IMMS 9

9TH INTERNATIONAL MESOSTRUCTURED MATERIALS SYMPOSIUM

17–20 August 2015

BRISBANE CONVENTION AND EXHIBITION CENTRE
QUEENSLAND, AUSTRALIA

WELCOME



It is a great pleasure to extend a warm welcome to you all as IMMS-9 participants and speakers.

Building on the success of previous IMMS meetings, the IMMS-9 aims to foster discussion on developments in the synthesis and characterization of mesostructured materials for a wide range of applications, such as energy and environment, biomedical, catalytic and adsorption processes, and thin films and functional structures.

Delegates from diverse backgrounds will have an opportunity to discuss new scientific findings, share knowledge, and advance ideas in this important field. The symposium will be a good forum to renew friendship, develop or strengthen collaborations and academic networking.

The IMMS-9 will begin in the afternoon of 17th August followed by a 3-day scientific program. It will feature plenary and keynote lectures, invited and oral talks, and poster presentations. Full papers presented at IMMS-9 will be published in two scientific journals – Microporous and Mesoporous Materials and Scientific Reports, subject to peer review. For detailed information on IMMS-9, please visit www.imms9.org.

We wish you a stimulating and productive conference as well as a most enjoyable stay in Brisbane and Australia.

Warm regards,

Professor G.Q. Max Lu,
Provost and Senior Vice-President, The University of Queensland

Executive Chair, The IMMS-9 Organizing Committee

DAY 1 - 17 AUGUST 2015

15:00-19:00	**Registration** Boulevard Auditorium Foyer
	Chair: Max Lu Boulevard Auditorium
18:00-19:00	**PL-01 Dongyuan Zhao**

DAY 2 - 18 AUGUST 2015

08:15-08:30	**Opening Ceremony** Chair: George Zhao Boulevard Auditorium	
	Chair: Thomas Bein Boulevard Auditorium	
08:30-09:15	**PL-02 Ulrich Wiesner**	
09:15-09:45	KL-01 Chang-Yuan Mou	
9:45-10:15	KL-02 Christopher W. Jones	
10:15-10:35	Coffee Break	
	Design & Synthesis Chair: Serge Kaliaguine Room B1	**Bio Materials** Chair: Andrea O'Connor Room B2
10:35-10:55	IT-01 Youchang Xie	IT-03 Peter Behrens
10:55-11:15	IT-02 Shunai Che	IT-04 Gordon Xu
11:15-11:30	OP-01 A.E. Garcia Bennett	OP-04 Julia G. Lyubovitsky
11:30-11:45	OP-02 Jo Changbum	OP-05 Yu Chen
11:45-12:00	OP-03 Lok Kumar Shrestha	OP-06 Jiwei Cui
12:00-13:15	Lunch	
	Catalysis Chair: T. Maschmeyer/ Yin Wan Room B1	**Energy** Chair: R. Caruso/ Yanquin Wang Room B2
13:15-13:35	IT-05 Peng Wu	IT-08 Quan Yuan
13:35-13:55	IT-06 Hideaki Yoshitake	IT-09 Eun-Bum Cho
13:55-14:15	IT-07 Ying Wan	IT-10 Yanqin Wang
14:15-14:30	OP-07 Trevor C. Brown	OP-10 Roland Marschall
14:30-14:45	OP-08 Su Seong Lee	OP-11 Lei Zhang
14:45-15:00	OP-09 Shuang Gao	OP-12 Jianping Yang
15:00-1520	Coffee Break	
	Chair: Peter Behrens Boulevard Auditorium	
15:20-16:05	**PL-03 Thomas Bein**	
16:05-16:35	KL-03 Qihua Yang	
16:35-17:05	KL-04 Martin Hartmann	
17:05-20:00	**Poster Presentation & Reception** Boulevard Auditorium Foyer	

DAY 3 - 19 AUGUST 2015

Chair: M. Thommes
Boulevard Auditorium

08:30-09:15	**PL-04 Ryong Ryoo**
09:15-09:45	KL-05 Jerry Y.S. Lin
9:45-10:15	KL-06 Bao-Lian Su
10:15-10:35	Coffee Break

	Design & Synthesis Chair: Shang-Bin Liu Room B1	**Adsorption & Environment** Chair: Ajayan Vinu Room B2
10:35-10:55	IT-11 Tatsuo Kimura	IT-13 Matthias Thommes
10:55-11:15	IT-12 Kean Wang	IT-14 Suresh K. Bhatia
11:15-11:30	OP-13 Shunsuke Asahina	OP-16 Gregory Knowles
11:30-11:45	OP-14 Peng Bai	OP-17 Jun Hu
11:45-12:00	OP-15 Benjing Xu	OP-18 David K. Wang
12:00-13:15	Lunch	
	Thin Films Chair: Jerry Lin/Shaomin Liu Room B1	**Functional Materials** Chair: M. Hartmann/Peng Wu Room B2
13:15-13:35	IT-15 Bishnu Prasad Bastakoti	IT-18 Chang-Sik Ha
13:35-13:55	IT-16 Igor Djerdj	IT-19 Alan Chaffee
13:55-14:15	IT-17 Shaomin Liu	IT-20 Yongsheng Li
14:15-14:30	OP-19 Yana Znamenskaya	OP-23 Jun Huang
14:30-14:45	OP-20 Ziqi Sun	OP-24 Xiangju Meng
14:45-15:00	OP-21 Xiaobo Li	OP-25 Zhangxiong Wu
15:00-15:15	OP-22 Indriana Kartini	OP-26 Lu Han
15:15-15:35	Coffee Break	

Chair: Bao-Lian-Su
Boulevard Auditorium

15:35-16:20	**PL-05 Kazuyuki Kuroda**
16:20-16:50	KL-07 Shinji Inagaki
16:50-17:20	KL-08 Karen J Edler
17:20-17:50	KL-09 Rachel A. Caruso
18:30-21:30	**Banquet Dinner** Boulevard Room Keynote Speech: Ove Hoegh-Guldberg

DAY 4 - 20 AUGUST 2015

Chair: Ryong Ryoo
Boulevard Auditorium

08:30-09:15	**PL-06 Markus Antonietti**
09:15-09:45	KL-10 Jianlin Shi
9:45-10:15	KL-11 Mietek Jaroniec
10:15-10:35	Coffee Break

	Adsorption & Environment Chair: Allan Caffee Room B1	**Catalysis** Chair: Michael Yu Room B2
10:35-10:55	IT-21 Serge Kaliaguine	IT-23 Hiromi Yamashita
10:55-11:15	IT-22 Shang-Bin Liu	IT-24 Hendrik Kosslick
11:15-11:30	OP-27 Yongde Xia	OP-30 Izabela Nowak
11:30-11:45	OP-28 Gaoke Zhang	OP-31 Fang Zhang
11:45-12:00	OP-29 Wei Teng	OP-32 Quanyi Wang
12:00-13:15	Lunch Dr Esther Levy's Presentation on Materials Science Publishing	

	Functional Materials Chair: M. Jaroniec/ Kean Wang Room B1	**ECR Session** Chair: Jun Huang/David Wang Room B2
13:15-13:35	IT-25 Xiaoming Chen	Yi Gu Meryem Bouchoucha Michael Dreifhe Qin Yue S. Loreto Yi-Wen Wang Yuxiang Liu Yun-Pei Zhu Biao Kong Yanlai Li Kun Che Kao Ali Shahtalebi Wei Luo
13:35-13:55	IT-26 Lianjun Wang	
13:55-14:15	IT-27 Yan Kong	
14:15-14:30	OP-33 Haihong Wu	
14:30-14:45	OP-34 Xiaomin Li	
14:45-15:00	OP-35 Yong Liu	
15:00-15:15	OP-36 Manas Pal	
15:15-15:35	Coffee Break	

Chair: Chung-Yuan Mou
Boulevard Auditorium

15:35-16:20	Dow Centre for Sustainable Engineering Innovation Lecture **PL-07 Galen Stucky**
16:20-16:50	KL-12 Sarah H. Tolbert
16:50-17:20	KL-13 Shilun Qiu
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Range4	140μA～5A	±1mA

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9TH INTERNATIONAL MESOSTRUCTURED MATERIALS SYMPOSIUM

Plenary Lecture Abstracts

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Interfacial Assembly and Engineering of Ordered Functional Mesoporous Materials for Applications

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Abstract

With recent progresses made in modern nanoscience and nanotechnology, ordered mesoporous materials have been one of the hottest research topics in scientific community spanned chemistry, materials science, physics and biology. The construction of mesoporous materials is mainly concerned with building monodispersed mesosized (2-50 nm) pore voids and arranging them in a long-range ordered array. Generally, two kinds of templates are used to produce the mesopores: supramolecular aggregates such as surfactant micelle arrays, and rigid preformed solids such as ordered mesoporous silica, carbon, and colloidal crystals. Noticeably, besides the templates, the interface also plays a central role in the synthetic process, because it provides a rich and crucial space for the assembly and construction of mesostructures. Generally, two kinds of interfaces involve in the synthetic system. The first one is at between surfactant templates and guest species, which has been extensively investigated. Another important interface is the two-phase (solid, liquid and gas) one, including liquid-solid, gas-liquid, liquid-liquid, gas-solid, and solid-solid interface, which has been well developed for the synthesis of ordered mesoporous materials. Compared with the one phase synthesis referring to homogeneous nucleation and growth, the introduction of a two-phase interface in the system can change the growth behaviors of mesoporous materials and lead to the formation of molding or multifunctional mesoporous materials. For example, mesoporous thin films or membranes have been widely fabricated on a substrate via an evaporation-induced self-assembly (EISA) method. Multifunctional core-shell structured mesoporous materials can be obtained by rationally depositing mesoporous shells on well-designed cores at the interface. Recently we have developed a novel facile approach i.e. a solvent evaporation-induced aggregating assembly (EIAA) to synthesize large pore mesoporous silica materials. In addition, the well-known hard-templating method for mesoporous materials is also a typical interface reaction.

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Mesoporous Materials from Block Copolymer Self-Assembly

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Abstract

The use of block copolymer self-assembly to structure direct various organic and inorganic materials into mesoporous materials is an area of intense research activity world-wide. Some of the interesting features of this approach include multiple materials formation avenues that are compatible with large-scale processing, tailoring of mesoporous materials morphology including co-continuous three-dimensional (3D) structures with improved mechanical properties over one- or two-dimensional (1D or 2D) structures, as well as tailoring of mesopore size typically in the range between 5 to 50 nm. In this talk progress in this field will be described focusing on work by the Cornell Wiesner group. Examples will include amorphous, polycrystalline, as well as single-crystal inorganic materials structure directed by equilibrium as well as non-equilibrium processes. The talk will describe efforts to develop a fundamental understanding of the respective structure formation processes supported by simulation work based on self-consistent field theory combined with density functional theory. Finally, after describing the degree of structural control achievable in various materials classes ranging from oxides to metals to semiconductors and from homogeneous structures to hierarchical and graded mesoporous structures, focus will turn to the study of entirely new and emerging property profiles of such mesoporous materials that are a direct result of the achievable structure control on the nanoscale.

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Multifunctional Mesoporous Nanoparticles for Drug Delivery

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Abstract

The integration of multiple molecular functionalities into mesoporous silica nanoparticles (MSN) enables the development of nanoagents for targeted drug delivery, particularly for anti-cancer drugs. We will first provide an overview on current research regarding the synthesis of mesoporous nanoparticles, approaches towards targeting certain cell receptors, as well as controlled molecular release systems based on internal (such as pH and redox potential) and external (light, temperature, etc.) stimuli. In the following we will discuss several recent examples from our research addressing the numerous challenges in targeted drug delivery.

Folate and epidermal growth factor (EGF) has been used for successful cell targeting with MSN. Considering triggered release in the endosome, a novel pH-responsive system has been created based on carbonic anhydrase (CA) gatekeepers (hydrodynamic diameter 5.4 nm). This system relies on the spatial control of functionalization available for our previously developed mesoporous silica core-shell nanoparticles. A pH-dependent CA inhibitor was covalently attached to the surface of the MSN, resulting in the desired opening mechanism caused by the endosomal pH change.

Addressing endosomal escape, we have covalently attached a red-light sensitive phthalocyanine photosensitizer to the MSN, surrounded by a lipid bilayer. Photoactivation leads to endosomal membrane rupture in cells causing cargo release from the mesopores into the cytosol. Moreover, we have exploited the proton sponge effect during acidification of the endosome with polymer-functionalized MSN to achieve endosomal release.

Finally, it is of great interest to expand the scope of bioactive cargo molecules that can be released from MSN systems. We have developed organically functionalized large-pore and medium-sized MSN with spatially controlled orthogonal functionalities that can reversibly adsorb oligonucleotides such as siRNA. Very high siRNA loading in the internal pore volume, efficient endosomal release and high biological activity was established.

These and other examples show that mesoporous silica nanoparticles represent a promising and flexible platform for numerous biomedical applications.

Development in Mesostructured Materials Science Based on Hierarchical Structure Directing

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Abstract

Mesoporous materials with various compositions have been contributing to many areas of modern science and technologies, such as catalysis, adsorption, electrochemical energy storage, and drug delivery. Among them, catalytic applications are still one of the most important issues in mesoporous materials science. In fact, the MCM-41 mesoporous silica was discovered by Mobil researchers in an attempt to synthesize large-pore zeolites. MCM-41 caused a big sensation, but the amorphous pore walls possessed insufficient acidity and hydrothermal stability as compared with crystalline zeolites. For two decades, there have been numerous works to synthesize mesoporous materials that are composed of truly crystalline zeolite frameworks. Owing to all those works, we are now in a stage to synthesize various zeolites possessing mesopores and micropores in a dual or hierarchical manner, using various routes. These progresses are shown in this lecture, with particular highlight on the recently developed synthesis routes using rationally designed surfactant molecules [1, 2] or random polymers [3].

The surfactant for hierarchical structure direction is an amphiphilic molecule that can assemble into micelle like an ordinary surfactant, but the molecule is functionalized with a particular zeolite structure-directing agent (SDA, typically, multiammonium group) [1, 2]. In an aqueous solution of silicates, the surfactant molecules and inorganic species are spontaneously assembled to form an organic-inorganic composite micelle, and consequently, a mesostructured material. Unlike the MCM-41 synthesis, however, the SDA group causes the formation of crystalline zeolite on the surface of the micelle. That is, a crystalline microporous zeolite structure (*e.g.*, MFI, MEL, MTW or beta) is built on the mesopore wall. Mesostructures obtainable in this manner are often layered nanosheets, house-of-card assembled nanosheets, and disordered nanosponges. The nanosponge exhibits a narrow distribution of mesopore diameters, despite the disordered pore arrangement. Our rational synthesis of such dually (or hierarchically) porous materials is now building a bridge between zeolite research field and mesoporous material science.

Another notable route to hierarchically porous materials is the use of random co-polymers or homo-polymers that are functionalized with SDAs for zeolites or other inorganic structures [3]. This synthetic method is particularly suitable for mesoporous materials with crystalline inorganic frameworks. The mesopores are generated by a mesoscale phase separation of polymer backbones from SDA-functionalized side chains during the inorganic crystallization. The synthesis has been demonstrated for a variety of materials, such as hierarchically nanoporous zeolites, their aluminophosphate analogues ($AlPO_4$), mesoporous TiO_2, SnO_2 and ZrO_2. The synthesis is expected to widen our ability to access unexplored mesostructured materials.

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Mesostructured Materials Design through Chemistry of Silica, Silicates, and Organosiloxanes

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Abstract

Creation of novel functional materials with organized structures at meso-length scale has been an important area of materials science. While pore wall composition has been widely expanded from silica to various compositions, including oxides, nonoxides, carbons, metals, alloys, hybrids, polymers, and metal complexes, silica has been most frequently studied as the pore wall composition of mesoporous materials. In this paper some recent developments and perspectives on mesostructured/mesoporous silica and related materials will be presented.

Layered silicates form organic intercalation compounds with various organic compounds and they can be recognized as lamellar mesostructured materials. Depending on the composition and structure some unique features can be expected. For example, kaolinte, a 1:1 type layered aluminosilicate, can form scroll type-nanotubes. Layered sodium polysilicates show a variety of reactions to form organically modified products. They can be converted to microporous and mesoporous silica.

Morphological control is quite important for applications. Colloidal mesoporous silica nanoparticles can be prepared by removing surfactants through dialysis. This route can avoid aggregation of colloids by sedimentation-redispersion. Surfactants can be removed while retaining the original colloidal state, which is applicable to the preparation of primary nanoparticles.

Mesoporous silica films with highly aligned cylindrical pores are prepared by the sol–gel method using a substrate with structural anisotropy. This method can be applied to titania–silica composite films. The obtained mesoporous titania–silica composite film exhibits a remarkable birefringence reflecting the highly anisotropic mesoporous structure and the high refractive index of titania.

Self-directing and building block approaches take quite different concepts. Self-directing processes using well designed organosiloxane precursors are recognized to induce mesostructures, depending on the molecular shape. Building block approach has been utilized for multiscale design. Depending on the demand of mesoporous silica with specific functions there will be further developments in the field of preparative methods of mesoporous materials.

The research field of mesoporous materials will continue to expand by involving interdisciplinary areas. Applications are really crucial for our community to develop researches on mesoporous materials. Recent advances should make this area more promising for practical applications. This trend will continue and multidisciplinary efforts will make this area more fruitful.

From Covalent Organic Frameworks over Novel C_nN_m-species to Porous N-doped Carbons: Polycondensation of New Porous Materials with Extreme Properties

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Abstract

Choosing the right organic starting products, (non-classical) ladder polymerization and copolymerization allows to generate a wider range of porous materials, ranging from regular frameworks over disordered systems with however well-defined pores to rather disordered porous functional carbons, while the electronic properties vary from wide bandgap semiconductors to organic metals within a rather similar family of components. At the same time, following distinct layout rules, such porous materials can be made to be "unexpectedly" stable, i.e. inert against pure oxygen at 500 °C or resistant against boiling sulfuric acid in an oxidative catalytic reaction.

I will report on our recent approaches to make such structures, mainly via novel condensation schemes of nitrogen containing monomers, such as nitriles, supramolecularily preorganized complexes, and ionic liquids. In addition, I will introduce the concepts of "salt flux synthesis" and "salt templating", in which ordinary salt as LiCl, ZnCl2, CsAc or KCl are used a porogenes to make super-high surface area materials with up to 4000 m2/g without any activation steps. This includes components such as "C_2N", one of the missing links between carbon and carbon nitride.

I will also report on first applications where such polymer scaffolds are used as catalysts, catalyst supports, as electrocatalysts, and for energy storage. In the latter case, simple systems with a polymer cathode and anode meanwhile show the potential to outperform classical lithium ion battery technology, pointing the way to so-called 3. generation battery systems based on sustainable carbons

Thoughts on the Current Path of Mesoscale Science from Discovery to Commercial Deployment

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Abstract

Our current ability to use the nanostructure assembly of inorganic/organic entities and non-equilibrium kinetics to create multiscale heterostructured materials presents an unprecedented opportunity to design and synthesize multicomponent systems; or, by adding high throughput experimental design, to rapidly optimize from an almost unlimited number of phase space possibilities a desired figure of merit response with simple processing. Historically the majority of breakthrough commercial successes have come about over a 15 to 25 year time frame from discovery to deployment. This is close to the current mesoscale timeline, which had its beginnings in the late 1980's and early 1990's. The bottom up synthesis of mesoscale-based materials or benchtop demonstrated expectations appears, however, to be far ahead of commercially verified applications. The purpose of this talk is to explore this hypothesis, to discuss some of the challenges of commercialization such as upscaling and validation, discuss the recent emphasis in the United States on the Materials and Mesostructured "Genome" programs, which have tightly integrated on a short time scale the relation between discovery and deployment as a prerequisite for funding; and, describe some examples that are being developed for large scale use or have been implemented by commercial companies.



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Keynote Lecture Abstracts

Water Confined in Mesoporous Silica

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Abstract

Water under nano-confinement is different from normal water. It is relevant to life and geoscience because much of the hydration phenomenon in nature occurs in narrowly confined water. We studied many properties of water confined in mesoporous silica by various experimental techniques.

Water under nano-confinement has a much a lower freezing point than bulk water. The abnormal properties of supercooled water, becoming more prominent at deep supercooling, were studied by neutron scattering techniques. These include equation of state information such as density(from SANS) and dynamic properties such as rotational relaxation(from QENS). SANS and SAXS experiments can measure the density of D2O and H2O down to 180 K. Both gave a density minimum at low temperature, a sign of low density liquid water.

Understanding solubility of a hydrophobic molecule such as Xe in water under nanoconfinement will impact several related problems, (a) solubility of methane in water within nanopores of rock under fracking condition, (b) understanding how hydrophobic effect would be changed in confined water, (c) how protein hydration would change under confinement. We studied hydration behavior of Xe in water confined in mesoporous silica using XeNMR technique. A major advantage of xenon in Xe-NMR study is its ability to respond to very subtle changes in its local environment. Xenon possesses a large and highly polarizable electron cloud, which translates into a large chemical shift range that is sensitive to the local electronic and magnetic environment. We studied Xe solvation in water as confined in mesoporous silica. It was found that in pore confined water, the hydration of Xe is more energetically favorable than in bulk water. The increased solubility of Xe in nanopore is in the same trend with computer simulation results of confined methane.

Engineering Nanoporous Oxides for CO_2 Separations

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Abstract

Carbon dioxide separation from gas mixtures is a critical process in several current and emerging energy-related industries, including in natural gas purification (CH_4/CO_2) and exhaust gas clean-up (CO_2/N_2). Amines are well known to bind strongly but reversibly with CO_2, making supported amine materials versatile solids for use in adsorptive or membrane CO_2 separation applications. Among the most well-studied supported amine materials are mesoporous oxide supported amines. It has been demonstrated that tailoring the nature of the support (porosity, surface area, composition, etc.) and amine groups (polymers, oligomers; primary, secondary, tertiary amines) can lead to the ability to fine-tune solids to have outstanding properties for CO_2 adsorption and separations. In this presentation, the design and characterization of nanoporous oxide-supported amine solids for the separation of CO_2 from simulated flue gases [1] or for the extraction of CO_2 from ambient air [2], will be described.

There are three primary types of oxide-supported amine materials used for CO_2 capture, as categorized based on the synthesis method [3]. Class 1 materials involve amines physically impregnated into the pores of porous supports, with no covalent bonds linking the amines to the support. Class 2 materials have small molecules that are covalently grafted to the oxide support, often with the use of aminosilane reagents. Class 3 materials are prepared by *in-situ* polymerization of amine-containing monomers off the oxide support surface, and contain covalent linkages to the solid oxide. All three material types will be discussed.

A practical adsorptive separation process for flue gas or direct air capture of CO_2 requires a solid adsorbent with suitable properties, including good thermodynamic behavior, kinetic behavior, stability (thermal, to gas contaminants, and most importantly, to water) and low cost. Furthermore, the material must produce a concentrated CO_2 product, and must be compatible with a scalable process. Too often, materials are designed for specific applications in isolation, without considering the process (gas-solid contacting strategy) to be used [4]. This presentation will address all of these issues with regard to the design of robust, scalable oxide-supported amine adsorbents for CO_2 separations.

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Assembly of Catalytic Active Species within Confined Nanospace

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Abstract

Porous materials, such as zeolites, mesoporous materials, MOFs and porous polymers, have been widely used in the field of catalysis. The catalytic reactions generally take place in the nanopore, the confined nanospace of porous materials. Thus, the assembly of catalytic active species in the confined nanospace has attracted much research attention. Recently, we focused on the development of methods for the assembly of different kinds of catalytic active species in the confined nanospace. The first example is that we have developed a silylation method for encapsulation of molecular catalysts [Co(Salen), Ru-BINAP, Binol-Ti, Fe(Salan), Ru-TsDPEN] in nanocages of mesoporous silicas.[1-3] Studies show that molecular catalysts confined in nanocages could move freely during the catalytic process. Thus, the asymmetric catalysis in nanopore exhibits homogeneous nature in nanoscale and could build up a bridge between homogeneous and heterogeneous catalysis. Moreover, it was found that the confined nanospace could enhance the cooperative activation effect to increase the catalytic activity of solid catalysts. This work provides a new opportunity for the design of efficient solid catalysts for the asymmetric reactions as well as many other reactions, which involve cooperative activation by separate catalytic centers or second-order kinetic dependence on the local concentration of catalysts.

In addition to molecular catalysts, a novel hybrid solid acid with a double-shell nanostructurewas fabricated via the self-assembly of PS-SO_3H in the confined nanospace of silica hollow nanospheres. [4] The acid strength of PS-SO_3H can be reversibly enhanced and decreased by expansion and aggregation of PS-SO_3H within the confined nanospace, which is confirmed by ^{31}P MAS NMR, ammonia adsorption calorimetry and TEM characterizations. In a series of important acid-catalyzed reactions, such as esterification of fatty acid, Friedel-Crafts alkylation of toluene and cumene hydroperoxide cleavage, the solid catalyst exhibits much higher activity than Amberlyst®-15, and in some cases even higher than liquid acid, H_2SO_4, under similar reaction conditions.

Very recently, we used two-step method for the synthesis of silica-based yolk-shell nanospheres confined with ultrasmall Pt NPs stabilized with poly(amidoamine), in which the interaction strength of Pt NPs and support could be facilely tuned. By ingenious utilization of silica cores with different surface wettability (hydrophilic vs. hydrophobic) as the adsorbent. The yolk-shell nanospheres possessing the weakest interaction strength between Pt NPs and the support show the highest catalytic activity (88500 h^{-1} and 7080 h^{-1} for the hydrogenation of cyclohexene and nitrobenzene, respectively), due to its unaffected freedom of Pt NPs for intrinsic properties retention.

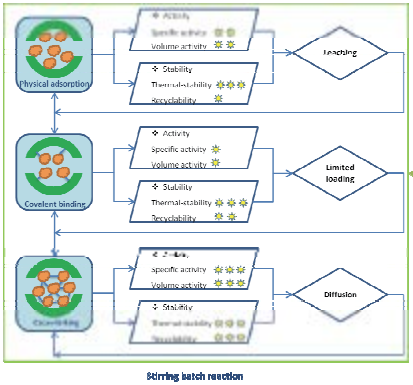
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Novel Strategies for Immobilization of Lipase on Porous Supports

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Abstract

In the last 15 years, ordered mesoporous materials (OMM) have shown large potential as supports for the immobilization of enzymes [1]. Periodic mesoporous organosilicas (PMO) are a novel branch of ordered hybrid mesoporous materials, in which the organic fragments are regularly distributed within the framework. PMOs have been studied as carrier for enzyme immobilization in recent years. In our previous studies, we have shown that periodic mesoporous organosilicas (PMO) are promising candidates for the adsorption of TLL providing an improved catalytic performance compared to free lipase and lipase immobilized in pure silica mesocellular foams (MCFs). However, a steady decrease of catalytic activity with every recycling step is found [2]. Therefore, different immobilization techniques are explored (Scheme 1). Leaching can be avoided by covalent bonding of TLL on modified PMOs, however, the limited loading results in low space-time-yields. Thus, the formation of cross-linked enzyme aggregates (CLEA) in the pores of PMOs was attempted to entrap TLL and increase the immobilized amount at the same time. Improved recyclability and activity was achieved by this method and the optimized biocatalysts were tested in transesterification reaction of 1-butanol with vinylpropionate. The catalysts were first tested under batch conditions and then transferred to fixed bed reactors. CLEAs in benzene-bridged PMOs always surpassed MCF-based CLEAs in both type of reactors (Fig. 1).
A novel strategy employing filter panels with hierarchical porosity [3] will also be presented.



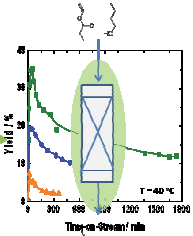


Figure 1. Fixed-bed reaction of vinyl propionate with 1-butanol (1:1 mol ratio, 0.5 M).
■PMO_CLEA_7.5U; ●MCF_CLEA_32U; ▲MCF_CLEA_

Scheme 1. Different pathways for lipase immobilization in mesoporous mateials.

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Mesoporous Inorganic Membranes for Conventional and Non-Conventional Applications

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Abstract

Mesoporous inorganic membranes include the legendary Vycor glass membranes with pore diameter of about 4 nm developed by Corning and modern inorganic membranes prepared by the sol-gel method. The sol-gel derived mesoporous membranes are used in conventional ultrafiltration processes or as the support for gas separation or reverse osmosis membranes. The sol-gel derived inorganic membranes, represented by gamma-alumina membrane, have an average pore diameter in the range from 3 to 10 nm, with very uniform pore size distribution. They are prepared as a thin film of about a few micron in thickness on macroporous support of asymmetric pore structure, thus offering high liquid or gas permeance. This talk will compare synthesis and structural and transport properties of several mesoporous inorganic membranes, including alumina, zirconia, titania, ceria and silica, that were studied in our laboratory. The talk will also discuss several new mesoporous membranes for non-conventional applications. These will include mesoporous silica membranes containing vertically aligned, segregated mesopores for molecular extrusion and mesoporous-microporous zeolite membranes as separator for lithium ion batteries.

Hierarchically Mesostructured Porous Materials: From Nanoscience to Catalysis and Energy Conversion and Storage

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Abstract

Over the last decade, tremendous research has been focused on the hierarchically mesostructured porous nanomaterials. This subject became a hot topic and will continue to prosper in the years to come. A large series of domains, from biotechnology, biomedicine, catalysis, energy, optics, and separation processes (gases, biomolecules, etc.) to the immobilization of biomolecules and bio-organisms, have a fervent interest in hierarchically mesostructured porous materials, with applications such as bone regeneration, heart tissue replacement, and adsorbents fueling this interest [1-9]. Hence, this rapidly evolving field is of great importance and has spurned much attention from both academia and industry alike.

This talk presents different synthesis strategies to hierarchically mesostructured porous materials: 1) self-formation phenomenon of hierarchy with multiple-scaled interconnected and mesostructured micro-meso-macroporosity on the basis of the chemistry of metal alkoxides and alkylmetals; 2) bottom up self-assembly of microporous nanoparticles. The obtained materials have great potentials in nanotechnology, photocatalysis, catalysis, gas sensing and energy conversion and storage. A particular example of hierarchically mesostructured porous nanomaterials obtained from our new bottom up self-assembly of microporous nanoparticles will be illustrated. The obtained nanomaterials have been used as photocatalyst in liquid phase dye molecuels photodegradation, as sensor in gas phase alcohol sensing and as electrode in Li ion battery.

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Mesoporous Organosilica Support for Efficient Heterogeneous Metal Complex Catalysis

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Abstract

Immobilization of metal complexes on solid supports is important for easy recovery and recycle uses and allows easy integration of different components for constructing highly functional systems. However, immobilization on conventional supports such as silica gel has often resulted in decreases in the performances of metal complexes, such as catalytic activity and selectivity, because the uniform environment of the homogeneous metal complexes is disturbed by unfavorable interactions with the solid surface and nonuniform fixation on the surface. Moreover, the diffusion limitation of substrate and product molecules has been a problem for porous supports due to a decrease in reaction efficiency in their narrow channels. Thus, the development of a new support preserving the inherent functions of metal complexes is still a challenge for realizing their practical applications.

Here, we report the successful synthesis of the crystal-like bipyridine-PMO (BPy-PMO) from 100% organosilane precursor $[(i\text{-}PrO)_3Si{-}C_{10}H_6N_2{-}Si(Oi\text{-}Pr)_3]$.[1] BPy-PMO had a well-defined pore surface structure where 2,2'-bipyridines were densely and regularly arranged and preserved the high coordination ability to metals. A variety of bipyridine-based metal complexes including iridium (Ir), ruthenium (Ru), rhenium (Re), and palladium (Pd) were easily formed on the pore surface (Fig. 1). Furthermore, we discovered the excellent ligand properties of BPy-PMO in heterogeneous Ir-catalyzed direct C−H borylation of arenes with bis(pinacolato)diboron and in heterogeneous photocatalytic hydrogen evolution from water using a Ru-complex and platinum integrated on the pore surface. These results demonstrate the great potential of BPy-PMO as a solid chelating ligand and a useful integration platform for construction of efficient molecular-based heterogeneous catalysis systems.

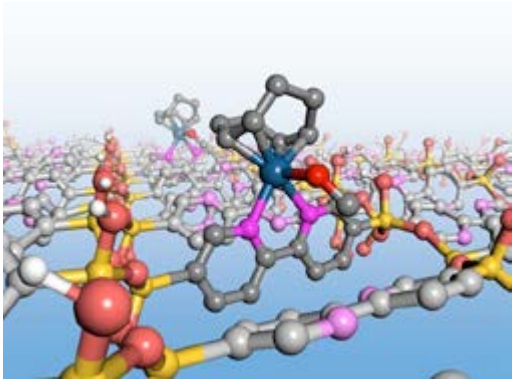


Fig.1 CG image of the pore surface of BPy-PMO immobilized with iridium complexes [Ir(cod)(OMe)(bpy)].

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Formation of Free-Standing Surfactant-Templated Films

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Abstract

Free-standing mesoporous films are of interest for the production of membranes for nanofiltration, high surface area sensors and catalysts and electrochemical devices. We have studied the formation mechanisms of surfactant-templated silica films growing at the air-solution interface from acidic solutions to develop mesostructured, crack-free self-supporting membranes. Although films can be grown using both cationic and nonionic surfactant template in this manner, the mechanisms of film growth show two distinct patterns; either slow growth from stable solutions which initially contain silica coated micelles or via a rapid particle formation mechanism where film growth and formation of a composite precipitate proceed simultaneously.[1, 2] We have used SESANS to study particle growth on micron length scales, while also probing interactions between solvent, silica and micelle headgroups using wide angle scattering and atomistic modelling methods.[3]

Resulting from our studies, we have suggested that there may be an analogy between polymerizing silica and polyelectrolytes[1] and, were thus able to also prepare solid mesostructured polymer-surfactant films which grow similarly at the interface.[4] These membranes grow on alkaline solutions, so we have now employed these polymer-surfactant films as novel templates for silica films grown from basic rather than acidic solutions. The resulting films are thick, contain well-ordered mesostructures and are far more robust than those grown from solutions containing only surfactant and inorganic precursor.

Silica films with a range of mesostructures can be obtained using either cationic surfactants[5] or cat-anionic surfactant mixtures[6] with different polyelectrolytes in these alkaline solutions. The film formation mechanism appears to involve both a steady state evaporation process driving material to the solution interface accompanied by continuing silica polymerization which locks the structure in place.[7] Surfactant can be removed by calcination or by solvent wash, leaving polymer functional groups in the inorganic pore walls as sites for further functionalization. Among other applications, these membranes are being developed as positron-positronium converters for experiments at CERN in collaboration with a group at Politecnico di Milano.



Figure 1: silica-surfactant film harvested onto plastic mesh of side 1cm.

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Controlling the Mesostructure of Titania for Application in Solar Cells

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Abstract

The structural properties of titania can be manipulated to significantly enhance its performance in applications of environmental importance. Considering the dye-sensitized solar cell, controlling the morphology of titania for use as the photoanode can influence a number of parameters: 1) The dye loading within the photoanode correlates to the surface area, and thus particle size and porosity, of the titania. 2) Electron diffusion in the photoanode requires good interconnectivity between the titania nanoparticles. 3) Electolyte infiltration into the photoanode is influenced by the porosity of the titania film, and 4) Light harvesting can be enhanced by increasing scattering within the film. Therefore, the efficiency of these cells can be improved by deliberate structural engineering of the photoanode. Likewise for the perovskite solar cells with a thin titania layer for electron transport, the titania structural properties influence perovskite crystallization, light harvesting and overall efficiency. In this presentation the synthesis of titania materials with varied structural properties, such as mesoporous beads and dendritic nanowires, will be discussed and correlated with the performance of solar cells containing these structures.

Mesoporous Silica Nanoparticle-Mediated Drug Delivery For Cancer Therapy

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Abstract

Drug delivery systems (DDSs) are expected to overcome most of the drawbacks of tranditional cancer thermotherapy. The synthesis and construction of DDSs by using nano-sized and monodispersed drug carrier for targeted drug delivery have attracted great interests recently. Mesoporous silica nanoparticles (MSNs) have been found to be capable of efficiently delivering anticancer drugs with sustained and controllable drug release features and possible targeting effects, and now become one of the most attractive research focuses [1-4]. One of the most interesting subjects is the possibility of overcoming MDR by using MSNs-based DDSs.

Most anti cancer drugs such as DOX act within the nuclei in killing cancer cells. We have found that when the diameter of MSNs is not larger than 50 nm, and MSNs is properly surface-modified with a certain kind of peptide (e.g., TAT), drugs can be directly delivered into the cancer cell nuclei and release therein. Such an intranuclear DDS not only demonstrate enhanced anticancer efficacy for common cancer cells, but can also kill MDR cancer cells with high efficiency [5,6].

A structure difference-based selective etching strategy was developed to synthesize hollow-structured MSNs (HMSNs) with excellent monodispersity. Different kinds of anticancer drugs, e.g., hydrophobic and hydrophilic drugs, can be respectively loaded in the hollow core and the mesopore channels. Such a DDS loaded with more than one kind of drugs was found to be effective in overcoming MDR [7, 8].

We found that common MSNs-DDS loaded with one kind of anticancer drug is capable of circumventing the drug pump-out mechanism in cytoplasm by MSNs-DDS to a certain extent, and part of the drug released within cytoplasm can diffuse into cell nuclei and thus kill the MDR cancer cells. [9]

Multofunctional MSNs-based nanocomposites have been constructed for drug delivery monitoring, theranostics, imaging-guided therapy, et al [10-11]

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Tuning Porosity In Carbon-Based Nanostructures

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Abstract

Since the beginning of 21 century there is a great interest in the development of carbons with well-developed and well-defined porosity (e.g., see pioneering review [1]) such as ordered mesoporous carbons (OMCs) obtained mainly by hard- and soft-templating (HT and ST). The HT synthesis involves the filling of pores of a hard template such as ordered mesoporous silica and colloidal silica crystals with carbon precursors followed by carbonization and template dissolution. In the case of the ST synthesis carbon precursors and block copolymers self-assemble to form ordered polymeric mesostructures, which upon carbonization are converted to OMCs. Both HT and ST OMCs are mainly mesoporous carbons (pore sizes between 2 and 50 nm), with some intrinsic irregular microporosity (pore sizes below 2 nm) depending on the carbon precursors used. One of the key questions in chemistry of nanomaterials, which refers to nanostructured carbons too, is how to design their properties for specific applications.

At present there is a great interest in the development of carbons with desired porosity for diverse applications ranging from gas storage, adsorption of biomolecules, removal of pollutants of different sizes, and heterogeneous catalysis to energy storage and conversion. For instance gas storage and capture require carbons with strictly defined microporosity, adsorption of dyes and biomolecules is more effective in mesoporous carbons, and hierarchically porous carbons, which consist of interconnected micropores, mesopores and small macropores (pores above 50 nm), are well suited for supercapacitors. The main objective of this work is to present recent advances in the synthesis of carbons and carbon-based nanostructures with tuned porosity. A special emphasis will be placed on the design hierarchical carbons and carbon-based nanostructures with well-defined porosity, and porous carbon-based materials with spherical morphology. The aforementioned HT and ST synthesis strategies are well suited for the development of nanostructured carbons with tuned porosity and morphology as well as with incorporated inorganic species. The aforementioned properties can be tuned by proper selection of carbon precursors and templating agents, adjustment of chemical composition and synthesis conditions, and controlled post-synthesis activation. For instance, hierarchically porous carbon nanostructures can be prepared by creating ordered mesopores by block copolymer templating, additional ordered mesopores or macropores by colloidal crystal templating, and micropores by organosilane-assisted synthesis and/or post-synthesis activation with various activating agents. Also, there are enormous opportunities in the development of organic-inorganic nanostructures with well-defined hierarchical porosity such as specially designed mesoporous metal-organic frameworks (MOFs) and their conversion to hierarchically porous carbon-based nanostructures.

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Using Nanoporous Materials for Application in Energy Storage

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Abstract

In this talk, we examine ways that nanoporous materials can be used to address issues of relevance to energy storage. We begin with solution phase self-assembly, which provides a powerful method to create complex nanoscale architectures through low-cost processing routes. For example, block-copolymer templating of sol-gel precursors or preformed inorganic colloids can be used to produce periodic nanoporous inorganic materials that combine high surface area, open porosity, and mechanical flexibility. Such materials can form the basis for high power electrochemical energy storage materials known as pseudocapacitors. In such materials polymer derived porosity can produce a very desirable combination of electrical connectivity, electrolyte access to the interior of the material, ample surface redox sites, and very short solid-state diffusion lengths for lithium ions. With idealized architectures, we have shown that a unique combination of high energy density and high power density can be achieved, in some case combined with reactivity toward ions other than Li^+. More importantly, by systematically controlling the architecture, we can learn about the architectural components needed for optimal pseudocapacitor performance.

Another route to produce nanoporous materials is by selective dealloying of metal alloys. This route is the ideal complement to polymer templating, as it can easily be used to produce thick samples with high electrical conductivity, but without the chemical variability that can be achieved using sol-gel or nanocrystal based methods. Here we will present recent results on the use of these nanoporous metals for both electrochemical energy storage and for electro-catalysis. Initially developed for noble metals, here we present results on a much broader range of systems including nanoporous Al and NiFe. Taken together, the results show how controlled nanoscale porosity has exciting potential to impact the global energy problem.

Micropore Engineering of Carbonized Porous Aromatic Framework for Supercapacitors

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Abstract

Micropore engineering of porous carbons on the effect of capacitance was explored using a carbonized porous aromatic framework (PAF-1).[1, 2] The porous carbons obtained through different carbonization methods show different pore structures enabling us to do this. The capacitance was measured both in aqueous electrolyte and different organic electrolytes. The porous carbons prepared by KOH activation show both high microporous volume, which is beneficial for charge storage, and mesoporous volume, which is devoted to fast ion diffusion in the pores; properties which are highly desirable. It shows capacitance value as high as 280 F g^{-1} and 203 F g^{-1} at a current density of 1 A g^{-1} in 6.0 M KOH and 1-ethyl-3-methyl -imidazolium bis(trifluoromethyl-sulfonyl)imide (EMImTFSI), respectively. We also demonstrate the effect of diffusion and that of geometric packing of the electrolyte ions in the pores, where a commensurate match of the electrolyte ions with the pores of carbonized materials control and influence significantly the capacitance of these materials.

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9TH INTERNATIONAL MESOSTRUCTURED MATERIALS SYMPOSIUM

Invited Talk Abstracts

Preparation of High-surface-area γ-Al_2O_3 by Assistance of Some Polar Organic Compounds Dispersed on the Support

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Abstract

Preparation of high-surface-area γ-Al_2O_3 economically has always been an important subject in the manufacture of many catalysts and adsorbents. Our group has found a wide-spread phenomenon of which many compounds can disperse onto the surface of a support as a monolayer [1]. We report here that a γ-Al_2O_3 with very high surface area can be obtained if some polar organic compounds are deposited on the surface of alumina hydroxide, and followed with calcination of the hydroxide. We believe that when the organic compounds decompose and be eliminated during the calcination, the sintering of γ-Al_2O_3 particles will be hindered owing to the existence of the monolayer- dispersed organic compounds. Four different polar organic compounds, sucrose, glucose, amylose, and polyethylene oxide have been explored as an additive to alumina hydroxide for the preparation of high-surface-area γ-Al_2O_3. Experiments had shown that all these four organic compounds were very effective to achieve high surface area of γ-Al_2O_3 in the preparation. The quantities of each additive for obtaining γ-Al_2O_3 with the highest surface area had been optimized and are reported below. As a baseline sample, an aluminum hydroxide precipitate is made by mixing aluminum nitrate and ammonia solutions, followed by filtration, washing, drying, and final calcination at 600℃ for 2 hours, a γ-Al_2O_3 with a surface are of 209 m^2/g, a pore volume of 0.18 cm3/g, and an average pore diameter of 3.1 nm is obtained. In comparison, when an optimal quantity of 0.2 mole sucrose per mole aluminum was added to the aluminum hydroxide after washing out ammonia nitrate and followed by calcination at identical conditions, a γ-Al_2O_3 with a surface area of 471 m^2/g, a pore volume of 0.44 cm3/g, and an average pore diameter of 3.8 nm was produced. In the case of glucose, the optimal quantity of addition is 0.8 mole of glucose per mole aluminum, and a γ-Al_2O_3 product with a surface area of 490 m^2/g, a pore volume of 0.44cm^3/g, and an average pore diameter of 3.1 nm has been obtained. For amylose (soluble starch), the optimum quantity of addition is 0.6 mole C_6 per mole of aluminum, and a γ-Al_2O_3 product with a surface area of 386 m^2/g, a pore volume of 0.45cm^3/g, and an average pore diameter of 4.6 nm has been obtained. For polyethylene oxide as the additive, the optimal quantity is 100 g of polyethylene oxide per of mole aluminum, and a γ-Al_2O_3 with a surface area of 506 m^2/g, a pore volume of 0.9 cm^3/g, and an average pore diameter of 5.1 nm has been obtained. In summary, the organic compounds used as additives to make γ-Al_2O_3 is cheap, the preparation process is simple and the increase of surface area is significant, so it is a very promising method for producing γ-Al_2O_3 with high surface area.

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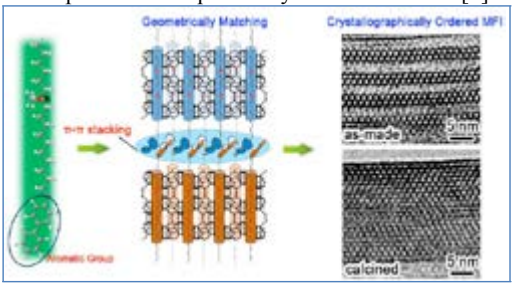
π-π Interaction of Aromatic Groups in Amphiphilic Molecules Directing for Mesoporous Zeolite

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Abstract

One of the challenges in material science has been to prepare macro- or mesoporous zeolite. Examples of their synthesis exist, there is a need for a facile yet versatile approach to such hierarchical structures. Our approach to designing feasible templates for the synthesis of hierarchical zeolites is to stabilise the micelle structure by introducing highly rigid segments (i) that have strong interactions with each other in the hydrophobic chain to block crystal growth by forming an extremely stable hydrophobic layer and (ii) that form an ordered orientation to provide a geometric match with the MFI zeolitic framework. Here, we introduce a concept for designing single-quaternary ammonium-head amphiphilic template with strong ordered self-assembling ability through π-π stacking in hydrophobic side, which stabilises the mesostructure to form single crystalline architecture with mesostructured zeolite nanosheets (SCZN) [1,2]. The concept was demonstrated for the formation of a new type SCZN join with 90° rotational boundary by the bolaform templates with bi-quaternary ammonium head, which resulted in a mesoporous zeolite with highly specific surface area even after calcination [1,2]. Low binding energies for this self-assembling system were supported by a theoretical analysis. Geometrically match between the arrangement of aromatic groups and the zeolitic framework was speculated for the formation of SCZN [1,2]. Finally, single-crystalline mesoporous ZSM-5 with three dimensional sheet-like mesopores, which possess not only *a-c* plane but also abundant *b-c* and *a-b* planes, was produced by using a triply branched template with bi-quaternary ammonium head [3].



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Nanoporous Materials in Tissue Engineering Applications

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Abstract

In the last years, several nanoporous materials like nanoporous silica have been established as non-toxic and biocompatible biomaterials [1,2]. Most of the investigations have focused on nanoparticles as drug delivery systems for the release of small drug molecules [1]. A current trend in medicine is regenerative tissue engineering, aiming at the reconstruction of tissue, i.e., the repair or replacement of partial or entire tissues. For this purpose, scaffolds have to be constructed on which suitable biochemical and physico-chemical factors are placed to instruct (stem) cells to the formation of a certain tissue or combination of tissues. Here, we show that nanoporous materials can be an important component in regenerative medicine. These materials can be applied as nanoparticles, as coatings on implants, or as a component in nanocomposite materials. Tissue-specific growth factors which control the differentiation of cells and can induce the formation of certain tissues, or adhesion molecules which allow certain cells to adhere, can be applied in sufficient quantities using the nanoporous materials. Typical examples are BMP2 (bone morphogenetic protein 2), a protein growth factor which induces osteogenic differentiation and the formation of bone, or BDNF (brain-derived neurotrophic factor) which supports the survival of nerve cells and encourages the growth and differentiation of new neurons and synapses.

In this contribution, the use of nanoporous materials for tissue engineering applications will be exemplified. Strong differentiation effects can be obtained, for example, by using BMP2 immobilized on nanoporous silica coatings or nanoporous silica nanoparticles [3,4], as exemplified in cell culture and animal experiments. The construction of scaffolds will also be demonstrated. By a simple infiltration technique, growth factor-loaded NPSNPs could be incorporated into collagen membranes where they attached strongly to the collagen fibers. Furthermore, difficulties in the use of nanoporous materials for the immobilization of sensitive proteins like growth factors will be discussed. These relate to the conservation of biological activity of the proteins as well as to problems with the application of well-established methods of molecular biology (e.g., ELISA: enzyme linked immunosorbent assay). When applied directly, these often fail, probably due to high adsorptive capacity of the nanoporous materials.

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Controlling Mesoporous Silica-coating of Layered Double Hydroxide Nanoparticles for Drug Delivery

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Abstract

Layered double hydroxide (LDH) nanoparticles (NPs) have found various potential applications in control delivery of therapeutics, including many negatively charged drugs, oligonucleotides and genes, peptides/proteins [1-3]. The current study investigated the surface coating with mesoporous silica ($mSiO_2$) for control and target drug delivery. Mg_3Al-Cl-LDH NPs were coated with $mSiO_2$ by varying preparation parameters, including the reagent concentration, the chain length of cationic surfactants, the coating temperature and time. Transmission electron microscope images and Fourier-transform infrared spectra evidenced the successful $mSiO_2$ coating onto the surface of LDH NPs. Within the investigated range of these parameters, the thickness of the coated $mSiO_2$ layer can be controlled from 5 to 20 nm and the pore size from 2.5 to 3.5 nm. We also demonstrated that the exchanging and intercalating properties of Mg_3Al-Cl-LDH NPs enabled the easy loading of anionic drugs and the controlled release of loaded drug molecules were resulted from combination of particular $mSiO_2$ pore structures and drug-LDH interactions [4,5]. We further showed that such hybrid nanoparticles were readily taken up by cells [5]. Thus we have established a foundation for the development of a multifunctional smart delivery platform.

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Design Synthesis of Zeolite-Based Microporous and Mesoporous Materials for Bifunctional Catalysis

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Abstract

Microporous and mesoporous materials, with hierarchical pore structures and integrated chemical compositions, combine together the merits of mesosilica and crystalline zeolites. With respect to zeolite-based materials, core/shell-structured zeolite@mesosilica [1] and mesoporous zeolites [2] have been developed. These materials are promising for bifunctional catalyses by taking the advantages of the large pores and confining effects of mesopores.

We found that coating mesosilica phase on the surface crystals of TS-1, either by conventional CTAB or P123 copolymer-assisted synthesis or with self-assembly in emulsion system, gave rise to core/shell-structured TS-1@mesosilica or TS-1@KCC-1 materials [3a, 3b]. The P123 copolymer-derived TS-1@mesosilica were converted readily into TS-1@mesocarbon through a nanocasting and selective silica etching strategy [3c]. By confining the Au and Pd nanoparticles (NPs) within the mesopores in shell parts, efficient bifunctional catalysts were prepared for direct epoxidation of propylene to propylene oxide with hydrogen and oxygen either in gas-phase or liquid-phase [3a, 3c]. The reaction took place in a tandem way, that is, *in-situ* formation of hydrogen peroxide on precise metal NPs and subsequent alkene epoxidation by the formed H_2O_2 on Ti active sites. On the other hand, the mesosilica shell coated over the crystals of Ti-MWW exhibited unique protecting effects for the core Ti-MWW active component in basic reaction media [3d]. Serving a sacrifice, the mesosilica retarded the desilication and prolonged greatly the lifetime of Ti-MWW in continuous ammoximation of cyclohexanone. On the other hand, immobilizing the $Rh(OH)_3$ species within the mesopores of TS-1@KCC-1 composite, a bifunctional catalyst useful for on-pot synthesis of benzamide from benzaldehyde, NH_3 and H_2O_2 was obtained [3e]. Selective and controlled desilication of zeolite crystals was realized by piperidine-assisted NaOH treatment, leading to mesoporous ZSM-5 with superior catalytic properties in hydrocarbon cracking [4a]. Moreover, hierarchical meso-ZSM-5@mesoaluminosilicate can be further prepared by self-assembling the dissolved aluminosilicate species onto the desilicated ZSM-5 crystals using triblock copolymer as template. Supporting Pt NPs inside mesopores resulted in efficient bifunctional hydrocracking catalysts [4b]. Bifunctional tandem catalysis was realized on multilamellar organic-inorganic hybrid zeolites with organic structure-directing agent (OSDA) molecules occluded within micropores. The OSDA species served as base active sites for the cycloaddition of epoxides and carbon dioxide independently [5a], or cooperated with the zeolite acid sites to catalyze the acid-base reactions [5b]. This would provide new ideas for taking full use of expensive and precise OSDA molecules.

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Reactions of α, β-unsaturated Aldehydes in Methanol on Mesoporous Gold-anatase

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Abstract

We prepare in this study "mesoporous titania-supported" gold catalysts, whose structure is agglomeration of nanocrystallites of gold and anatase with similar diameters. These catalysts appear as a mesoporous solid with a uniform pore size. The catalysts were prepared by a simple deposition-precipitation method using mesoporous anatase pre-calcined at various temperatures. This heat treatment results in the growth of anatase crystallites. After the decomposition-reduction of precipitated gold salt, the catalysts were heated again for various duration to enlarge the size of gold particles.

Figure 1 shows a typical TEM photograph of the catalyst. Dark particles attributable to gold have almost the same crystallite size with the light particles of anatase. The nitrogen adsorption-desorption and pore size distributions revealed that the porous structure of mesoporous anatase before combining with gold nanoparticles was not significantly changed in gold-anatase after heating 1 h. However, the pore size distributions become broad and large with heating time of post-heating. This is clearly caused by the growth of gold particles.

The catalytic reactions of acrolein, crotonaldehyde and methacrolein were carried out in methanol at 273 K. We found the products of dehydration coupling reactions (methyl methacrylate and its derivative molecules) in addition to those of the addition of methanol to C=C double bond (methoxyaldehydes). In the methyl methacrylate formation from acrolein, the selectivity varies from 0 % to 78 % according to the pre-calcination temperature of mesoporous anatase. In the formation of methyl crotonate from crotonaldehyde, no side products are found, while the activity becomes the largest when using the catalyst from mesoporous anatase calcined at 673 K and at 723 K (, where the data are almost the same,) and no products are found on the catalysts from mesoporous anatases calcined at 823 K and 873 K. The selectivity increases with the calcination temperature of mesoporous anatase when the substrate is methacrolein. These results of catalytic reactions will be discussed with the XPS spectra of gold, UV spectra of anatase and porous structure.

Since the reactivity of these three aldehydes are considerably different due the position of methyl group, while each substrate is sensitive to slight differences of the structure of catalyst supports, these reactions can be applied various types of supported gold catalysts.

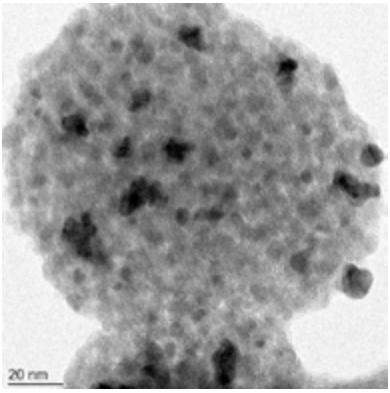


Fig. 1. Au supported on mesoporous anatase pre-heated at 723 K.

Aggregation-free Gold Nanoparticles in Ordered Mesoporous Carbons: Towards Highly Active and Stable Heterogeneous Catalysts for Selective Oxidation of Alcohols

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Abstract

Carbon-supported catalysts have appeared more active than un-supported nanoparticles in oxidation of polyhydroxylated compounds, highlighting the importance of the relative affinity of the substrate and the support for aqueous media. However, activated carbon has been seldom used for gold deposition due to the facts that traditionally used methods for metal catalysts are unfeasible for gold nanoparticles.[1] Here we will present a coordination-assisted self-assembly approach for the intercalation of aggregation-free and monodispersed gold nanoparticles inside ordered mesoporous carbon frameworks (Figure 1).[2] By tuning the thiol group concentration and adopting a two-step carbinization, the gold particle sizes can be easily tuned from 3 to 17 nm.

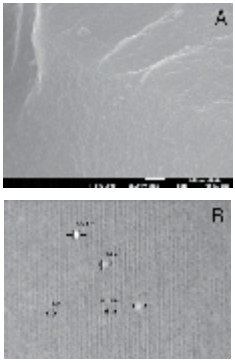


Figure 1. HRSEM images for Au/C with nanoparticles size of about 9 nm surface (A) and after cross section polishing (B). The particle sizes are labeled with solid line, the primary mesopore size is labeled with dot line

Using potassium hydroxide as a base, the selective oxidation of benzyl alcohol with molecular O_2 in water reaction over the Au/C catalyst having 9 nm gold nanoparticles is rather fast under 90 ºC and 1 MPa. An almost complete conversion of benzyl alcohol to benzoic acid is achieved within 60 min. A mild condition of 60 ºC and atmospheric pressure was then adopted. The initial reaction rate reduces to 115.2 mmol $g^{-1}h^{-1}$. But benzyl alcohol can still almost complete selectively oxidized to benzoic acid within 12 h. We also tested the initial reaction rate (within 0.5 h) and conversion of benzyl alcohol to benzoic acid at 12 h in successive runs in the presence of a thiol-containing mesoporous silca(SH-SBA-15) as a trapping agent. Obvious changes are undetected for catalytic performance after five runs. These results indicate that the gold-containing mesoporous carbon catalyst is stable and can be reused. Interestingly, this catalyst is highly poisoning-resistance. Even with a molar ratio for thiocyanate:Au of 33, about 37% activity can be remained. The high activity and stability can be assigned to aggregation-free metallic gold nanoparticles, highly exposed surface by bimodal pores, confinement of nanoparticles by stable carbon mesostructure, and large carbon mesopores with the relatively hydrophobic surface facilitating the selective adsorption of substrate in water and mass transfer.

A reduction of gold particle size from 9 to 3.4 nm in the catalyst leads to a high activity toward the selective oxidation of benzyl alcohol to benzyl acid and toward the reduction of p-nitrophenol to p-aminophenol at low temperatures such as 0 °C. The catalyst exhibits TOF value of 478 and 31.2 h^{-1} at 25 and 0 °C, comparable to, and much higher than an 8.9 nm gold-supported nanocatalyst, respectively, for the water-mediated selective oxidation of benzyl alcohol. These results highlight the improvement in the sorption of dioxygen species on surface atoms of gold nanoparticles at low temperatures due to electronic modification by the reduction of the particle size. [3]

The atomic economic reaction with a 100 % yield in the presence green solvent of water under atmospheric pressure shows great advantages in green chemistry.

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Mesoporous Inorganic Materials for Advanced Electrochemical Capacitance Storage

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Abstract

Due to the characteristics of mesostructure-based materials, it exhibits brilliant optical, magnetic, catalytic, electrical and other physicochemical properties. Regular and adjustable pore structure, large surface area together with a certain degree of size and shape selectivity make it suitable for the study of some physical effects and multi-functional materials, which will lay the groundwork for conducting academic research of catalytical and electrical applications of mesostructured materials.

Based on the principle of coordination chemistry, an anion assisted synthesis routes for synthesis of mesoporous inorganic nanomaterials was developed. By regulating the hydrolysis of metal ions in the self-assembly process, a series of mesoporous nanomaterials with specific surface structures were successfully obtained. [1,2] In addition，the confined channels of the ordered mesoporous material was utilized to stabilize rare earth nano-catalyst, which obtained nanocomposite with good thermal stability and catalytic activity. [3,4] In details, the designed pore structure of ordered mesoporous alumina prevented CeO_2 nanoparticles with a size smaller than 5 nm from aggregating and forming secondary large particles. As a result, thermally stable ceria nanoparticles with a uniform small size and improved catalytic properties were synthesized. Recently, a three-dimensional carbon nanotube (CNT) skeleton was embed into mesoporous SiO_2 (m-SiO_2) to fabricate bulk, robust sponges, which enhanced the mechanical strength and internal molecular exchange. Taking the advantage of CNT's flexibility, bulk m-SiO_2 didn't crack or shrink due to the improvement of structure instability. Besides, hierarchical porous structures containing both mesopores and macropores improved molecular diffusion and mass transportation inside the m-SiO_2 monoliths remarkably. [5] For further application, hierarchical porous electrode nanocomposite was prepared by using carbon nanotube sponge as a three-dimensional template. The deposition of a m-SiO_2 layer onto CNT resulted in a CNT@m-C core–shell hybrid structure. The introduction of CNT sponge broke the limitation of mesoporous carbon's inherent fragility and low electrical conductivity. Consequently, the synthesized macro/mesoporous carbon frameworks possessed wonderful capacitances. [6] Three-dimensional hierarchical porous nanocomposite reveal inspiring potential in electrochemical energy storage.

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Mesoporous Ceria-Silica/Poly(Ether Sulfone) Composite Membrane for Fuel Cell Electrolyte Application

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Abstract

Hydrocarbon-based electrolyte polymer membranes have been investigated to be used as an electrolyte membrane for fuel cell application because fluorine-based polymer membrane is not economic and is hard to process. However, long-term stability of hydrocarbon-based polymer membrane is known to be weakened by attacking of hydroxyl radicals formed during cell operation. Thus, it has been necessary to increase antioxidant ability of hydrocarbon-based polymer. In this study, ceria-containing mesoporous silica were prepared via sol-gel chemistry and sPES50 (poly(ether sulfone) with 50% degree of sulfonation) based polymer composite membranes were prepared using mesoporous ceria-silica powders.

The SPES50 membranes were prepared by the solution-casting method. SPES50 was dissolved in an organic solvent (7 mL, 10 wt% in DMSO), and was poured on a clean glass plate. The glass plate was dried on a hot plate at 70°C for 12 h, and then in a vacuum oven at 80°C for another 6 h to give a homogeneous membrane of 50–60 μm thickness. Acidification of the membrane was carried out by treating with 5 M HCl solution for 8 h at 80°C followed by deionized water for 4 h. The composite electrolyte membranes with cerium ions were prepared by the mixing method as follows. First, mesoporous silica was dispersed in SPES50 solution of in DMSO (10 wt%). Concentration of mesoporous silica was controlled to have 2.5, 4, 10, and 30% against the concentration of the sulfonic acid groups. The mixture was stirred vigorously under sonication. Then, the homogeneous solution was poured in glass plate at 70°C hot plate for the 12h to remove solvent. Then, the membrane was washed with deionized water to remove the residual solvent and impurities. Finally, we obtained mesoporous silica composite membranes with different ceria contents.

The antioxidant effect of ceria-containing composite membranes were investigated by Fenton test and hydrogen peroxide exposure, which were examined by measuring residual weights using a balance and molecular weights using GPC, respectively. Also, proton conductivity was measured for fuel cell application.

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Mesoporous NbOPO4: Synthesis and Application in Biomass Conversion

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Abstract

The production of liquid fuels and fine chemicals from renewable biomass resources is particularly attractive and great efforts have been devoted worldwide to converting renewable biomass into fine chemicals and transportation fuels. Nb_2O_5 and $NbOPO_4$ have been studied as water-tolerant solid acids and would have good performance in the hydrolysis and dehydration during biomass conversion.

In our laboratory, mesoporous $NbOPO_4$ was synthesized with CTAB as template and used for (1) the dehydration of carbohydrates to 5-hydromethylfurfural (HMF), (2) the dehydration of sorbitol to isosorbide, (3) the hydrolysis of cellulose to levulinic acid, (4) the alcoholysis of cellulose to esters of levulinic acid, and (5) the hydrodeoxygenation of biomass derived compounds to alkanes. In all these process, mesoporous $NbOPO_4$ showed high activity and long-term stability as solid acid or as support, which is attributed to its strong acidity and tolerance to water. More importantly, NbOx as an early transition metal oxide has the ability to cleavage C-O bond during hydrodeoxygenation of biomass or biomass derived compounds to alkanes.

Table 1 The results of direct hydrodeoxygenation of various raw woody biomass over $Pt/NbOPO_4$.[a]

Entry	Biomass	Mass yield of liquid alkanes [wt%][b]				Carbon yield of liquid alkanes [%]		
		Pentane	Hexane	ACHs	Total	Pentane	Hexane	ACHs
1	Larch	4.78	20.4	2.62	27.8	66.9	77.7	13.8
2	Fir	3.66	16.0	2.28	21.9	65.2	69.2	10.0
3	Camphor	7.33	15.2	5.09	27.6	54.2	63.4	33.6
4	Poplar	7.06	9.67	5.13	21.9	45.9	40.2	33.5

[a] The reactions were conducted at 190 ^oC and 5 MPa H_2 for 20 h.

Therefore, $NbOPO_4$ is a good solid acid catalyst in the conversion of biomass and related compounds and more surprisingly it has the ability to cleavage or assistant to cleavage C-O bond, which can be extended to other reactions.

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Compositional Design for Exploring the Possibility of Unique Reticular Type Porous Structures

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Abstract

Porous materials design has been developed increasingly by using the self-organization properties of amphiphilic organic molecules. A huge number of ordered mesoporous materials have been reported using various surfactants (e.g., cationic, anionic, nonionic), with precise controls of mesostructure, composition and morphology. Following the successful fabrication of semiconducting oxide (e.g., TiO_2, SnO_2, ZnO) films by using the self-assembling process of asymmetric block copolymers like polystyrene-*b*-poly(oxyethylene) (PS-*b*-PEO),[1] I have recently proposed a new organic templating using flexible PS-*b*-PEO colloids combined with shrinkage of frameworks.[2] A unique reticular type oxide network showing very high surface area can also be designed in oxide films using PS-*b*-PEO. Until now, some uniqueness of this reticular type porous structure has been confirmed by photodegradation of organic molecules and adsorption of bulky biomolecules.

If this reticular type porous structure is designed by a variety of compositions, uniqueness of the porous structure will be investigate further, and then this kind of research is accelerated for considering potential and/or practical uses. From the viewpoint, herein, I introduce promising synthetic methods for the compositional design of the reticular type porous films. As shown in Figure 1 with preliminary experimental data, several pathways are considered for obtaining compositionally designed films with reticular type porous structures.

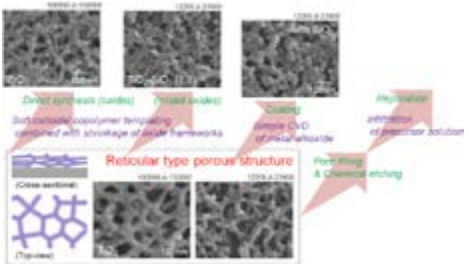


Figure 1. Synthetic methods and processing for the compositional design of reticular type porous oxide films.

In my previous paper,[2] I have reported that a similar structure was fabricated in a zirconia film but not in silica and alumina films. However, a similar film of titania-silica with the Si/Ti molar ratio of 1.0 can be prepared on the basis of the synthetic procedure for the reticular type titania film, revealing a possibility of continuous design between titania and silica up to the Si/Ti molar ratio of 1.0. The direct synthesis has not been established yet, but silica coating of reticular type porous titania films is proposed through a simple chemical vapor deposition (CVD) of silicon alkoxide, which would widely provide the opportunity to utilize reticular type porous films with different compositions. Toward the replication of reticular type porous structures, complete carbon filling and subsequent chemical (e.g., HF) etching of the titania frameworks will afford the carbonous hard-templates that are promising for obtaining a wide variety of reticular type porous inorganic solid films. In this context, I believe that potential applications of the reticular type porous structures will be designed and investigated through these experiments.

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Surface Functionalized Carbon Microspheres for Refinery Water Treatment

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Abstract

Carbon microspheres (CS) were synthesized from glucose solution at 170^0C and different reaction time. Four CS samples were synthesized at 12h, 14h, 16h and 19h, respectively. A portion of the samples were surface activated by the treatment with 0.5M NaOH, the other portion treated with 0.5M CH_3COOH, and the remaining samples were left untreated (native). All samples were characterized. Batch adsorption experiments were carried out at room temperature to remove heavy metal ions (Ag^+ and Cu^{2+}) from aqueous solutions. It was found that increasing reaction time resulted in CS with a lower amorphous content and lowered adsorption capacity, NaOH-treated CS had the highest adsorption capacity of ~450 mg Ag^+/g and ~170 mg Cu^{2+}/g, while CH_3COOH-treated CS had a lower Ag^+ and Cu^{2+} uptake than native CS. The adsorption isotherms were well fit by the Langmuir isotherm equation (for base-treated CS) and the Freundlich isotherm equation (for acid-treated CS). The adsorption mechanisms of each type of CS were discussed with respect to their experimental data.

Physisorption of Gases with Special Reference to the Evalulation of Surface Area and Pore Size Distribution: New IUPAC Recommendations

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Abstract

Gas adsorption is an important tool for the characterization of porous solids and fine powders. Major advances in recent years have made it necessary to update the 1985 IUPAC recommendations on *Reporting Physisorption Data for Gas/Solid Systems* (K.S.W Sing et. Al, Pure Appl. Chem 57 (1985)), which had been broadly accepted by the scientific and industrial community.

The aims of this new IUPAC report are to clarify and standardize the presentation, nomenclature and methodology associated with the application of physisorption for surface area assessment and pore size analysis and to draw attention to remaining problems in the interpretation of physisorption data

References:

Matthias Thommes, et al. "Physisorption of Gases, with Special Reference to the Evaluation of Surface Area and Pore Size Distribution". *Pure and Applied Chemistry*

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All information including figures/tables/references should be included in **one page** only.

Adsorption and Transport of Light Gases in Hierarchical Materials

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Abstract

In recent years a new class of adsorbents with a 'hierarchical' structure has been the subject of much interest, due to the potential of such materials to dramatically improve yield in those processes where the critical dimensions of the pore and the fluid are similar. In these hierarchical structures, a mesoporous network is purposefully embedded into the microporous material structure, in order to improve its transport properties. We analyze here our recent experiments on mass transfer in hierarchical CHA-like zeolite, microporous SAPO-34, having embedded mesopores as transport pathways providing access to intra-crystalline micropores. We use effective medium theory (EMT), where no topological configuration of the phases is assumed other than they mix in an isotropic manner. Our results suggests that, while hierarchical materials yield significant improvement of mass transfer in nanoprorous crystals, the magnitude of such improvement is heavily influenced by the connectivity and availability of the transport pores. If the mesopore volume-fraction is below the percolation threshold, there will exist microporous regions in the crystals where access of adsorbate cannot occur through an adjacent mesopore, slowing transport to a point where the difference between the diffusivity in the purely microporous and the mesopores-enhanced crystal will differ by no more than one or two orders of magnitude. Molecular simulation is used to predict the diffusion coefficients of ethane and propene in the microporous zeolite, providing results that compare well with the experimental data as long as the correct combination of framework/force field is chosen. Thus, molecular simulation methods and EMT can potentially be combined to theoretically investigate hierarchical materials.

Polymeric Micelle Assembly: A New Way for Synthesis of Functional Mesoporous Materials

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Abstract

Polymeric micelles are formed in solution when the hydrophobic portions are driven to an interior structure while hydrophilic portions are turned outward facing toward the water. So far, the polymeric micelles have been utilized for various applications, such as adsorbents, drug carriers. Recently, we have focused on the polymeric micelles as stable and rigid templates for obtaining mesoporous materials with ultra large pore sizes.[1-3] Our 'polymeric micelle assembly' approach is highly useful for preparation of novel mesoporous materials which are not easily obtained by general synthetic approaches. As one example, mesoporous gold (Au) films with tunable pores are expected to provide fascinating optical properties stimulated by the mesospaces, but they have not been realized yet because of the difficulty of controlling the Au crystal growth. Very recently, we reported a reliable synthesis of mesoporous Au films using stable micelles of polystyrene-*block*-poly(oxyethylene) (PS-*b*-PEO) diblock copolymers, with electrochemical deposition advantageous for precise control of Au crystal growth.[3] In the electrolyte solution, $HAuCl_4$ is dissolved into H_3O^+ and $AuCl^{4-}$ ions and then interacts with the EO shells of the micelles through hydrogen bonding. This interaction favours H_3O^+ rather than $AuCl_4^-$, and consequently creates positively charged micelles that can be directed to the working electrode surfaces, where the $AuCl_4^-$ ions are reduced to metallic Au with the electrochemical deposition of the micelles. The resultant mesoporous Au films actually exhibit high scattering performance and thus high activity for molecular sensing. Significantly, enhanced electric field (E-field) amplitude is clearly seen inside or at the perimeter of the mesopores. The E-field amplitude and LSPR frequency are readily tunable by simply tuning the pore size and we demonstrate the new methodology for tailoring the optical functionality. In this presentation, we would like to introduce our recent progress on new mesoporous/nanoporous materials as well.[4, 5]

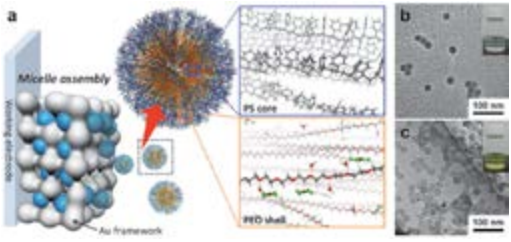


Fig. 1 | (a) Schematic illustration for the fabrication of mesoporous Au films by using polymer micelle assemblies. (b, c) TEM images of PS-*b*-PEO micelles formed in aqueous solution (b) without and (c) with $HAuCl_4$ source. The Tyndall effect is also shown as an inset image.

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Hexagonal Rare Earth Orthoferrites Stabilized on the Nanometer Scale in Polymer-Templated Mesostructured Thin Films and Powders

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Abstract

We report the polymer templating synthesis and thorough structural, optical and magnetic characterization of single phase hexagonal rare earth orthoferrites (*h*-$RFeO_3$; R = Yb, Lu) in the form of thin films and powders with cubic mesoporous morphology, nanocrystalline wall structure and high thermal stability. The contribution aims to show that large amphiphilic diblock copolymers are ideally suited as structure-directing agents for the preparation of metastable compounds, having honeycomb-like networks of open pores, due to their ability to form supramolecular structures and interact with inorganic building blocks. Based on results from DFT geometry optimization and constrained Rietveld refinement, the crystal structure of $YbFeO_3$ at room temperature is concluded to be a hexagonal with the non-centrosymmetric space group $P6_3cm$ and lattice parameters a =5.9948(5)Å and c =11.732(2)Å. We also demonstrate that these metastable orthoferrites can be readily deposited on both silicon and quartz glass substrates, with a high degree of crystallographic alignment along the *c*-axis. In contrast, conventional epitaxy techniques like metal-organic chemical vapor deposition (MOCVD) require specific single crystalline substrates (e.g., Y_2O_3-stabilized ZrO_2) to achieve the stabilization of such exotic transition metal oxides with preferred crystal orientation.

Dual Phase Ceramic Membranes for Air Separation and High Temperature Oxidations

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Abstract

Mixed ionic-electronic conducting (MIEC) ceramic membrane is a highly active research topic given its potential to replace the conventional high cost oxygen production method by a novel cost-effective membrane separation technology. MIEC ceramic membranes have been majorly classified into single phase perovskite oxides and dual phase membranes. These perovskite membranes are successfully developed for pure oxygen production solely due to the relatively mild operating conditions for air separation. Unfortunately, the stability of these perovskite membranes is weak and cannot be applied in atmosphere containing reducing or acidic gases like CH_4, H_2, CO and CO_2 due to the reactions of the perovskites and these gases thus they cannot be more economically applied in recently emerging markets-clean energy technologies and syngas synthesis. The robust dual phase ceramic membrane with strong chemical stability has the potentials to fill up this gap. This presentation will be focusing on the working principles of dual phase membranes and design strategies to address the issues of membrane stability and gas permeation flux rates. Hopefully, the present talk can provide new understanding towards the long-standing ambition to realize robust membranes or membrane reactors for clean environment and greener chemical synthesis.

Snap-top Nanocontainers for Selective Recovery of Nickel Ions from Seawater

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Abstract

The design of high performance nanomaterials that possess unique and distinctive properties has attracted for numerous applications concerning human health and environmental importance. Successful reports about the recovery of metals from various sources are suffering from some kinds of difficulties. The recovery of metals in a selective way is the only remedy to overcome this problem. The outer surface of the as-synthesized spherical MCM-41 was tailored by N-[3-(trimethoxysilyl)propyl]aniline (TMSPA) and further locked with β-cyclodextrin(CD) to preserve the included cryptand[211] (C211) molecule, after removing the surfactant (CP-MCM-41). Various analysis techniques have been used to ensure the formation of MCM-41 and successful modification. X-ray diffraction and transition electron microscopy evidenced the formation of mesoporous material with well-ordered spherical morphology. ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectral analysis revealed the silicon environment of the synthesized and modified materials. N_2 sorption experiments showed the functionalized and surfactant removed MCM-41 has large surface area (1107 $m^2 g^{-1}$), acceptable pore diameter (2.5 nm) and affordable pore volume (0.65 $cm^3 g^{-1}$) to accommodate the guest molecules inside the pore channels. Organic functionalization was determined by ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy. The metal adsorption ability and selectivity were examined by the introduction of CP-MCM-41 in various metal solutions including artificial and real seawater. The highly selective (99 mole %) recovery of nickel ions was achieved by CP-MCM-41 from natural seawater through ICP-OES analysis, even though the C211 prefers lithium-cryptate formation according to the previous reports. X-ray photoelectron spectroscopy (XPS) confirmed the chemical states of the nickel-cryptate and external surface compositions of CP-MCM-41.

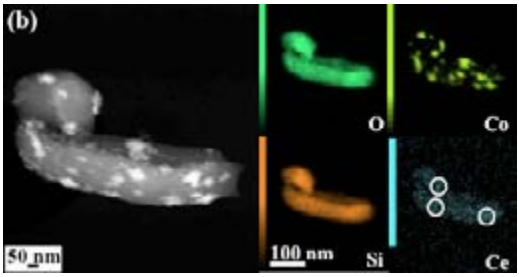
The Morphology and Catalytic Behaviour of Co_3O_4 Supported on Meosporous SBA-15

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Abstract

We have been investigating the potential of cobalt oxide supported on mesoporous silica SBA-15 as a robust heterogeneous catalyst system for the selective oxidation of organic substrates. For catalysts prepared by the 'two-solvent' method we observed the formation of cobalt oxide 'patches' which are larger in diameter that the SBA-15 channels [1]. This phenomenon is attributed to the fact that SBA-15 mesopores are interconnected by micropores that facilitate extended crystallite growth. As a result, catalysts of this type prepared with lower cobalt content exhibit higher oxidation activity (e.g., for cyclohexanol to cyclohexanone), due to the better accessibility of the reactants to more catalytic sites [2]. X-ray diffraction revealed that the cobalt oxide patches were crystalline with a spinel structure.

In recent work we synthesised analogous Ce-doped cobalt oxide composite catalysts. The liquid phase catalytic performance of the Ce-doped composites was found to be higher than either the un-doped composites or analogous Ce-composites. This is attributed to the improved dispersion of Co_3O_4 species in the Ce-doped composite, such that more active surface area becomes available for the organic substrates to access. Also, the extent to which CeO_2 covers over the surface of Co_3O_4 species appears to cause a synergistic effect and thus improve the redox properties of the catalytic system.



STEM image and elemental mapping profiles of a Ce-doped cobalt oxide on SBA-15 composite catalyst.

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Hierarchically Porous MBG-based Scaffolds for Enhanced Bone Tissue Repairing and Regeneration

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Abstract

The aim of this study is to develop a novel kind of porous MBG-based scaffold (MBGS), N-MBGS or C-MBGS, with sufficient compressive strength and porous architecture suitable for bone tissue regeneration, which were prepared via a simple powder pressing method and a post-grafting modification with amino or carboxylic groups. *In vitro* cell culture with bone marrow stromal cells (BMSCs) and *in vivo* rabbit femur defect models were employed to evaluate the osteogenetic capacity of the as-synthesized hierarchically porous scaffolds. It is revealed that both scaffolds could significantly promote the proliferation and osteogenic differentiation of BMSCs *in vitro* by improving their bone-related gene expression (alkaline phosphate (ALP), runt-related transcription factor 2 (Runx 2), osteocalcin (OCN) and bone sialoprotein (BSP)) and osteogenetic efficacy *in vivo*. Furthermore, N-MBGS presents the most significant promoting capability due to the hydrophilicity and positively charged surface. Thus, it is anticipated that this new scaffold system could acquire practical applications in the field of tissue engineering.

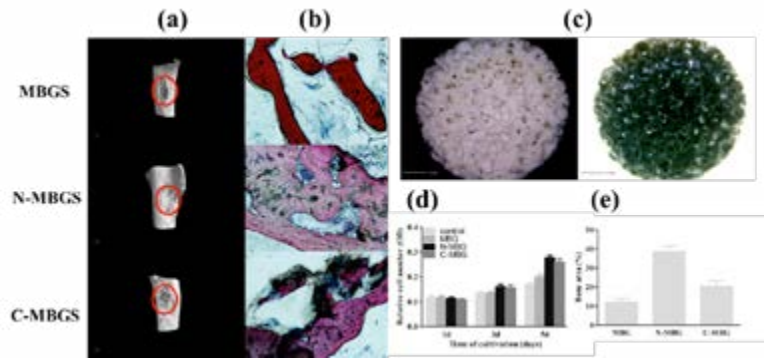


Figure 1 Bone regeneration in a femur cavity defects by Micro-CT analysis(a) andhistological evaluation (b), micrograph of MBGS(c), proliferation of bMSCs cultured with different scaffold (d) and quantitative analysis of the new bone area after 12 weeks.

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The Design and Application of Mesoporous Materials for the Processes of CO_2 Capture and Separation

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Abstract

It is widely accepted that climate change is being exacerbated by increasing atmospheric concentrations of greenhouse gases, and fossil fuel combustion electrical generation plants represent a major source of anthropogenic CO_2 accounting for one third of global CO_2 emissions. One possible approach is the capture of CO_2 from flue gas followed by its sequestration in geological formations. The purpose of CO_2 capture is to produce a concentrated stream of CO_2, preferably at high pressure, so that it can readily be transported to a storage site. Two types of solid looping cycles for CO_2 capture and separation, chemical-looping combustion (CLC) and CaO-based CO_2 looping cycles (CaL), are proposed. The common characteristic of these two processes is the use of solids that circulate between two different chemical environments with fluidized bed combustion (FBC) systems as an optimal technology.

It is well accepted that extremely low-cost CaO-based solid sorbents are good adsorbent candidates for capturing CO_2 in CaO-based CO_2 looping process due to their high reactivity with CO_2, and high capacity. The major and most investigated challenge for CO_2 looping cycles is the decrease of reversibility for the carbonation reaction, which is typically explained by sintering of the involved calcium based materials. In our recent research, we have fabricated mesoporous core/shell structured CaO-based pellets with a tunable thickness (1 to 5 μm) of mixed or pure oxide sorbents shell (silica, zirconia, alumina, ceria) for cyclic high temperature (700-850 C) CO_2 capture. These oxide shells and in particular the porous zirconia also infiltrated the inner void of the pellets isolating the CaO crystal grains and forming a unique segregation effect during the high-temperature CO_2 capture process. The core/shell pellets exhibited better CO_2 adsorption stability over 30 repeated carbonation/ decarbonation cycles than their original cores. This enhanced stability is due to this segregation effect which prevented the contact of CaO crystal grains. Moreover this core/shell sorbent also exhibited the best attrition resistance among different selected sorbents.

Chemical looping combustion (CLC) is a rather new combustion technology that has recently gained increased attention since it was found as having inherent advantages for CO_2 separation compared to the conventional technologies, where the CO_2 produced is diluted with atmospheric nitrogen. Aiming at this CLC process, two types of perovskites, $LaCoO_3$ and $LaMnO_3$, prepared by the reactive grinding and nanocasting methods were investigated as oxygen carriers. They demonstrated high reactivity and stability of CH_4 combustion under CLC conditions, negligibly coke formation but an undesirable agglomeration of particles. In our further study, $LaMn_{0.7}Fe_{0.3}O_{3.15}$@$mSiO_2$ core−shell materials were prepared by coating a layer of mesostructured silica around the agglomerated perovskite particles. It was found that this core−shell structured carrier showed much higher reactivity and stability over 10 repeated redox cycles compared to the pristine core due to a protective role of the silica shell against sintering.

The two series of work demonstrated critical and original applications of mesostructured materials in this socio-economically significant technological developments.

Polyamine-Immobilized SBA-15 as Solid Adsorbents for CO_2 Capture: A NMR Study

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Abstract

Capture of CO_2 via polyamine-modified SBA-15 mesoporous silica has attracted considerable attentions due to its high adsorption capacity and superior durability. Herein, we explore the sorption mechanism of CO_2 on an as-synthesized tetraethylenepentamine (TEPA)-modified SBA-15 by means of various solid-state NMR techniques. Results obtained from 2D $^{29}Si\{^1H\}$ FSLG-CP HETeronucleus CORrelation (HETCOR) NMR experiments revealed that, upon a mild loading of TEPA (ca. 10 wt%) onto SBA-15, resonance peaks responsible for couplings of hydroxyl groups and the surfactant template (triblock copolymer; P123) with the Q^3 [$Si(OSi)_3OH$] and Q^4 [$Si(OSi)_4$] surface silica sites of the support were completely replaced by signals arising from interactions between the grafted amines and the surface silicas. This indicates the presence of strong hydrogen bonding ($C\text{-}NH_x\cdots H\text{-}O\text{-}Si$) between the latter two tends to expel the P123 template from the silica surfaces. The 2D $^{29}Si\{^1H\}$ FSLG-CP HETCOR NMR spectrum of CO_2 uptake TEPA-modified SBA-15 is also analyzed and the spectrum shows that the spatial correlation between ^{29}Si and ^1H is much similar to that of TEPA-modified SBA-15 before CO_2 uptake, indicating the surface silanol group has negligible effect on the overall CO_2 uptake. A more sophisticated solid-state NMR technique, namely $^{13}C\{^{14}N\}$ S-RESPDOR was also employed together with DFT calculations to explore the carbamate species formed by $^{13}CO_2$ chemisorbed on a 50 wt% TEPA-modified SBA-15. Accordingly, two types of adsorption species, namely, secondary and tertiary carbamates as well as distant ammonium groups with a relative concentration of 7:3 were identified together with a $^{13}C\text{–}^{14}N$ internuclear distance (ca. 1.45 Å), and relevant ^{14}N quadrupolar parameters, revealing that the distribution of surface primary and secondary amines readily dictates the CO_2 uptake/release properties of the adsorbent.

Design and Applications of Plasmonic Catalysts for Efficient H_2 Production from Ammonia Borane

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Abstract

Nanostructured noble metals such as Au, Ag and Cu are attractive materials that strongly absorb visible light owing to their localized surface plasmon resonance (LSPR). On the other hand, hydrogen is regarded as a promising fuel due to its high energy content per mass and non-pollution. Ammonia borane (NH_3BH_3) is an attractive chemical hydrogen storage candidate. In this study, we demonstrated that the plasmonic nanostructures, including color-controlled Ag nanoparticles and MoO_{3-x} nanosheets, can be used as highly efficient catalysts for H_2 production from NH_3BH_3 under visible light irradiation.

The supported Ag nanoparticles were prepared on SBA-15 mesoporous silica by microwave-assisted alcohol reduction in the presence or absence of sodium laurate. MoO_{3-x} nanosheets were prepared by oxidizing metal molybdenum powders with hydrogen peroxide followed by the solvothermal treatments in ethanol solution. The catalytic performances were investigated for dehydrogenation of NH_3BH_3 in aqueous suspensions with plasmonic catalysts under argon gas atmosphere. The activity for H_2 production from NH_3BH_3 was greatly enhanced by the visible light irradiation induced by LSPR especially on the rod type Ag nanoparticles with lager aspect ratio. Addition of Pd metal on Ag nanoparticles could enhance the activity. Under visible light irradiation, plasmonic MoO_{3-x} nanosheets also displayed dramatically enhanced H_2 production.

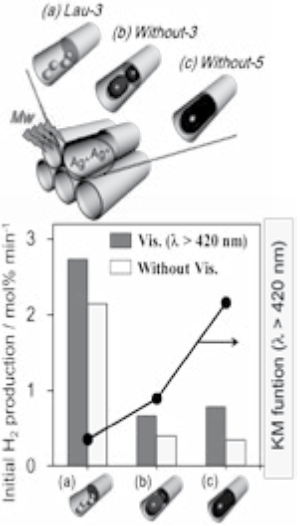


Figure. 1 The H_2 production from NH_3BH_3 on Ag/SBA-15 prepared by (a) Lau-3, (b) Without-3 and (c) Without-5 under dark condition or light irradiation.

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Selective Catalysis with Rh-supported Porous Metal-Organic Frameworks

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Abstract

Porous metal-organic frameworks (MOFs) have been attracted high attention due to their unique properties like extraordinary specific pore volumes, micro- and meso-sized pores and cages as well as the large tunable chemical and structural diversity allowing tailor-made preparation of materials for application in e.g. catalysis and adsorption [1]. A possible drawback of these new materials is the organic-inorganic hybrid nature of MOFs, which may limit chemical and thermal stability. Porous MOFs have been shown to catalyze a couple of different chemical reactions. However, in depth studies of the catalytic performance are still rare. This presentation aims to highlight the impact of structural and textural properties of MOFs on the activity and selectivity in the hydroformylation of olefins in order to derive structure-property-relationships. Additionally, a possible influence of the linker will be discussed.

This paper deals with the preparation and characterization of different sized Rh-supported MOFs and catalytic testing in the hydroformylation of olefins to corresponding aldehydes using different sized and shaped olefins [2]. A representative set of different structured porous MOFs namely MIL-77. MIL-96, MOF-5 IRMOF-5, MIL-101 and Meso-MIL-101, containing small, medium, large, and extra-large pores with sizes ranging from *ca*. 4 to 300 Å, have been selected and synthesized and supported with rhodium. The samples were characterized by XRD, TEM/SEM, FTIR, TG-DSC as well as nitrogen ad- and desorption in order to derive information on structural and textural properties. The catalytic performance was studied using different test molecules as *n*-hexene, *n*-heptene, *n*-octene, *n*-decene, *n*-dodecene, *n*-hexadecene, 2,2,4-trimethyl pentene, cyclohexene, and cyclooctene. The reaction was performed in stainless steel autoclaves using toluene as solvent at 100°C and a synthesis gas (CO/H_2) pressure of ca. 50 bar. The reaction products were analyzed by GC/MS.

The characterization data confirmed high crystallinity, porosity and sufficient (mechanical) stability of MOF catalysts. All Rh-supported MOFs show high catalytic activity with turn-over-numbers of *ca.* 50.000 (based on rhodium). The high activity is assigned to the high accessibility of active sites in MOFs and a high, probably atomic, dispersion of the rhodium in the hybrid structure provide strictly uniform and separated metal oxide building units. The porosity has a severe impact on activity and selectivity conclusively showing that the catalysis takes place in the porous MOF. Surprisingly, the large porous MIL-101 behaves highly selective by excluding strictly conversion of intermediate formed internal olefins. This finding points to a location of the Rh at the microporous super tetrahedral units (STU). Overall, MOFs are highly potential catalysts for chemical reactions in non-aqueous media. MOF catalysts can be recovered and reused.

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Luminescent Metal-Organic Frameworks for Molecular Oxygen Sensing

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Abstract

Porous metal-organic frameworks (MOFs) composed of metal ions (or clusters) and organic bridging ligands have many applications, such as adsorption/separation, catalysis, and sensors, which may attributed to their useful characteristics, such as high crystallinity, high porosity, designable frameworks, and modifiable pore surface [1].

The sensing of molecular oxygen plays an important role in environmental monitoring, biological, medical, analytical, and industrial chemistry. The sensing materials are usually composed of expensive noble metals. Such materials were usually noble metal complexes because of their excellent photoluminescence. However, they have to be fabricated into organic porous matrixes for practical applications. On the other hand, the first MOF for oxygen-sensing contains high concentrations of noble metal, or iridium, was reported a few years ago [2]. Nevertheless, it is still a great challenge to design and synthesize high-performance MOFs for O_2 sensing with cheap and stable materials for reduced cost and different applications.

Therefore, we have recently developed several new approaches to address the above-mentioned questions, which include doping with less expensive Ru(II) ions in low concentration [3], and metal-coordination [4] into the frameworks and pores, respectively, as well as using strongly photoluminescent MOFs with cheap Cu(I) and Zn(II) ions [6]. The progress will be given in this presentation.

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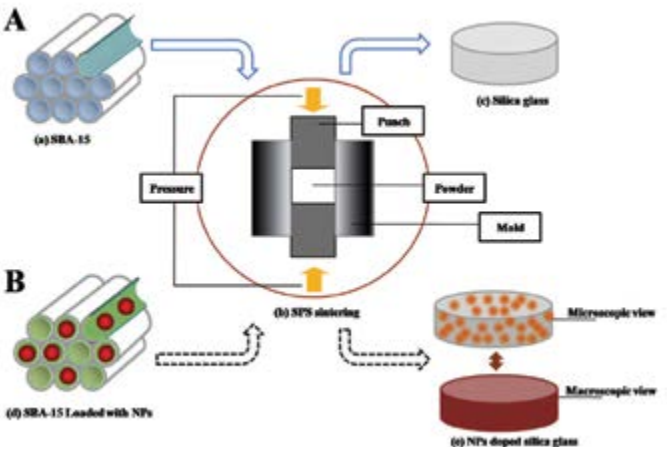
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A Facile Strategy for Fabricating Optical Silica Glasses Derived from SBA-15

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Abstract

Silica glasses containing noble metal nanoparticles are of great interest due to the surface plasmon resonances of these nanoparticles which behave as optically functional phases. These composite materials are expected to be exploited in photonic devices. Despite the prospects of application, the traditional fabrication methods impair homogenously nucleation of nanoparticales resulting in an obstacle to control the size and dispersion of nanoparticles dopnant. Here, a new versatile processing strategy based on solid-state sintering is reported for preparation such bulk transparent glass composite. Mesoporous silica SBA-15 powders encapsulating Au, Ag and Pt nanoparticles are prepared via host-guest synthesis method and then dynamically consolidated to form a bulk transparent specimen by Spark Plasma Sintering(SPS). The whole sintering process takes place under much lower temperature (1020°C) and within very short times (10minutes) than traditional melting-quenching method. The obtained composite glasses show different colors due to the surface plasmon resonance differences from Au, Ag, Pt nanoparticles and exhibit large nonlinear optical susceptibilities (ranging in 10^{-12}~10^{-11} esu) regarding with the extreme low dopnant (ca. 0.05 wt%). This approach should be applicable to the synthesis of silica glasses embedded with a wide variety of nobel metal and semiconductor nanoparticles.



Highly-dispersed Crystalline Metal Oxide confined in the Channel of Mesoporous Silica via a Novel Templating Route

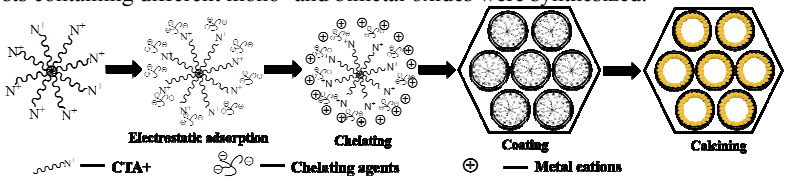
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Abstract

The statues of active sites on the surface of support are essential to improve the catalytic activity. Preparing supported catalysts with high-loading and complete monolayer dispersed metal oxides as active species is a great challenge, especially on mesoporous silicate.

Herein, a novel one-step $S^+L^-M^+I^-$ route was employed to incorporate highly-dispersed and controllable amount of crystalline metal oxide in the intra-pores of mesoporous silica in which chelating agent (L^-) first interacted with cationic surfactants (S^+) by electrostatic interaction subsequently metal cations (M^+) coordinated with L^-. Finally, silicates (I^-) was deposited and coated on the metallomicelles. By this method, functional mesoporous silica catalysts containing different mono- and bimetal oxides were synthesized.



Scheme 1. Synthetic schematic of mesocomposites via direct-templating route

Typically, MCM-41 encapsulating monometal V, Cu or bimetal (V-Cu) oxides were fabricated. Characterization results demonstrated the ordered mesostructure, increasing coverage and high dispersion of metal oxides on the pore-wall. High catalytic activity was acquired as expected. Interestingly, bimetal-loading samples exhibited a high activity for the direct oxidation of benzene to hydroquinone by H_2O_2.

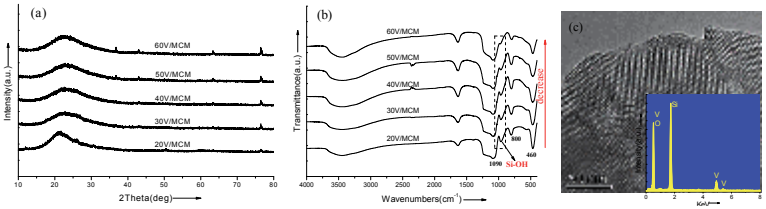


Figure 1. High-angle XRD(a), FT-IR spectra(b), TEM image(c) and EDS(inset) of Pvanadium-containing mesoporous silica

This work was supported by the National Natural Science Foundations of China (21276125, 21476108 and 20876077).

Advanced "Meso" Materials: 9 Years On

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Abstract

The field of mesostructured materials has advanced rapidly over the past few years. This presentation reflects on developments in this research area from the perspective of the *Advanced Materials* editorial office. Trends in submissions and publications are examined and hot topics identified. Insight is given into the peer-review process and tips are provided on how to enhance the prospects of publishing in your journal of choice.

Bio

Esther Levy is Consulting Editor for Wiley's leading materials science journals *Advanced Materials*, *Advanced Functional Materials*, and *Small*. She is also an Editor of the premium open-access general science journal *Advanced Science*. After completing her Ph.D. in physical organic chemistry at Cambridge University (UK) in 1997, Esther joined the Advanced Materials editorial team (Wiley-VCH, Germany) where she was appointed Editor-in-Chief in 2002. In January 2007, Esther relocated to Sydney to take up the position of Senior Commissioning Editor for Wiley's physical sciences book and journal publishing program in the Asia-Pacific region. She has been in her current role since 2011.

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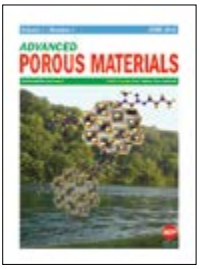
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Synthesis and Properties of Supramolecular Templated Mesoporous Silica Materials

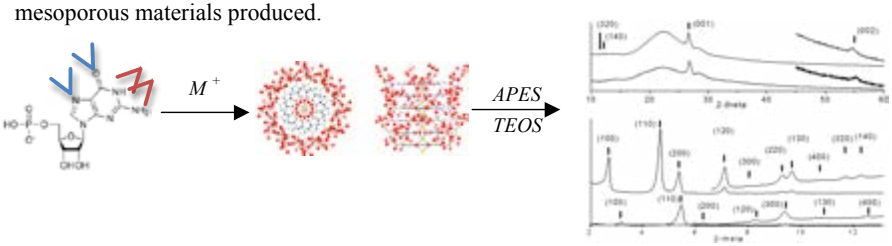
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Abstract

In recent years new approaches to the synthesis of mesoporous materials have been developed focusing on the use of non-surfactant templates that can offer new functions within the mesoporous produced without the need to eliminate the pore forming agent.[1] Such functions may include the use of pharmaceutically active compounds as pore forming agents or the use of chiral compounds to transcribe a chiral surface within the pores. Furthermore, avoiding the need to remove the pore template by calcination has both environmental and economic consequences.[2]

Recently we reported the synthesis of mesoporous material NGM-1 (*nanoporous guanosine material-1*) which is prepared through the use of supramolecular template guanosine monophosphate (GMP), a nucleotide monomer in messenger RNA.[3] The supramolecular assembly of GMP occurs via the formation of G_4-quartets, hydrogen bonded species that supported via pi-stacking interactions form chiral hexagonal columnar species. These are stabilized via the formation of cations (cations (Na^+, K^+, Rb^+, Sr^{2+}) which may direct the formation of various supramolecular structures.[4]

The synthesis and structural properties of a variety of GMP template materials will be reported, highlighting the effects that the pore template has on the pore surface. Evidence based on a variety of techniques including X-ray diffraction, transmission electron microscopy and circular dichroism as well as other spectroscopic methods will be utilized in order to show the chiral transcription of the template within the pores of the ordered mesoporous materials produced.



Guanosine monophosphate (left) and it's self-assembly via donor and acceptor hydrogen bonding (arrows) for the formation of supramolecular templates in the synthesis of ordered mesoporous materials. Right: XRD diffraction pattern of as-synthesised samples of NGM-1, showing the high structural ordering of the pore template.

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Surfactant-Directed Synthesis of Zeolite Nanosponges using Bulk Crystal Seeds

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Abstract

Mesoporous MFI zeolite was hydrothermally synthesized using di-ammonium surfactants with the addition of a small amount of bulk MFI zeolites as the seed.[1] The synthesized MFI zeolite was in a form of nanosponge morphology, in which 2.5-nm thick MFI zeolite layers were self-supporting each other to generate three-dimensionally interconneted mesopores with uniform diameters (~ 4 nm). The mesoporous architecture was retained after removal of surfactants by air calcination. In addition, the required period for crystalization of MFI zeolite using bulk crystal seeds was five times shorter than that of the non-seeded MFI synthesis. For example, the MFI zeolite synthesis took less than 3 d at 150 °C even at Si/Al = 20. The bulk zeolite additives completely disappeared in the final product, indicating that the bulk zeolite might be fragmented for the usage as seeds. We believe that the bulk crystal seeding would be effective to produce various surfactant-directed zeolites with uniform mesopore diameters.

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Nanoporous Fullerene Nanomaterials with Crystallized Framework

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Abstract

Self-assembled single crystalline fullerenes (C_{60} or C_{70}) nanostructures exhibit excellent physicochemical and optoelectronic properties including high electron mobility, high photosensitivity [1,2]. Owing to these appealing feature together with excellent electron accepting properties, dimensionally controlled nanostructures of fullerenes have received considerable interest for the possible applications in diverse fields such as material engineering and optoelectronic device fabrications including flexible optoelectronics device, field effect transistors, light emitting diodes, photovoltaic cells, sensors, and photodetectors [3,4]. Introduction of pores structures in the fullerene crystals is expected to increase the effective surface area drastically, which is expected to offer a great utility in many applications (*e.g.*, high-power solar cells and capacitors, large hydrogen storages, highly-active photocatalysts, highly-sensitive chemical and physical sensors) [5]. In this contribution, we discuss new synthetic route to the production of new class of fullerene (both C_{60} and C_{70}) crystals consisting of nanoporous structure with crystallized frameworks (Fig. 1). These novel materials offered enhanced electrochemically active surface areas compared to pristine fullerenes. Textural properties of the materials could be controlled by adjusting the synthetic condition. We also discuss our recent results on the thermal conversion of single crystal fullerene into high surface area with graphitic microstructure [7].

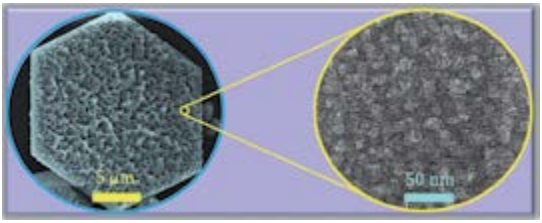


Fig. 1: Electron microscopic images of nanoporous fullerene crystal with crystallized frameworks.

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Collagen Hydrogel Preparation Method and Embryonic Stem Cell Behavior

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Abstract

We have been characterizing the colloidal collagen structures (fibers) within hydrogels used in tissue engineering and regenerative medicine applications with multiphoton imaging. Multiphoton imaging employs two-photon fluorescence (TPF) and second harmonic generation (SHG) contrasts. This technology is uniquely suited to non-invasively investigate self-assembly in highly hydrated soft supramolecular systems in 3D.

The paper reports on our efforts to evaluate collagen hydrogel preparation methods on the formation of collagen fibers and interconnected channels that stabilize these materials along with behavior of embryonic stem cells cultured on them. It emphasizes that polymerization, cross-linking chemistries and material degradation processes are critically important parameters for preparation and maintenance of cell-containing collagen formulations.

3D hydrogels were prepared from different initial collagen concentrations (2 g/l or 4 g/l) and polymerization temperatures (27 °C or 37 °C). In a separate experiment, 2 g/l 37 °C hydrogels were stabilized through the nontoxic cross-linking with carbodiimide (EDC), EDC/*N*-Hydroxysuccinimide (NHS) or genipin. Overall, nine envisioned conditions of how stem cells could be set up to interact with scaffolds in tissue engineering and regenerative medicine applications were evaluated.

In 37 °C polymerized hydrogels, the elastic modulus G' is significantly higher then the viscous part G". The dynamic mechanical properties for hydrogels prepared at 27 °C are more variable. The increase in the moduli for the 2 g/l 37 °C cross-linked hydrogels correlates with the degree of cross-linking. All cross-linkers reduced the viscous part G" of the modulus, implying that cross-linked materials are more rigid and non-flowing compared to not-cross-linked hydrogels. Genipin led to a highest degree of cross-linking and a sizable increase in the elastic modulus of the prepared hydrogels.

The cells encapsulated or placed on top of 4 g/l hydrogels extended slower compared to cells interfaced with 2 g/l materials. Initial collagen concentration and cross-linking both affected the embryonic stem cells' behavior in a topographic model.

Hollow Mesoporous Silica Nanoparticles for Biomedical Applications

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Abstract

Hollow mesoporous silica nanoparticles (HMSNs) show the promising application in drug delivery for chemotherapy due to their well-defined mesopores and large hollow interiors.[1] We will introduce our recent researches on the rational design, elaborate fabrication and biomedical applications of HMSNs. A facile and efficient "structural difference-based selective etching" strategy was developed for the synthesis of highly dispersed HMSNs with controllable particles size,[2] pore size[3] and multifunctionality.[4] Importantly, the composition of HMSNs was tuned by incorporating functional-organic groups into the framework of HMSNs, endowing them with the specific features of improved biocompatibility, stimuli-responsive drug-releasing pattern and enhanced chemotherapeutic efficiency.[5-6] In addition, the applications of HMSNs in reversing the multidrug resistance of cancer cells, inhibiting the metastasis of cancer cells, molecular imaging, gene delivery, HIFU-based synergistic imaging will be discussed in detail.

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Hard Mesoporous Silica Templates in the Nanoengineering of Soft Polymer Therapeutic Particles

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Abstract

Polymer carriers with finely controlled and responsive properties have received a great interest in therapeutic delivery systems for biomedical applications.[1] Mesoporous silica (MS) particles are attractive candidates as templates for the preparation of such polymer carriers, due to their facile preparation method, high loading capacity, and tunable template properties including surface area, pore size, and diameter. Recently, we have developed a technique using MS particles as templates to make polymer carriers with customised material properties allowing for control over the particle elasticity, the types of therapeutics loaded, and the different biological stimuli (e.g., enzyme, pH, reduction) capable of triggering release.[2-4] The soft polymer particles can be easily prepared by infiltrating polymers into hard MS particles, followed by cross-linking of the polymer chains, and subsequent removal of the templates. The elasticity of the soft polymer particles, with a Young's modulus from 0.2 to 25 kPa, can be controlled by tailoring the polymer composition and/or the cross-linking density. The deformability of the soft polymer particles in a microfluidic blood capillary model can be tuned to be similar to that of red blood cells, which is favourable for increasing particle circulation time *in vivo*.[5,6] For therapeutic delivery, both hydrophilic (e.g., doxorubicin) and hydrophobic (e.g., paclitaxel or thiocoraline) anticancer drugs have been encapsulated in the MS-mediated polymer particles, which led to cytotoxicity in cancer cells. In addition, vaccine particles with effective dendritic cell stimulation could also be prepared using this general method, which highlights the potential of nanoengineered polymer particles for vaccine delivery.[7] The reported technique is a facile and versatile method to prepare cargo-loaded soft polymer particles, which represents a novel paradigm for the delivery of drugs and vaccines.

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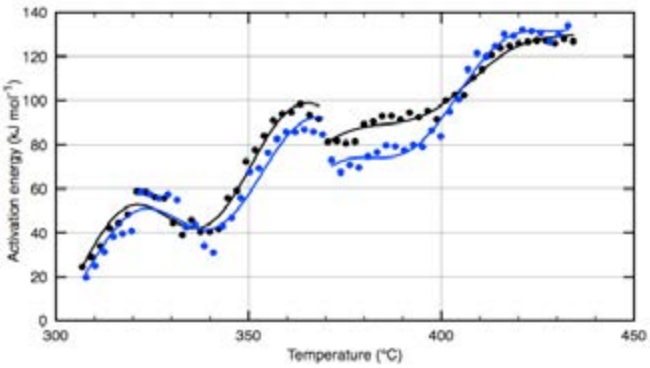
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Variable Activation Energies during Isobutane Selective Oxidation over Mesostructured Heterogeneous Catalysts

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Abstract

The kinetics of the selective oxidation of isobutane to methacrolein over phosphomolybdic acid ($H_3PMo_{12}O_{40}$) and copper (II) phosphomolybdates in the absence of gas-phase oxygen has been investigated using low-pressure steady-state and temperature-programming techniques [1]. Under these conditions proton, electron transfer and oxygen atom insertion leads to methacrolein formation and catalyst deactivation. Outer-sphere lattice oxygen ions may be replaced by solid-state diffusion [2]. Variable, oscillating and increasing activation energies with increasing temperature are apparent for consecutive runs over $Cu_{1.25}H_{0.5}PMo_{12}O_{40}$. Variations are compensated by pre-exponential factors.



The concept of variable activation energies during temperature-programming has been controversial [3]. Phosphomolybdate catalysts show activation energy variations with either consecutive single-wavelength oscillations (see above) for catalysts with high Brønsted acidity or three oscillations for low Brønsted acidity [4]. Linear regression, for each oscillation, shows increasing activation energies, with increasing temperature for all mesostructured catalysts. The two or three discontinuous waves indicate re-oxidation of the catalyst outer-sphere during temperature programming. Such broad ranges of activation energies and large wave amplitudes indicate wide distributions of active site strengths and environments. Inclusion of copper enhances substrate stability and reduces activity.

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Packed Bed Reactors with Mesoporous Silica-Supported Catalysts for Flow-Type Reactions

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Abstract

Mesocellular siliceous foam (MCF) accommodates the fixation of various objects including homogeneous organometallic or organic catalysts and bulky biocatalysts and facilitates various transformations of numerous types of substrates with high catalytic activity and recyclability, associated with its uniform, ultralarge, and 3-dimensionally interconnected pores. Particularly, its good mechanical strength and high porosity make it highly suitable for a packing material in a packed bed reactor, potentially utilized as a continuous flow reactor which is environmentally friendly. Upon immobilizing the homogeneous organometallic or organic catalysts, silica is not a popular support material due to the reactive silanol groups on surface, which may lead to lowering catalytic activity and selectivity.

Spherical MCF microparticles have been successfully prepared by a simple modification of conventional method. They show excellent performance as a stationary phase in reverse-phase column chromatography and size exclusion chromatography (SEC) in conjunction with a potential usage as a good packing material. Using the spherical MCF, we have successfully developed various heterogeneous catalysts by immobilizing a variety of homogeneous organometallic catalysts, organocatalysts and biocatalysts. To minimize the influence of free silanol groups, we have developed a simple method of partial pre-capping. Using this efficient method, MCF-supported chiral bisoxazoline catalysts show comparable selectivity and reactivity to the homogeneous counterparts through immobilization. The immobilized homogeneous catalysts have been applied to a packed bed reactor for flow-type reactions. The partial pre-capping method has been successfully applied to immobilization of homogeneous ruthenium-based metathesis catalysts achieving high reactivity and good recyclability and then flow-type reaction with a packed bed. Another method has been developed by using simply the pressure to immobilize enzymes in hydrophobically modified cage-like nanopores. The immobilized enzymes show excellent catalytic activity and selectivity as well as reduced leaching and excellent thermal selectivity. This system has been also applied to a continuous flow reaction. In addition, uniform dispersion of metal oxide catalysts on the MCF surface led to efficient conversion of ethanol to 1,3-butadiene through gas phase reactions in packed beds. Our results demonstrate that the MCF is a very useful support material for flow-type reaction systems with packed beds.

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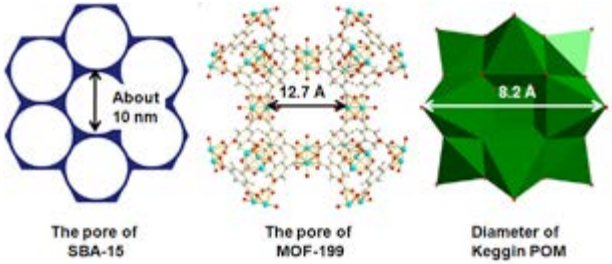
Facile Synthesis of POM@MOF Embedded in SBA-15 as a Steady Catalyst for the Hydroxylation of Benzene

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Abstract



Scheme1 The pores sizes of SBA-15, MOF-199 and the diameter ofKeggin PMo_9V_3 POM.

Polyoxometalates (POMs) are anionic early transition metal-oxygen clusters and have diverse applications in catalysis, electrochemistry, photochemistry, bioscience and material science because their active sites can be designed and manipulated at molecular and atomic levels [1]. However, POMs are difficult to be recovered directly from the liquid reaction phase because they are highly dispersed in the reaction medium.Metal organic frameworks (MOFs) as a promising class of hybrid crystalline materials are constructed by bridging organic ligands between their metallic moieties[2]. By means of covalent or electrostatic interaction, POMs can be encapsulated into appropriate metal organic frameworks (POM@MOF)[3], forming orderly arranged organic framework encapsulated POMs. Furthermore, based on the size of POMs and MOF frameworks, we believe that the hybrid POM@MOF catalyst could be finely fitting with the right size in the SBA-15 pores as indicated in Scheme 1.

Herein, a new hybrid material (POM@MOF@SBA-15, PMS) in which metal organic framework (MOF) MOF-199 encapsulated Keggin polyoxometalate (POM) catalyst (names as POM@MOF) confined in mesoporous SBA-15 was facile synthesised. Cycling experiments of the PMS catalyst were carried out in the direct synthesis of phenol from benzene and demonstrated unprecedented stability of this new type PMS catalyst.

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Mesoporous and Nanostructured Photocatalysts for Clean Hydrogen Generation

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Abstract

Mesoporous oxides are a fascinating class of porous materials. Since the discovery of ordered mesoporous SiO_2 via soft-templating already two decades ago, a large variety of mesoporous oxides either by soft- or hard-templating has been reported for a vast number of different applications including (photo-)catalysis and sensors. Photocatalytic water splitting induced by solar irradiation on a semiconductor's surface is considered as an attractive solution for sustainable solar energy conversion. The challenge of current research is to develop and investigate semiconducting materials with photocatalytic activity under visible light and with high surface area.

Mesostructured complex semiconductor oxide materials to improve photocatalytic activity for H_2 generation will be presented in this contribution. Mesoporous and fibroid photocatalysts exhibit shortened charge carrier diffusion lengths and enhanced surface area for improved photocatalytic performance.

Different synthesis strategies for the preparation of mesoporous $CsTaWO_6$ and its photocatalytic performance are presented. $CsTaWO_6$ is a semiconductor with a band gap of 3.6 eV[1] which can be decreased via nitrogen doping to approx. 2.3 eV.[2] Via evaporation-induced self-assembly (EISA), the as-synthesized mesoporous $CsTaWO_6$ show high crystallinity at moderate calcination temperatures (450-550 °C) with an average crystallite size of approx. 20 nm. The BET surface areas measured by N_2 physisorption are up to 78 $m^2\ g^{-1}$ and the pore size and pore volume calculated by NLDFT are 10 nm and 0.24 $cm^3\ g^{-1}$, respectively. The improved surface area strongly enhanced the photocatalytic hydrogen production rates of the material.

For hard-templating inside KIT-6, the resulting mixed metal oxide is formed 'in-situ' inside the pores using precursor mixtures from a citrate-based complexing route.[1] After various steps of infiltration with intermediate drying and calcination the silica template is removed, resulting in surface areas between 100 to 140 $m^2\ g^{-1}$ depending on the used KIT-6 template. Still, impurities of WO_3 and Ta_2O_5 still have to be removed, and the pore ordering has to be improved.

We have moreover prepared nanofibers of the (111)-layered perovskite photocatalysts $Ba_5Ta_4O_{15}$, $Ba_5Ta_2Nb_2O_{15}$ and $Ba_5Nb_4O_{15}$ via electrospinning.[3] This class of materials is very interesting since their band gap can also be reduced into the visible light range via nitrogen doping to approx. 1.75 eV.[4] The formation mechanism of the nanofibers was investigated in detail, indicating the intermediate formation of barium carbonate strengthening the nanofiber morphology for calcination. Superior photocatalytic activity for hydrogen generation and overall water splitting was found compared to simple powder samples, the latter upon photodeposition of a Rh-Cr_2O_3 co-catalyst system.

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Iron-Oxide-Based Advanced Anode Materials for Lithium-Ion Batteries

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Abstract

Iron oxides, such as Fe_2O_3 and Fe_3O_4, have recently received increased attention as very promising anode materials for rechargeable lithium-ion batteries (LIBs) because of their high theoretical capacity, non-toxicity, low cost, and improved safety. Nanostructure engineering has been demonstrated as an effective approach to improve the electrochemical performance of electrode materials. One effective method relies on the design and synthesis of nanostructured electrode materials with various morphologies, configurations, porosity, and a combination of micro- and nanostructures, which are all expected to promote the electrochemical processes and maintain the good structural integration. Another approach is to integrate carbonaceous matrix into the metal oxide active materials to form hybrid nanostructures, which can better buffer the volume strain due to the elastic feature of carbon supports and increase the electrical conductivity. I will introduce the novel approaches to the construction of iron-oxide-based nanostructures and the importance of proper structural and compositional engineering that leads to improved physical/chemical properties of iron oxides for efficient electrochemical energy storage (Figure 1).[1-4]

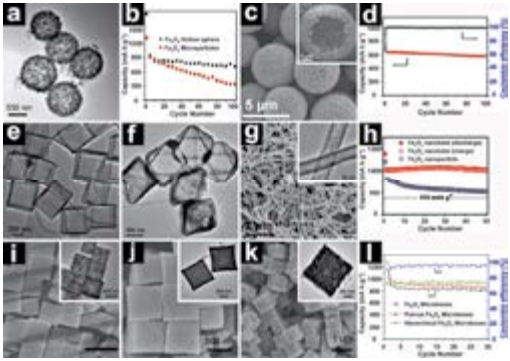


Figure 1. a) TEM image and b) cycling performance of the α-Fe_2O_3 hollow spheres. c) FESEM images and d) cycling performance of Fe_3O_4 hollow microspheres constructed by nanoplate building blocks. e,f) TEM images of $Fe(OH)_x$ nanoboxes (e) and octahedral α -Fe_2O_3 nanocages (f). g) FESEM and TEM (inset) images, and h) cycling performance of α -Fe_2O_3 nanotubes. i–k) FESEM and TEM (inset) images and l) comparative cycling performance of Fe_2O_3 microboxes (i), porous microboxes (j), and hierarchical microboxes (k).

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Yolk-Shell Silicon-Mesoporous Carbon Anode with Compact Solid Electrolyte Interphase Film for Superior Lithium-Ion Batteries

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Abstract

Silicon (Si) has a high theoretical capacity ($Li_{4.4}Si$ = 4200 mA h g^{-1}), still limits its application on Si-based anodes due to the problems of low electric conductivity, large volume change (~ 400 %), continuous formation of unstable SEI layer, and easy fracture during lithiation and delithiation process.[1] To overcome the resultant rapid capacity decay, an effective carbon coating strategy is introduced as a conductive and buffered layer. However, the dense carbon layer hampers the fast diffusion of lithium ion, results an unsatisfactory rate-capability for silicon-carbon nanocomposites.[2] Furthermore, the crucial impact of solid electrolyte interphase (SEI) is usually be neglected and the formation of SEI is hard to control. Importantly, if a stable and compact SEI is constructed, the electrolyte molecules would not penetrate through SEI layer into the active material for further growth, thereby avoiding continual lithium loss and ensuring higher Coulombic efficiency.

Here, we have engineered unique void-containing mesoporous carbon-encapsulated commercial silicon nanoparticles (NPs) in yolk-shell structures. This unique design has multiple attractive advantages: (i) the special design of the void spaces (10 and 50 nm) between the silicon NPs and the mesoporous carbon shells highlights the superiority of the unique yolk-shell structure and allows us to optimize the cycling stability while maintaining a reasonable storage capacity; (ii) the open-ended mesoporous carbon shells with accessible channels are able to facilitate the fast diffusion of Li^+ ions, and guarantee the full immersion of active materials in the electrolyte, thus contributing to excellent rate capability; (iii) our *ex-situ* characterization clearly reveals for the first time that a favorable homogeneous and compact solid electrolyte interphase (SEI) film is formed along the mesoporous carbon shells, retaining the internal void space for silicon yolk expansion and rendering superior capacity retention at a high current density. With this design, such elegant mesoporous carbon-encapsulated Si yolk-shell NPs address the challenges of rapid capacity decay and unsatisfied rate capability for Si-anodes, and deliver a high reversible capacity of ~ 1000 mA h g^{-1} with outstanding cyclability during 400 long-deep cycles, as well as superior rate-capability of 62.3% capacity retention at a very high current density of 8.4 A g^{-1}.

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Mesostructured Materials Analyzed by Low-Voltage High-Resolution SEM

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Abstract

Scanning electron microscope (SEM) has very large focus depth and images of secondary electrons (SEs) and back-scattered electrons (BSEs) can provide surface selective and atomic number-dependent information, respectively. Electrons with low impact energy can reduce both "charging-effect" in insulators without metal coating and rate of beam damage although we need to sacrifice spatial resolution. However, we have recently succeeded in obtaining low-voltage high-resolution SEM (LV-HRSEM) images by taking deceleration method, for overcoming blurring through chromatic and spherical aberrations at low electron energy. Here, we will present power of LV-HRSEM showing some examples, and also discuss advantages for characterization of meso-structured materials of LV-HRSEM.

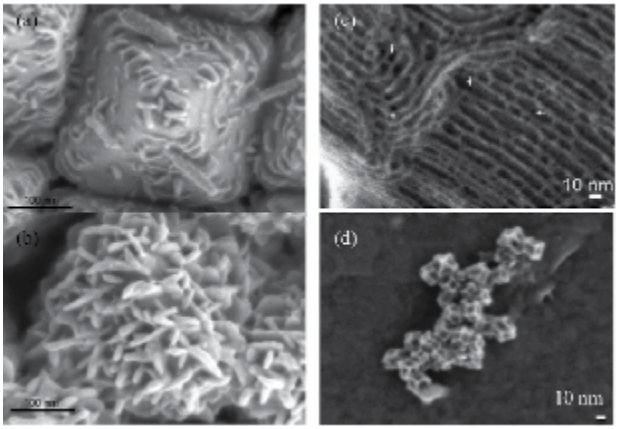


Fig.1 LV-HRSEM images. O_h-nano-Ag⊂MOF obtained from ALD Alumina, 1 cycle (a) and 5 cycles (b), which show plate-like MOF crystallites growing vertically on silver nanocrystals. SBA-15, white arrows indicate some of the pore openings at inter walls (c) [2]. Pt_3Ni nanoframes prepared from $PtNi_3$ nanocrystals (d) [3]. Images were taken by SEs with a landing energy of 300 eV (a -c) and 500 eV (d) after applying a specimen bias at -5 kV.

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Synthesis and Catalytic Application of Mesoporous Alumina and Hierarchically Porous Zeolites

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Abstract

Alumina is an important industrial chemical, widely applied in catalysis, adsorption and ceramics. However the poor textural properties of the traditional alumina have strictly limited its application in catalysis. A considerable amount of efforts have been devoted to the preparation of mesoporous alumina with superior structural properties. And the adopted strategies are commonly template approaches. In our group, mesoporous alumina materials with different pore structures, varied morphologies and modified surface acidities were synthesized. Catalytic evaluation results showed the prepared mesoporous alumina materials exhibits excellent catalytic performance in several catalytic reactions, such as the aldol condensation of cyclohexanone and catalytic cracking of heavy oils. The excellent catalytic performance of mesoporous alumina is attributed to its superior structure and unique surface properties.

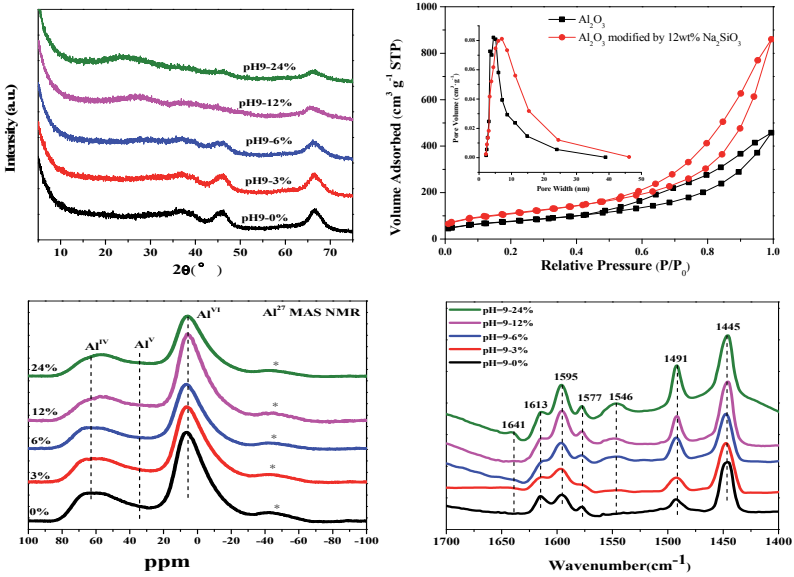
Besides, a hierarchically porous ZSM-5 zeolite was synthesized using a dual-templating method. The two kinds of templates were found to work in a cooperative way in the organization of the hierarchical pores (macropores, mesopores and micropores). The hierarchical zeolite exhibits superior catalytic performance in Claisen-Schmidt condensation of benzaldehyde and acetophenone, self-condensation of cyclohexanone and has a remarkably high selectivity to dimethyl ether in the methanol conversion reaction at relatively low temperatures, which was attributed to the fast mass transport in the three-dimensional hierarchical pore network. A cooperative assembly mechanism accounting for the formation of the hierarchical zeolite was proposed based on experimental results.

Synthesis and Characterization of Thermally Stable Mesoporous Alumina Modified by Water Glass

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Abstract

Silica-doped aluminas were prepared by using the cation-anion double hydrolysis method[1], the relationship between surface acid as well as textual properties of silica-doped aluminas and Si/Al ratios of 3, 6, 12, 24wt% was investigated. Sodium silicate as an effective pore-expanding agent greatly improved surface area and pore volume of these samples, though leading to significant decline in crystallinity. As the amount of sodium aluminate increased, more 4-coordinated and 6-coordinated aluminum were transformed to unsaturated 5-coordinated aluminum, which attributed to the strongest Lewis acid. Furthermore, the Brønsted acid site concentration increased by increasing the silica content in the 3%<6%<12%<24% samples calcined at 550 ◦C because of more silicon atoms existing on the surface as an separate silica phase[2]. Interestingly, for silica-doped aluminas, based on the results of NH_3-TPD, it was found that the total acid concentration (Brønsted and Lewis sites) was actually in proportion to the surface area.



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Shaped Silica-Polyethyleneimine Composites for CO_2 capture

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Abstract

Solid amine sorbents are of particular interest to facilitate the economic capture of CO_2 from mixed gas streams such as post combustion flue gas, towards mitigating global warming [1-2]. Mesocellular siliceous foam (MCF) – polyethyleneimine (PEI) composites have been found to provide a simple, highly CO_2 selective, and water tolerant, high capacity sorbent option for potential application to the post combustion capture (PCC) of CO_2 [2-3]. However, most studies of such materials have been concerned with the sorbent in powder form, rather than shaped as preferred for industrial processing [3-5]. Furthermore, the shaping of such products has been found to be problematic [3]. Recently we demonstrated the relevance of novel shaping technology developed to overcome these problems to prepare a broad range of silica–amine composites [6].

Mesocellular siliceous foam (MCF) and polyethyleneimine (PEI) were combined at various loadings to form a range of composite MCF-PEI powders. These powder products were then shaped into pellet form via both a manual hydraulic press [3,7], and via an automated single punch tablet press (SPTP) [6], in accord with the novel shaping method [7]. These shaped products were then subjected to isothermal CO_2 partial pressure swing adsorption processing (PPSA) at various temperatures, to assess their potential to facilitate CO_2 capture via pressure swing adsorption (PSA) and thermal swing adsorption (TSA) process technologies. The shaped products were found to exhibit good sorption capacities and kinetics at 105 °C, exhibiting up to ~5 wt % and ~14 wt % CO_2 working capacity for PSA and TSA processing respectively, at 105 °C.

The heats of adsorption for such sorbents, and the longer term process stability of one such sorbent in a simulated flue gas (containing ~15 % H_2O), were also studied.

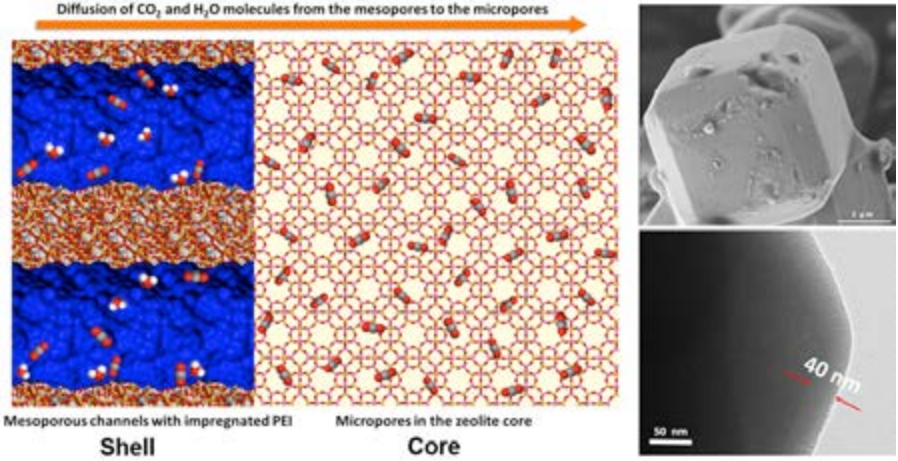
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Dynamic Reaction-induced Hindrance Effect on Moisture for CO_2 Capture in the Presence of Water on the Hybrids of Core-shell Zeolite@Mesoporous Silica with Amine-Impregnated

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Abstract

Humidity, a perennial problem in the real industrial process of CO_2 capture, can be solved by a simple and efficient approach of the dynamic reaction-induced hindrance effect of a core-shell Zeolite@Mesoporous Silica with polyethylenimine (PEI) impregnated. By a surfactant-directed sol-gel and coating processes, the core-shell micro-mesoporous 5A@MCM-41-PEI hybrids were fabricated. Under humid conditions, the amino groups of PEI in the shell can react with H_2O and CO_2 to form carbonates, which effectively prevented H_2O from diffusing into the inner core of 5A zeolite, and thus to maintain its excellent CO_2 adsorption capacity. Based on this, we proposed the dynamic reaction-induced hindrance effect of moisture for CO_2 capture. Increasing the amount of PEI loading would increases this effect and also make a great contribution for improving CO_2 uptake, but also would block the channels for CO_2 transfer. Among series hybrids, 5A@MCM-41-PEI-30 was demonstrated to be the most promising candidate for CO_2 capture in the presence of water, with the CO_2 uptake as high as 5.05 mmol/g from the simulated humid flue gas (with 15% CO_2 and 70% relative humidity at 298 K). In addition, the adsorbent also exhibited good stability and regeneration ability over 5 adsorption-desorption cycles. Therefore, the novel strategy of utilizing the dynamic reaction-induced hindrance effect through a core-shell structure with amine-impregnated would be a good solution for improving the CO_2 separation performance in practical applications.



Designing Titania Carbon Composite for Photocatalytic Membranes

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Abstract

In the last 50 years, membrane research and development have gained a significant interest for separation applications and technology. The major advantages of membrane technology are better separation efficiency, smaller footprint and ease of maintenance.[1] Furthermore, inorganic membranes have excellent mechanical, chemical and thermal stability, and durability over the conventional polymeric membranes.[2] In particular, titanium dioxide (TiO_2) membranes with separation ability could also offer other attractive functions, such as, adsorption, anti-microbial activity, catalysis and oxidation.[3]

Advanced membrane technology that can treat polluted water and separate fresh water simultaneously is of serious commercial and political interests. In this work, we demonstrate three series of photocatalytic membranes consist of high-strength titania carbon hollow fiber with excellent control of structure-property-performance relationship can be easily fabricated by controlling the sintering conditions for photo-degradation of organic dye, and simultaneously, separate fresh water. One of the major breakthrough is that we were able to overcome the trade-off between the photocatalytic efficiency and mechanical strength. These membranes were found to be produced within a critical window of sintering temperature and time. As seen in Fig. 1, the optimized hollow fiber membranes with a very high proportion of the anatase TiO_2 phase (79%) reached a 90.4% photo-degradation of acid orange 7 (AO7) with a bending modulus of 52 MPa. Furthermore, the maximum water permeation of the hollow fibre membranes varied between 6.94 (deionized water), 1.79 (AO7 feed/no UV) and 7.93 kg m^{-2} h^{-1} (AO7 feed with UV). As a consequence, we believe these hollow fibers can significantly reduce the processing and energy requirements of water treatment applications.

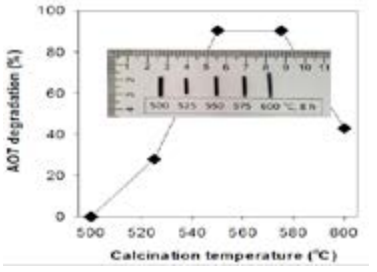


Fig 1. AO7 degradation by TiO_2 carbon composite hollow fiber membranes after 1 h under UV irradiation.

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Deposition of SBA-15 Layer and its Hydration

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Abstract

Mesoporous SBA-15 silica consists of 2D-hexagonally ordered primary mesopores with occasional plugs and unordered intrawall pores that interconnect the primary mesopores.[1] SBA-15 particles can be synthesized with platelet morphology with the mesopores running parallel to the short axis of the particle.[2] We have deposited SBA-15 platelets on hydrophilic or cationic surfaces, using a simple drop deposition method,[3] acquiring a stable monolayer of particles (see inset in Fig 1). Recently we have also succeeded in obtaining a close packed monolayer on larger areas using Langmuir-Blodgett methodology (Fig 2). We have investigated the hydration effect on the monolayer, obtained with drop deposition, using humidity scanning quartz crystal microbalance with dissipation (HS QCM-D),[4] and compared this with data from sorption calorimetry on the corresponding bulk material.

The monolayer shows the same sorption behavior as the bulk material (see isotherms from QCM-D and calorimetry in Fig 1), demonstrating that 1000 times lower amount of the sample (on the sensor) is sufficient to produce a reproducible isotherm. Further, it is clear that the particles have retained their properties during the deposition and that the sorption characteristics are unaffected by the supporting surface. The sorption-desorption of the monolayer is kinetically independent (see QCM-D isotherms at two time faster scan rate in Fig 1), and the characteristics are unaffected after several experimental cycles. We foresee that the results from our study are of relevance for bio-sensing and controlled release applications.

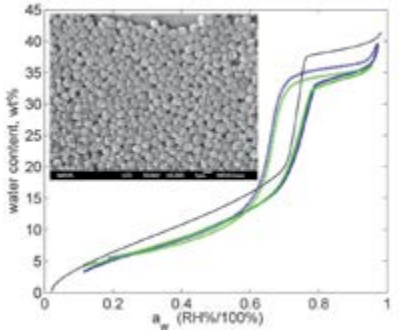


Figure1. *Water sorption (solid)/desorption (dashed) isotherms of SBA-15, obtained by QCM-D at scan rates of 50 (green) and 100 (blue) µl/min, and isotherm, obtained by sorption calorimetry (black). The inset is an SEM image of drop deposited SBA-15 platelets on hydrophilic silica sensor.*

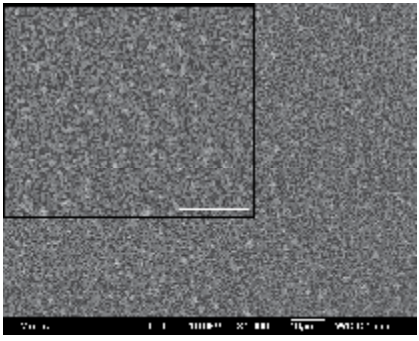


Figure2. *SEM image of SBA-15 platelets, deposited on a hydrophilic silica surface using Langmuir-Blodgett technique. The inset is a zoomed area of the image. The scale bar is 10µm.*

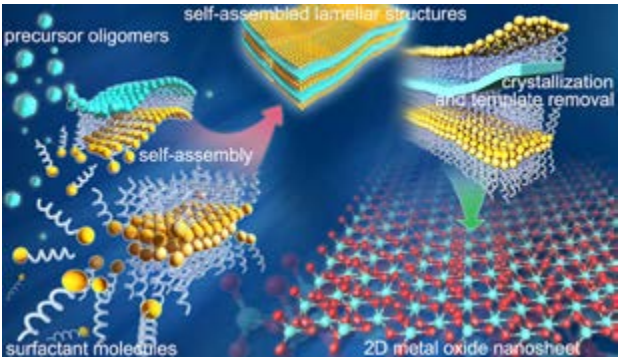
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Bottom-up Assembly of Ultrathin 2D Metal Oxide Nanosheets from Lamellar Reverse Micelles

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Abstract

Ultrathin two-dimensional (2D) nanostructures are highly desirable for obtaining superior catalytic, photovoltaic, and electrochemical performances, due to their large surface-to-volume ratio and confined thickness on the atomic scale. Although transition metal oxides have been widely studied as functional materials so far, they are mainly obtained in the forms of 0D (nanodots and fine nanoparticles), 1D (nanowires and nanotubes), and 3D mesoporous structures and nanoclusters. In contrast, 2D nanomaterials, especially those with confined thickness, have remained conspicuously absent until the recent emergence of delamination of layered compounds into single layers, referred to as "exfoliation" or "top-down" synthesis. In this presentation, we will report a novel, generalized synthesis strategy for surfactant self-assembly or "bottom-up" growth of various ultrathin 2D transition metal oxide nanostructures from molecular precursors, in which amphiphilic block copolymers and short-chain alcohol cosurfactants are intelligently employed as structure-directing agents to confine the stacking and growth of the metal oxide along the chosen direction. The obtained unique ultrathin 2D nanostructures can be the fundamental basis for emerging applications in not only energy generation/storage systems, but also electronic devices and sensors.



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Solar Hydrogen from Graphitic Carbon Nitride System

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Abstract

The development of photocatalytic systems for solar hydrogen production from water that avoid the use of expensive and/or toxic elements is highly desirable, considering scalability, cost and environmental issues involved when moving towards actual application.

To achieve an efficient photocatalytic system, co-catalysts, commonly noble metal and oxide are usually added to serve as heterogeneous electron transfer reaction sites, accelerating the oxidation–reduction kinetics. We recently reported a class of structurally fully characterized molecular cobaloxime complexes as co-catalysts for photocatalytic H_2 evolution in combination with C_3N_4 photocatalysts. The introduction of molecular co-catalysts rather than heterogeneous inorganic co-catalysts, which intrinsically leads to some inhomogeneities, when comparing different photocatalysts, guarantees that any differences are mainly due to the properties of the photocatalyst itself. Evidenced by using two different co-catalysts, *in situ* photodeposited Pt and molecular cobaloxime, we found the limit of the photoactivity of C_3N_4 is mainly due to the inherently low charge separation and mobility, not the surface area. The activity of C_3N_4 can be greatly improved by the introduction of slight disorder in the C_3N_4. A low surface area, silica template induced slightly disorder C_3N_4 exhibits a greatly improved photocatalytic hydrogen evolution rate, as compared to that of conventional bulk C_3N_4, resulting from much greater number of delocalised electrons and a suppressed recombination probability (as evidenced by fluorescence spectroscopy). In addition, by introducing the disorder via controllable post-modification, we can rationally modify the morphology and disorder content of C_3N_4 concurrently, yielding an improved C_3N_4 photocatalysts.

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Hydrothermal Engineered Zinc Oxide Nanorods on Glass Substrates

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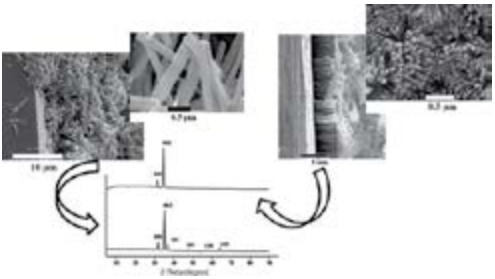
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Abstract

Vertically aligned zinc oxide (ZnO) nanorods on glass substrates were prepared hydrothermally in a two steps technique involving the preparation of ZnO seed layer and hydrothermal deposition of ZnO on the seeded-glass substrates. Post-washing treatments and quenching of the as-deposited ZnO nanorods films were proposed to hinder excessive deposition and engineer the growth of ZnO nanorods. It was shown that washing treatment and quenching process is an effective method to reduce and prevent the formation of randomly oriented growth of ZnO nanorods on glass substrates. The XRD patterns shows only the existence of (002) and (100) peaks of ZnO after treatments with increased textural coefficients on (002), TC_{002} from 3.94 to 5.23. This indicates suppressed growth of ZnO crystallites along (101). Nanorod diameters, length and density were then engineered hydrothermally through alternating hydrothermal temperatures. High hydrothermal temperatures reinduced the growth of random orientation of ZnO crystallites along (101). The TC_{002} increases with the hydrothermal temperature to reach a maximum of ca. 4.62 at 40 minutes, and then decreases with further increase of the temperature. It was also observed the rise on the density of nanorods as the temperature increase. Bandgap energy of the resulted ZnO nanorod thin films ranging from 3.69 to 3.79 eV. These results demonstrate that the growth of ZnO nanorod on glass substrates can be engineered by hydrothermal treatments leading to the formation of highly-oriented ZnO nanorods films. Hydrothermal technique with post-treatment offers a robust and efficient technique to prepare vertically-aligned ZnO nanorod potential as photoanodes for dye-sensitized solar cells.



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High Efficient Nanocatalysts based on Mesoporous Silica via Rapid Synthesis

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Abstract

Mesoporous silica materials featured with large surface area and ordered mesopores such as MCM-41 and SBA-15 are widely used as catalysts or the supports in heterogeneous catalysis. During the past decades, numerous routes for the synthesis of MCM-41 materials have been developed. Recently, we developed a one-step method for the synthesis of [Si]MCM-41 and [Al]MCM-41 materials with different silica/alumina ratios at room temperature. This type of [Si]MCM-41 contained the high amount of OH groups with weak acidity, which could initiate the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam with the highest activity compared with other types of silica [paper in preparation]. [Si]MCM-41 materials doped with Al were able to enhance the acidity of SiOH groups and generate Brønsted acidity in [Al]MCM-41, which were found to be catalytically active sites for phenylglyoxal conversion in alcohols and contributed the much higher turnover frequency (99.3/h) than a dealuminated zeolite Y (1.7/h) [1]. The high density of weakly acidic OH groups could enhance the Ni dispersion on the internal surface of [Si]MCM-41 to promote the hydrogen production and minimize the coke formation during biomass gasification [2]. The location of Ni particles within MCM-41 support had influenced the catalytic performance [3]. One significant advantage of our one-pot synthesis was to rapidly alter the surface property of MCM-41 for better multi-functional catalysts. For example, the open and close of support acidity had been tuned for the higher performance of Ni/MCM-41 catalysts in CO_2 reforming of methane [4]. After the well design of surface acidity of [Al]MCM-41, it was observed that the ionic effects to Pt surface were generated by the covered acid sites rather than free acid sites and the late only enhanced the hydrogenation conversion of aromatic ketones [5]. In addition, the rich base sites on MCM-41 could stabilize the catalytically active single-sites Pt-O(OH)x- and Au-O(OH)x- species for the low-temperature water-gas shift reactions [6,7].

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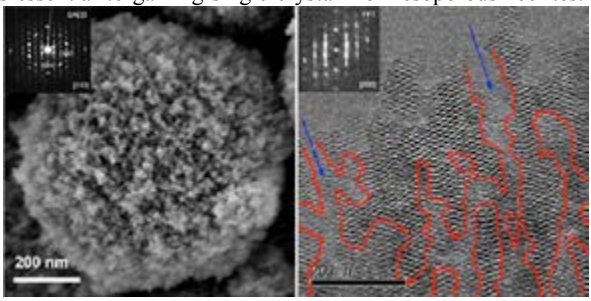
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Mesoporous Zeolites Templating by Nonsurfactant Cationic Polymer and their Enhanced Performance in Catalytic Combustion of Toluene

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Abstract

Mesoporous zeolites are useful solid catalysts for conversion of bulky molecules because they offer fast mass transfer along with size and shape selectivity [1-3]. We report here the successful synthesis of mesoporous aluminosilicate zeolite Beta from a commercial cationic polymer that acts as a dualfunction template to generate zeolitic micropores and mesopores simultaneously [4]. Using high-resolution electron microscopy and tomography, we discovered that the resulting material (Beta-MS) has abundant and highly interconnected mesopores. More importantly, we demonstrated using a three-dimensional electron diffraction technique that each Beta-MS particle is a single crystal, whereas most previously reported mesoporous zeolites are comprised of nanosized zeolitic grains with random orientations. The use of nonsurfactant templates is essential to gaining single-crystalline mesoporous zeolites. The single-crystalline nature endows Beta-MS with better hydrothermal stability compared with surfactant derived mesoporous zeolite Beta. Beta-MS also exhibited remarkably higher catalytic activity than did conventional zeolite Beta in acid-catalyzed reactions involving large molecules.



Furthermore, we also found that mesoporous Beta (Beta-MS) zeolite-supported Pt catalyst has high activities and superior catalyst life as well as low apparent activation energy in the catalytic combustion of low concentration toluene, compared with conventional Beta zeolite-supported Pt catalyst [5]. These results could be positively related to the presence of mesoporosity in the Beta-MS zeolite, which is favorable for mass transfer and dispersion of Pt particles. The excellent catalytic performance of Pt–R/Beta-H would be potentially important for the catalytic combustion of VOCs in the future.

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Aerosol-Assisted Assembly and Processing of Functional Mesoporous Microspheres via a Micro-Fluidic Jet Spray Drying Technology

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Abstract

Aerosol route is a general method for assembly and processing of particulate materials, including mesoporous particles.[1, 2] This method can strongly couple chemistry and process, thus attracting broad interests to explore functional materials. However, conventional aerosol methods for the synthesis of porous particles often lead to relatively small-sized (sub- to a few micrometers) particles with very wide particle size distributions. Herein, we demonstrate a unique micro-fluidic jet spray drying technology for the fast assembly and processing of mesoporous microspheres with large (a few to a few hundred of micrometers) and highly uniform particle sizes (Figure 1). By adopting this technology, we reported versatile approaches (such as the "surface locking" approach) for the synthesis of mesoporous carbon and carbon-based microspheres (either solid or hollow) with ordered mesostructures, hierarchical pores, high surface areas and large pore volumes.[3] Combining sol-gel chemistry and self-assembly, we reported the synthesis of a series of uniform mesoporous oxides (silica, alumina, and titania) and MOFs microspheres (microparticles).[4,5] By controlling chemical nucleation and growth during fast drying, we demonstrated one-step synthesis of mesoporous metal-doped functional microspheres, such as magnetic carbon microspheres.

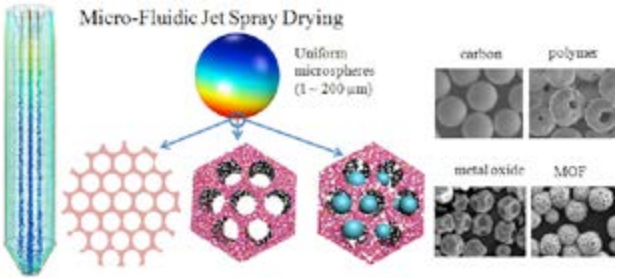


Figure 1. Illustration of the synthesis of mesoporous microspheres via the micro-fluidic jet spray drying technology

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Formation of the Photonic Macroporous Architectures Using Multilayer Core-shell Microphase-Templating Method

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Abstract

Ordered macroporous materials with the pore diameters comparable to optical wavelength and expected to have unique optical properties such as photonic bandgaps and optical stop-bands.[1] To drive the self-assembly process into the macroporous scales, we developed a delicate method using the multilayer core-shell microphase-templating route through the self-assembly of amphiphilic ABC triblock terpolymer and a silica source in a mixture of tetrahydrofuran and water.[3] A hollow double diamond architecture is synthesized first, which exhibits structural color that ranged from violet to blue in the visible wavelength range. The structure shows a porous system separated by two sets of hollow double-diamond frameworks shifted along <001> and adhered to each other crystallographically due to the loss of the mutual support in the unique synthesis, forming a tetragonal lattice ($I4_1/amd$). Calculations demonstrate that this is a "runner-up" photonic structure with complete band gap. Besides, we showed that electron crystallography is the only way to solve the complex structure. By using different template molecules, various mesoporous and macroporous architectures, including spherical close packing, 2D cylindrical packing, minimal surface-type diamond and primitive with different shift, have been synthesized. The structures, photonic properties and the formation mechanism of these materials have been investigated in detail. These results could provide significant opportunities in various research areas and open new horizons in developing new materials in chemistry and materials science.

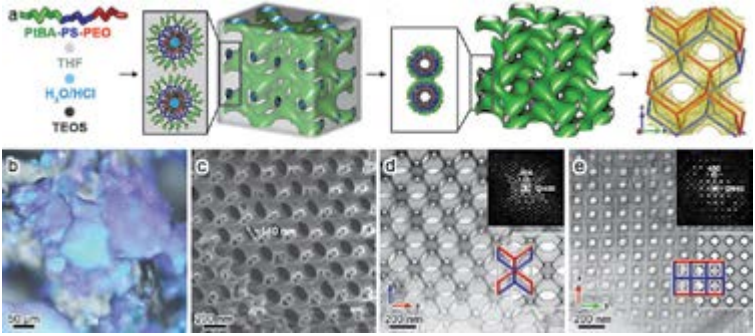


Figure 1. Schematic drawing (a), optical micrograph (b), SEM image (c) and TEM images (d-e) taken from the macroporous silica.

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Atomic Homogeneous Dispersed ZnO/N-doped Nanoporous Carbon Composites via Water Steam Carbonization of ZIFs with Enhanced CO2 Uptake Capacities and High Efficient Organic Pollutants Removal from Water

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Abstract

Porous carbon–metal oxide nanocompositess have attracted huge interest due to their promising potential in environmental applications such as gas sorption and contamination removal from water. Reducing CO_2 emission is a key environmental challenge due to its potential effect on global warming. In addition, removal of organic pollutants from industrial and household wastewater is also an important environment issue and carbon-semiconductor composites have been explored for organic pollutants removal from wastewater.[1] However, the components in these porous carbon-metal oxide composites usually cannot achieve homogeneous dispersion since they were frequently prepared by mechanical or physical mixing the metal oxides with the porous carbon materials. Recently, metal organic frameworks (MOFs), have emerged as promising precursors for the preparation of porous carbon based metal or metal oxide composites.[2,3] Due to the inorganic-organic molecular-like crystal structure of the parental MOFs, the generated metal or metal oxide can be retained homogeneously within the nanoporous carbon matrix.[4] However, their performance in targeted applications rely on the selected materials synthesis and product strategies.

In this work, we developed a mild, green and one-step carbonization of zeolitic imidazolate framework-8 under water steam at high temperatures to generate atomic homogeneous dispersed ZnO/nanoporous N-doped carbon composites. The use of water steam during the carbonization process holds the key to obtaining the fine and homogeneously dispersed ZnO nanoparticles within the functionalised nanoporous carbon matrix. The resulting advanced functional composite possessing a higher specific surface area, a larger pore volume and abundant oxygen-containing hydrophilic functional groups, exhibits exhibited excellent CO_2 uptake capacities, efficient adsorption and photodegradation performance in the removal of methylene blue from water under visible light irradiation with excellent recyclability.

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Facile Synthesis of Graphene Doped Iron Sludge by Fenton's Reagent Method and it's Application for Removal of Organic Contaminants through Heterogeneous Fenton Degradation

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Abstract

Graphene-iron sludge composites were synthesized using little amount of graphene doped with the iron sludge which generated from Fenton process. XRD, XPS and Raman analyses clearly showed the existence of graphene in the composite, the iron sludge in the composite was mainly FeOOH. FESEM showed the smooth and uniform structure of the Fe-G-0 sample and the particle size was 1-2 μm. The surface area and the corresponding pore size of the composites were affected by the graphene content in the sample. Under optimum conditions (0.03 g of graphene doping, 1 g/L of catalyst dosage and 10 mmol/L of H_2O_2 dosage), the Fe-G-3 showed much higher catalytic degradation efficiency of RhB as compared to the Fe-G-0, which could be ascribed to the increased pore size and enhanced adsorption property toward RhB. The degradation of ARG and MB confirmed the catalytic property of the Fe-G-3. Photoluminescence and capture experiments indicated that •OH radicals were the main active species for the heterogeneous degradation process.

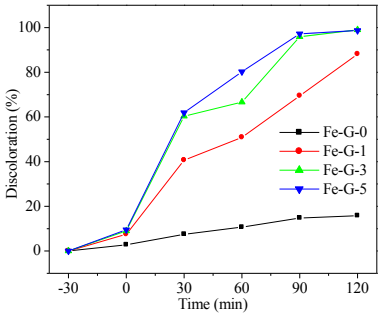


Fig. 1. Effect of graphene content in the composite for the discoloration RhB by Fe-G/H_2O_2.

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Amino-functionalized Ordered Mesoporous Carbon for the Separation of Toxic Microcystin-LR

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Abstract

Microcystin-LR (MC-LR), a type of cyanobacterial toxins, is a major risk factor in drinking water with its large monocyclic molecular size (length of 1.9 nm) and structural stability[1,2]. A reliable process to remove MC-LR from water sources is of urgent need, especially in eastern and southwestern China where many lakes are heavily polluted. Ordered mesoporous materials offer a totally new strategy for water purification[3].

Amino-functionalized ordered mesoporous carbon materials with high surface areas are fabricated from bimodal mesoporous carbons as the matrix and functionized with a three-step chemical modification of oxidation, acylation and amidation[4,5]. The mesostructural regularity, textural evolution, property and density of the surface functional groups are characterized. The obtained amino-functionalized mesoporous carbon possesses an ordered mesostructure, a high surface area (1,063 m^2/g), a large pore volume (0.7 cm^3/g) and mesopores (2.3 and 4.8 nm). More importantly, the surface is positively charged under neutral pH. This type of nanomaterials is designed for sorption and separation of negatively charged large molecules due to the synergic advantages of positively charged amino groups, high surface area, and interconnected large mesopores. Batch and column experiments demonstrate its outstanding adsorption capability (580 and 334 mg/g respectively) for the removal of Microcystin-LR (M_W = 995), much better than conventional activated carbon (<64 mg/g). Furthermore, this material can be effectively regenerated by methanol.



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The Effect of Microwaves on the Oxidative Properties of Niobosilicates and Nioboorganosilicates

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Abstract

Periodic mesoporous silicas containing niobium (Nb-PMS) represent a new class of materials suitable for a broad range of applications, i.e. catalytic reactions. In addition, the incorporation of various organic groups into these materials provides enormous possibilities to tune their chemical and physical properties. Especially, the introduction of specific functionalities into the walls of mesostructured silicas has received an immense attention in order to improve interactions at the water (oxidant)-organic interface. The main goal of this work was to evaluate the potential of microwave heating for the liquid catalytic oxidation process.

A direct synthesis route was used to prepare promising functionalized materials, ordered mesoporous niobosilicates (Nb-PMS) and nioboorganosilicates (Nb-PMO). The nanostructured Nb-PMSs have been synthesized by the use of tetraethyl orthosilicate, while Nb-PMOs by using the bridged silsesquioxane precursors containing two different organic bridging groups ($(C_2H_5O)_3Si\text{-}R\text{-}Si(OC_2H_5)_3$, R – ethylene (denoted as Nb-PMO-E) or octylene (Nb-PMO-O). The new materials exhibited high surface area and quite uniform mesopores of width ca. 8-19 nm. It is worthy to add that the use of large organosilanes as the exclusive silicon source has led generally to amorphous materials, while in our case (Nb-PMOs) the highly porous materials were obtained.

Since Nb-PMOs were expected to find application as a water-tolerant solid catalyst for reactions that require weak acidic sites and low temperatures, they were tested for various oxidation reactions with hydrogen peroxide as oxidant. It was shown that the novel Nb-containing organosilica materials are suitable for epoxidation of olefins. The activity in cyclohexene oxidation was found to be higher for Nb-PMO-O than for Nb-PMO-E materials. The new hydrophobic catalysts showed better performance (almost twice increase in epoxide selectivity) when compared to the niobosilicate catalyst although they had similar structural/textural properties, but only slightly improved the olefin conversion. An increase in the chain length of organic precursor was a contributing factor for higher hydrophobicity and thus a better selectivity. The microwave-assisted cyclohexene oxidation over Nb-PMOs was completed within 60 min whereas the conventional oxidation took at least 36-40 h for completion. The epoxide yields obtained from microwave-assisted synthesis was slightly higher than from the conventional process.

The catalysts were also used for hydroxylation of phenol with H_2O_2. The effect of contents of catalysts and H_2O_2 were investigated. The results show that Nb-PMOs are the promising candidate for industrial output due to their high catalytic activity, low tare formation and easy physical separation.

A Nanospherical Ordered Mesoporous Lewis Acid Polymer for Direct Glycosylation of Unprotected and Unactivated Simple Sugars in Water

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Abstract

The continued depletion of fossil reserve and the increasing environmental consciousness stimulate our society towards the search for the alternative renewable sources for chemical synthesis. One special opportunity to meet the challenge is the utilization of simple sugars, which are abundant, inexpensive and renewable.[1] In this regard, the fabrication of robust solid catalysts which can selectively synthesize highly functionalized carbohydrate derivatives from unprotected and unactivated simple sugars in water have attracted significant interest in recent years. Nanospherical ordered mesoporous materials are considered as the good candidates for chemical transformations because of their high surface area and nanoscale channel length.[2] Recent elegant studies have shown that nanospherical mesoporous silica-based catalysts exhibited superior catalytic performances compared to traditional mesoporous catalysts with irregular shapes in various chemical transformations. To the best of our knowledge, the use of nanospherical ordered mesoporous catalysts for efficient synthesis of sugar derivatives has not yet been reported. In this work, Herein we described the preparation of a novel nanospherical ordered mesoporous Lewis acid polymer ($Sc(OTf)_2$-NSMP) through converting the phenyl groups in the mesoporous phenol-formaldehyde polymer framework to Scandium triflate-functionalized polymeric skeleton (Figure 1a). In the C-glycosylation reaction between D-glucose and cyclohexane-1,3-dimedone over $Sc(OTf)_2$-NSMP, the conversion of D-glucose was 99% and the yield to xanthone-C-glucoside reached 92% after 2 d (Figure 1b), which exceeded the best results previously reported in the literature. Meanwhile, it can be generalized to obtain other xanthone glycosides from various sugars with moderate to good yields. Furthermore, it could be easily recovered and reused at least seven times without loss of its catalytic activity.

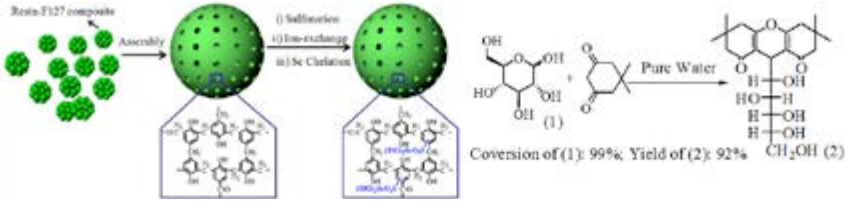


Figure 1 (a) Schematic illustration of the procedure of $Sc(OTf)_2$-NSMP, and (b) the C-glycosylation reaction between D-glucose and cyclohexane-1,3-dimedone.

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Synthesis of Mesoporous ZSM-5 Catalysts using Different Mesogenous Templates and their Catalytic Performances

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Abstract

Two kinds of mesoporous ZSM-5[1,2] were synthesized successfully via a hydrothermal method by the utilization of different soft templates - dimethyl octadecyl [3 - (trimethoxysilyl) propyl] ammonium chloride ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Cl$, TPHAC) and hexadecyl trimethyl ammonium bromide ($C_{16}H_{33}(CH_3)_3NBr$, CTAB). The obtained mesoporous ZSM-5s were compared with conventional ZSM-5 and the effect of different surfactants usage during the synthesis of mesoporous ZSM-5 on the physicochemical and catalytic properties were systematically investigated. Multiple techniques, such as XRD, SEM, N_2 adsorption techniques, HP ^{129}Xe NMR, ^{27}Al MAS NMR, ^{29}Si MAS NMR, and ^{1}H MAS NMR were employed in characterization.

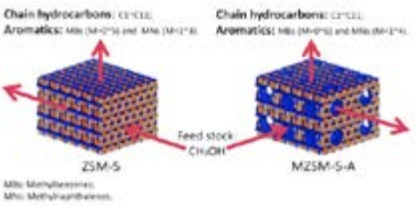


Fig 1. Schematic description of methanol conversion over ZSM-5 and MZSM-5-A.

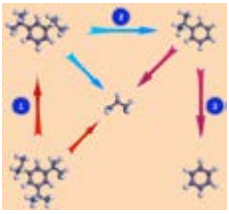


Fig 2. Main reactions during 1,3,5-TiPB cracking.

Even the synthesized MZSM-5s were with equal surface area, they presented different crystallinity, morphologies, pore size distributions, micropore-mesopore inter-connectivity, framework atom coordination states and acidity. When using these synthesized ZSM-5s as the catalysts of methanol conversion, the MZSM-5 templated with TPHAC exhibited extremely long catalyst lifespan compared with conventional ZSM-5, while MZSM-5 templated with CTAB showed no advantage in the catalyst life prolongation during the reaction. The differences in the catalytic life and reduction of coke deposition were correlated to the variation of acidity and porosity with the mesopore generation in the ZSM-5 catalysts by the usage of different structure directing agents. During catalytic cracking of 1,3,5-TiPB, the MZSM-5s showed similar conversion, as well as different product selectivity.

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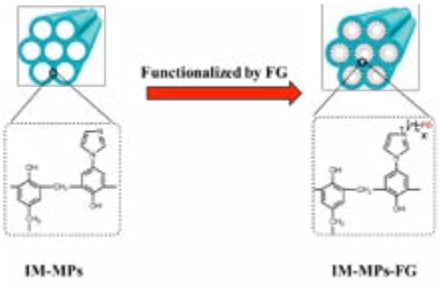
Controlled Synthesis of Imidazolium-based Ionic Liquids Functionalized Ordered Mesoporous Polymers as Novel Heterogeneous Catalysts

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Abstract

Mesoporous phenolic resins have attracted increasing attention in catalysis, electrodes and adsorbents due to their unique textual properties, such as high surface area, tunable mesostructures and the merits of organic polymers.[1, 2] Particularly, it has been demonstrated that FDU-type mesoporous polymers supported imidazolium-based ionic liquids employed as efficient heterogeneous catalysts for chemical fixation of carbon oxide (CO_2).[3] However, the multistep post-modification method inevitably suffered from the low imidazole loading and the inhomogeneous distribution of active species.

Very recently we discovered a simple and efficient method to directly synthesized ordered imidazolyl-functionalized mesoporous polymers (IM-MPs). [4] In view of imidazole structural feature, IM-MPs can be easily functionalized by a wide variety of useful organic functional groups (FG), which enables their potential application. Based on our previous studies in functionalized mesoporous polymers in acid- or base-catalyzed condensation reactions. [5, 6]. Herein, we prepared a series of functionalized IM-MPs, serving as heterogeneous catalysts with controllable FG content, which show good catalytic activities in various reactions and the advantages of easy recycling and reuse.



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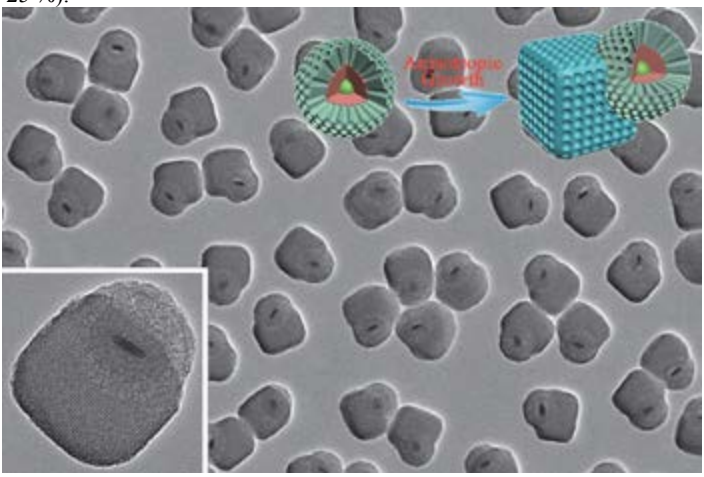
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Anisotropic Growth-Induced Synthesis of Dual-Compartment Janus Mesoporous Silica Nanoparticles for Bimodal Triggered Drugs Delivery

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Abstract

Multi-functional dual-compartment Janus mesoporous silica nanocomposites of UCNP@SiO_2@mSiO_2&PMO (UCNP = upconversion nanoparticle, PMO = periodic mesoporous organosilica) containing core@shell@shell structured UCNP@SiO_2@mSiO_2 nanospheres and PMO single-crystal nanocubes have been successfully synthesized via a novel anisotropic island nucleation and growth approach with the ordered mesostructure. The asymmetric Janus nanocomposites show a very uniform size of ~ 300 nm and high surface area of ~ 1290 m^2/g. Most importantly, the Janus nanocomposites possess the unique dual independent mesopores with different pore size (2.1 nm and 3.5 ~ 5.5 nm) and hydrophobicity/hydrophilicity for loading of multiple guests. The distinct chemical properties of the silica sources and the different mesostructures of the dual-compartments are the necessary prerequisites for the formation of the Janus nanostructure. With the assistance of the near infrared (NIR) to ultraviolet/visible (UV/Vis) optical properties of UCNPs and heat-sensitive phase change materials, the dual-compartment Janus mesoporous silica nanocomposites can be further applied into nano-biomedicine for heat and NIR light bimodal triggered dual-drugs controllable release. It realizes significantly higher efficiency for the cancer cell killing (more than 50 %) compared to that of the single triggered drugs delivery system (~ 25 %).



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Radially Oriented Mesoporous TiO_2 Microspheres with Single-crystal-like Anatase Walls for High-efficiency Optoelectronic Devices

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Abstract

Highly crystalline mesoporous materials with oriented configurations are in demand for high-performance energy-conversion devices. We report a simple evaporation-driven oriented assembly method to synthesize three-dimensional (3D)-open mesoporous TiO_2 microspheres with a diameter of ~800 nm, well-controlled radially oriented hexagonal mesochannels, and crystalline anatase walls. The mesoporous TiO_2 spheres have a large accessible surface area (112 m^2/g), large pore volume (0.164 cm^3/g), and highly single-crystal-like anatase walls with dominant (101) exposed facets, making them ideal for conducting mesoscopic photoanode films. Dye-sensitized solar cells (DSSCs) based on the mesoporous TiO_2 microspheres and commercial dye N719 have a photoelectric conversion efficiency of up to 12.1 %. This evaporation-driven approach can create opportunities for tailoring the orientation of inorganic building blocks in the assembly of various mesoporous materials.

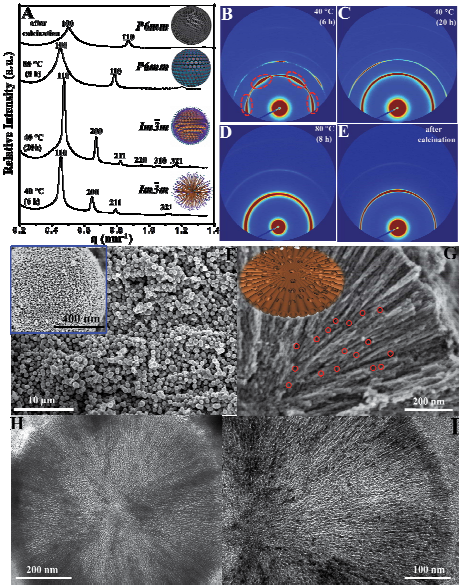


Fig.1 Microstructure characterization of the radially oriented mesoporous TiO_2 microspheres.

One-pot Synthesis of Mesoporous Titania and its Nanocomposites with High Surface Area using Spray-drying Technique at Low Temperature

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Abstract

Mesoporous TiO_2 has several potential applications due to its unique electronic and optical properties, although its structures and morphologies are typically difficult to tune because of its uncontrollable and fast sol-gel reaction. In this study we have coupled the template-directed-sol-gel-chemistry with a low-cost, scalable, and environmentally benign aerosol (spray-drying) one-pot preparation technique for the fabrication of hierarchically nanostructured TiO_2 microspheres and its nanocomposites. The parameters during the pre-hydrolysis and spray-drying treatment were varied to successfully control the bead diameter, morphology, monodispersity, surface area and pore size for improving their effectiveness for better application. The as-synthesized microspheres have a size distribution from 500 nm to 5 μm, specific surface areas larger than 160 m^2g^{-1} and mean pore sizes of several nanometers (3 ~ 4 nm). Other physicochemical properties with the experimental detail will be discussed during the presentation. Also it can be effectively separate-out the desired size-partition of mesoporous TiO_2 microspheres by a low speed centrifugation from the continuous and comparatively broad spherical size range.

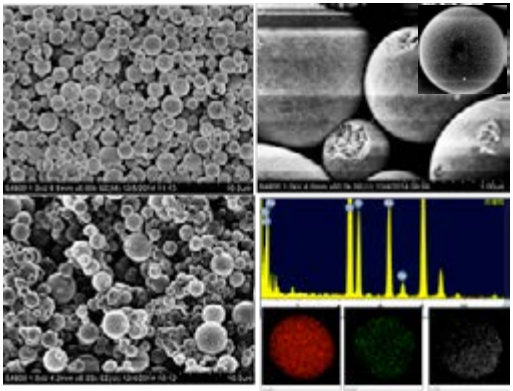


Figure: SEM images with EDAX and mapping of the as-synthesized TiO_2/nanocomposites microspheres

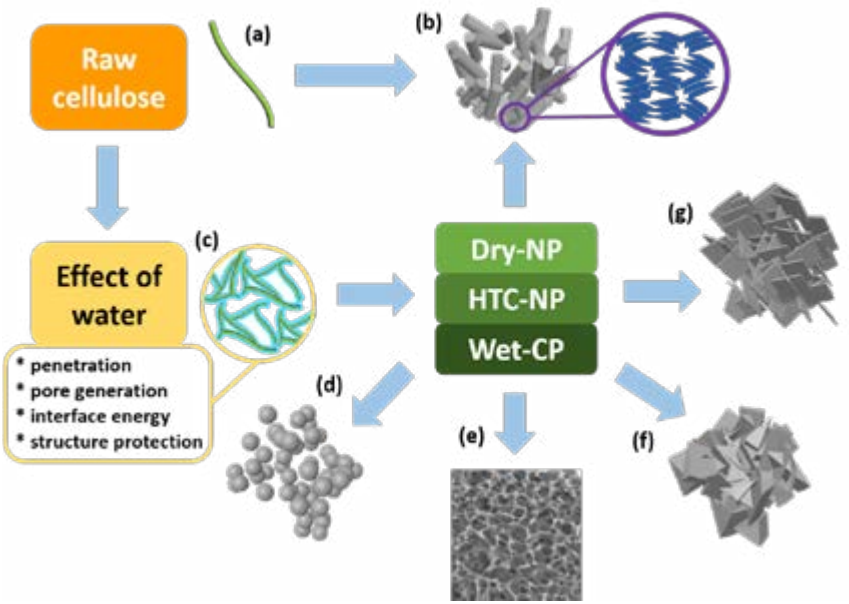
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A Study of Morphology Control of Porous Carbons Derived from Microcrystal Cellulose

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Abstract

Converting naturally available biomass into carbon structures is attracting intense scientific attention recently. A wide range of biomass materials sourced out from agriculture and industrial wastes are shown to be suitable precursors to be converted into carbon. A particular interest focuses on cellulose, one of the major components of plant constituents, as a model biomass precursor. However, it has not been clearly shown the control over morphology on the produced carbon materials. In this work, we studied the "morphology pathway" of carbon materials from microcrystal cellulose. Both pyrolysis and hydrothermal carbonization methods were used. The influence of additives, including H_2SO_4, KOH, $FeCl_3$, and $ZnCl_2$, has been investigated. The effect of water has been examined. With the proposed morphological transforming pathways as illustrated in Scheme 1, we will discuss carbonization mechanism of cellulose. Understanding the mechanism will inspire the design of novel carbon materials for different applications.



Scheme 1. Morphology pathways of cellulose.

Mesoporous Silica Nanoparticles: Selective Surface Functionalization and Particle Size Control for Optimal Theranostic Performances

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Abstract

The new generation of therapeutic systems is based on the engineering of theranostic nanomaterials which combine simultaneous therapeutic and diagnostic capabilities. Among the nanomedicine platforms which are currently under development, mesoporous silica nanoparticles (MSN) have emerged as promising materials for drug delivery and imaging applications due to their unique porosity and surface caracteristics[1]. The present communication will present a selective surface functionalization of MSN (MCM-48-type) with MRI contrast agent (DTPA-Gd) and polyethylene glycol (PEG) as a straightforward and efficient strategy that leads to the design of potential theranostic nanoparticles without porosity loss and with high drug loading capacity. The DTPA and PEG grafting procedures reported thus far have resulted in significant pore obstruction, which is detrimental to the drug delivery function of MSNs. This usually induces a dramatic decrease in porosity, thus limiting drug loading capacity. Therefore, these molecules must be selectively positioned at the outer surface of MSNs. The resulting nanoparticles not only show high colloidal stability and a remarkable and optimal MRI positive contrast enhancement but also could serve as efficient drug carriers for cancer treatment, as demonstrated *in vitro* with a model of daunorubicin as anticancer drug[2]. Moreover, this communication will present particularly efficient synthesis methods for size control of MSNs (down to 40 nm) which enable to generate small mesostructured nanoparticles with high porosity, narrow particle size distribution and high colloidal stability. The size effect of MSNs on controlled drug release as well as accumulation and diffusion into tumor will be also discussed and demonstrated *in vitro*[3].

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Designing Enzyme Cascades for Cofactor Regeneration

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Abstract

Due to their high selectivity enzymes are efficient biocatalysts but their application in organic syntheses is expensive since harsh reaction conditions can lead to enzyme denaturation. Therefore researchers try to stabilize enzymes by immobilization on suitable host materials with high retention of activity. Within the last decade mesoporous silicas have established as support material for enzyme immobilization. The pore structure of mesoporous cellular siliceous foams (MCF) is well suited to immobilize larger enzymes, since it consists of a disordered 3-D pore structure with cage-like cells (20-50 nm) interconnected by smaller windows (9-26 nm).[1-3] Surface modification of the MCF initiates hydrophobic, polar or covalent interactions between the protein surface and the surface of the MCF. Affected by the pore walls enzyme immobilization in general can lead to a higher stability compared to the free enzyme.[2] Not only the reusability of immobilized enzymes is important for upscale processes or industrial applications but also a recycling of the cofactors is desirable.

Here we present an enzyme cascade using immobilized enzymes, employing the nicotinamide adenine dinucleotide phosphate ($NADP^+$) dependent glucose-6-phosphate dehydrogenase (G6PDH), 6-phosphogluconate dehydrogenase (6PGDH) and alcohol dehydrogenase (ADH). G6PDH catalyzes the oxidation of glucose-6-phoshate (G6P) to give 6-phosphoglucono-δ-lactone (6PGL) which immediately hydrolyzes to 6-phosphogluconate (6PG), whereas 6PGDH enables the oxidation of 6PG to ribulose-5-phosphate (Ru5P). Both enzymatic reaction steps are accompanied by the reduction of an equivalent $NADP^+$ to NADPH, respectively.[4] $NADP^+$ can be regenerated from NADPH due to an ADH-catalyzed oxidation with concomitant reduction of 6-methyl-5-hepten-2-one (sulcatone) to 6-methyl-5-hepten-2-ol (sulcatol).[5] Related to the respective protein sizes we tailored the synthesis of MCF to obtain pore sizes of 18.5 nm (windows) and 30.8 nm (cells) respectively. As qualified support material for the immobilization of G6PDH aminopropyl functionalized MCF has established.[2,6] To initiate attractive interactions between the surface of 6PGDH as well as ADH and the silica host material, the pore walls of MCF have been functionalized with alkyl and aminoalkyl residues consisting of different chain lengths ($-C_3$, $-C_5$, $-C_7$, $-C_{11}$ as well as $-C_3NH_2$, $-C_5NH_2$, $-C_7NH_2$, and $-C_{11}NH_2$).[7] Enzyme uptakes, loading densities, longtime stabilities and Michaelis-Menten kinetics of the enzymes immobilized onto the above-named silicas were investigated. Furthermore, each modified MCF has been analyzed by nitrogen physisorption, thermal analysis and zeta potential titrations.

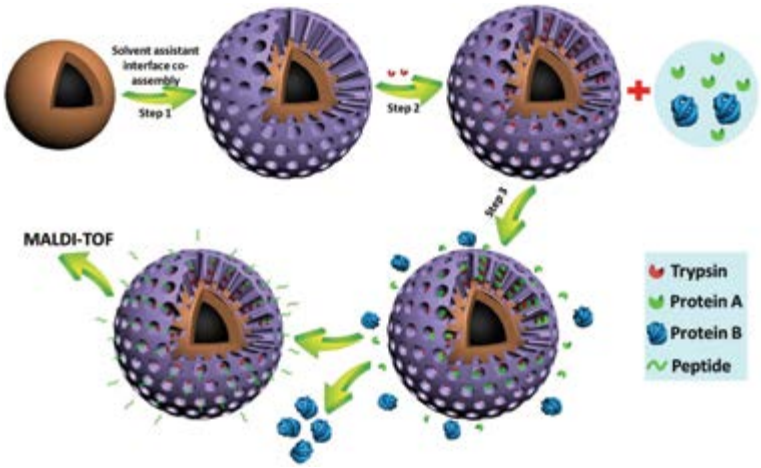
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Highly Dispersed Magnetic Mesoporous Silica Microspheres with Well-controlled Large Pores by Solvent Assistant Interface Co-assembly Method for Size Exclusion Proteolysis

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Abstract

We developed a solvent assistant interface co-assembly method to synthesize highly dispersed core-shell/yolk-shell magnetic mesoporous silica with large mesopores for enzyme immobilization and size exclusion proteolysis. This method is achieved by hydrolysis of tetraethyl orthosilicate (TEOS), interface assembly of Cetyltrimethyl Ammonium Bromide (CTAB) and silica oligomers with hexane/ether involved for enlarging the micelles onto pre-synthesized resorcinol-formaldehyde (RF) resin coated magnetic nanoparticles. The obtained core-shell magnetic mesoporous silica microspheres denoted as CSMS exhibit uniform and highly dispersed spherical morphology, well-defined sandwich structure, and large perpendicular mesopores with well-controlled pore size from 5~50 nm. Trypsin, a globular enzyme with molecular size of 3.8*3.8*3.8 nm^3, was successfully immobilized into the GLYMO functionalized mesopores of CSMS with a high loading capacity up to 97μg/mg by a simple aqueous reaction, marked as CSMS-T. The obtained CSMS-T was used for size exclusion proteolysis and exhibit excellent enzymolysis selectivity for low molecular proteins and high cycling stability.



Scheme 1: Schematic illustration of the synthesis of CSMS-T and size exclusion proteolysis
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Incorporation of Globin Proteins in Mesoporous (designed) Titania for Biosensor Applications

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Abstract

Mesoporous materials are ideal substrates for the incorporation and immobilization of proteins due to their high surface area, high pore volume and the possibility to obtain a very homogeneous, controllable pore size. Mesoporous silica is the most used substrate for the adsorption of proteins due to its large surface area and highly ordered mesopores structure.[1,2] Alternatively the use of semiconductor metal oxides such as TiO_2 could be very promising with respect to the possible join effect of semiconductor TiO_2 and redox active proteins. However the controlled synthesis of titanium dioxide is more challenging than silica due to the comparably fast hydrolysis of the precursors often leadings to disordered mesoporous structures and non-uniform pore networks.[3]

In this work, different protocols[4,5] for the synthesis of mesoporous titania have been improved to obtain highly ordered mesoporous structures and homogeneous pore sizes, that can be selected in a wide range of sizes, using different acids, allowing the encapsulation of different proteins. While adjusting the synthesis of mesoporous titania to create the required structural control for immobilization of proteins, a peculiar synthesis mechanism was observed. In a narrow range of synthesis conditions, organic titanium (IV) complexes, stable above 450°C have been revealed, resulting in new signals in the UV DR spectrum at 404 and 407nm due to the ligand-to-metal charge transfer (LMCT) between oxygen and titanium.[6] The impact of the stable organic group in the matrix has been evaluated by photo catalytic experiments.

In addition, in this work the adsorption of Horse Heart Myoglobin on commercial mesoporous titania (Millennium P500), as well as on the impact of the incorporation/immobilization on the proteins stability. Furthermore, the kinetics of the adsorption have been revealed to proceed in distinct steps. Several techniques have been used for this purpose both standard characterization tools such as UV vis and IR spectroscopy, and different continuous-wave and pulsed paramagnetic resonance (EPR) methods, which provide information about the structure around the HEME iron. The adsorption of Horse Heart Myoglobin on different designed mesoporous titania and the electrochemical analysis of the incorporated proteins are the next step of this work.

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High Density Heteropoly Acid inside Mesoporous Silica Nanoparticles for Gold Reduction and Catalysis Application

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Abstract

Inorganic polyoxometalate nanoclusters, such as phosphotungstic acid (PTA), show strong acidity and redox capacity simultaneously proton. A preparation of small gold nanoparticle with photoreduction of $AuCl4^-$ catalyzed by PTA in confinement space is designed with mesoporous silica.[1] Here we employ mesoporous silica nanoparticles (MSN) with highly ordered pore diameters (4-6 nm) to confine growth dimensions of PTA in various loading concentrations. Mesoporous silica nanoparticles were functionized with (3-Aminopropyl)trimethoxysilane (APTMS). High loading of PTA inside individual mesochannel was identified by TEM/HRTEM images and EDX analysis. Hexagonal packing of mesochannels having periodic PTA nanoparticle assembly was directly evidenced in the reduction intensity of the small-angle XRD patterns. Under exposure of UV light, PTA is able to reduce very small gold nanoparticles quickly in the nanochannels of mesoporous silica nanoparticles. Solid acidity of the Au-PTA/MSN was characterized by ammonia TPD, and pyridine-DRIFT studies. We also tested the efficiency of high-density Au-PTA nanoparticle system in catalytic oxidation/cracking of glycerol in H_2O_2 aqueous solution. The major product was formic acid. The catalytic mechanism will be discussed.

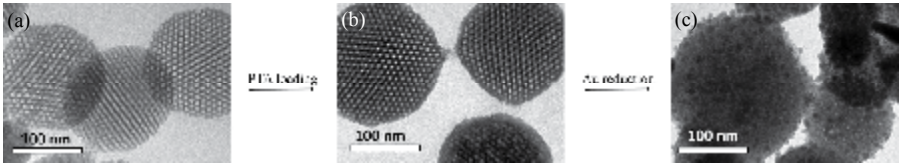


Figure 1. TEM images of (a) APTMS functionized MSNs, (b) MSNs after loading PTA and (c) after Au reduction.

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Aging Treatment to Control the Hierarchical-pore-structured of SAPO-11 Zeolite

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Abstract

Dry gel preparation is an essential step to synthesize zeolite by dry gel method. Several aging methods (e.g. microwave treatment and ultrasonic treatment) are employed to regulate pore structure, morphology, and acid character of SAPO-11 molecular sieves. X-ray diffraction, scanning electron microscopy, N_2-adsorption, pyridine-adsorbed fourier transform infrared spectroscopy, and ^{29}Si MAS NMR were employed to investigate the effects of aging treatments on SAPO-11 products. Mesopore structure is enhanced after aging, which is formed as wedge-shaped hole. In addition, these treatments effectively affect depolymerization/ polycondensation reaction of silicon species and growth rate of different crystal planes. Hydroisomerization catalysts (Ni/ SAPO-11) with hierarchical pore structure and appropriate acid characters exhibit a higher conversion of heptane and an excellent selectivity for iso-hydrocarbon.

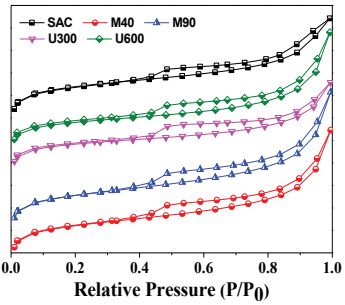


Fig. 1 N_2 adsorption- desorption isotherms of samples

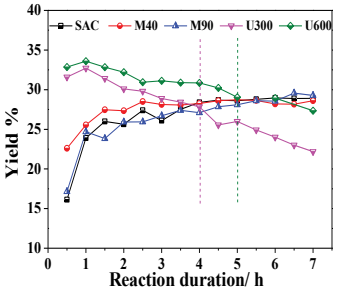


Fig. 2 Hydroisomerization performance of catalyst with different SAPO-11 support

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Metal-free Heteromatom-doped Mesostructured Carbons for Efficient Electronic Oxygen Reduction

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Abstract

Carbons represent a persistent area of research interest due to the fascinating variety and versatility, extensive availability, and intriguing physicochemical properties, exhibiting crucial potentials for sustainable energy and environment.[1] Although great progress has been achieved in exploiting methods for synthesizing heteroatom-modified carbons, the intentional regulation of dopant species and the corresponding concentrations is still highly challenging through present methods. As a consequence, it is considerably desirable to explore a general and efficient protocol to engineer heteroatom-doped carbons and the related composites. We have devoted ourselves to rationally design organic-inorganic multifunctional hybrid materials.[2,3] One step further on the basis of the organic functionalities can achieve extensively marvelous materials.

Phosphorus-doped mesoporous carbons (PDMC) electrocatalysts could be directly synthesized through soft templating method, in which organophosphonic acid serves as phosphorus source. PDMC possesses high doping level, large surface area and interconnected mesopore system, ensuring the sufficient exposure and availability of catalytic sites to realize considerable catalytic activity for oxygen reduction reaction (ORR) in alkaline media (**Figure 1**).[4] More importantly, PDMC shows much better tolerance for methanol oxidation, higher durability, and comparable Tafel slopes as compared with the commercial Pt/C catalyst.

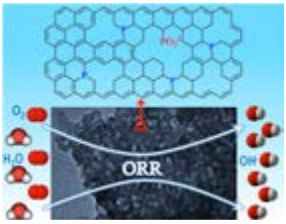


Figure 1. Scheme of PDMC for efficient ORR.

Furthermore, a novel and universal methodology based on acid-base polymerization consideration is proposed for the preparation of a wide variety of porous heteroatom-doped carbons based on.[5] The dopant species in the carbon matrixes can be facilely adjusted by judiciously regulating the acid types and the resultant concentrations can be efficiently tuned via controlling carbonization time and precursor ratios. The resultant carbocatalysts with large surface areas and well-structured porosity exhibit high oxygen reduction activity through a desirable four-electron pathway, strong durability, and methanol tolerance capability. The proposed strategy is promising for the design and development of carbon materials for fuel cells, metal-air batteries, and other renewable energy devices.

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High Performance Smart Nanoporous Hetero-Interfaces

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Abstract

High-Performance smart hetero-interfaces have recently attracted considerable interest due to unique properties, including their highly anisotropic geometry, large surface-to-volume ratio, and carrier and photon confinement.[1] Three-dimensional (3-D) nanoporous hetero-interfaces have been one of the hottest research topics in physics, chemistry, biology, and material science, due to their easily accessible pore structures and tailorable surface functionalities for applications, including energy storage and conversion, bio-tissue engineering, multi-scale drug delivery, multi-phase separation, and multi-phase catalysis.[2]

Currently, tremendous efforts are devoted to the rational synthesis of advanced porous heterostructures. Yet, if functional devices are to be made from these materials, precise control over their composition, structure, morphology, and dopant concentration must be achieved. Their fundamental properties must also be carefully investigated since the presence of a large surface and interfacial area can profoundly alter their performance.

Herein, different types of smart heterointerfaces are studied, with the aim to understand how the porosity, composition, structure, morphology, and doping of nanoporous heterostructured materials influence their performances for biomedical applications. The objective will be achieved by fabricating hetero-interfaces including 3-D porous ultralight hydrophilic and hydrophobic, porous bioinspired antenna-like structure, and porous oriented plasma gold nanopyramid arrays via an interfacial growth and self-assembly.[3-5]

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Porosity Induced Emission: Exploring Color-controllable Fluorescence of Porous Organic Polymers and their Chemical Sensing Applications

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Abstract

Fluorescent materials has spurred flourishing research interests, for they lie at the crossroad of a wide range of applications, such as light-emitting motifs, fluorescent sensors and probes, and various luminescent displays[1]. While most organic dyes, which exhibit excellent fluorescence in solutions or in suspensions, are non-luminescent in the solid state, which is known as "aggregation caused quenching" (ACQ) effect[2].

We proposed a new strategy as "Porosity Induced Emission" as an alternative way to circumstance ACQ effect. 4-diketopyrrolo[3,4-c]pyrrole (DPP), a commercial dye with the strong red light emission, was covalently incorporated into copolymerized into the skeleton of a melamine-based porous fluorescence network via a facile and catalyst free procedure to form porous organic polymers (POPs) with dual light-emission. Tuning the DPP fraction in the skeleton of these POPs would range the emission covering from red to blue in both solid-state and suspension. More importantly, the combination of fluorescence and porosity would provide more space to transduce the molecular interaction between adsorbed analytes and fluorophores to the detectable changes in light emission, leading to the fluorescence-off or fluorescence-on detection of electron-deficient or electron-rich analytes.

The "Porosity Induced Emission" approach can be an effective way to design materials with the solid-state fluorescence. This approach would be extensively applied for the common dye molecules to be emissive in the solid-state, which would be further applied as chemical sensors.

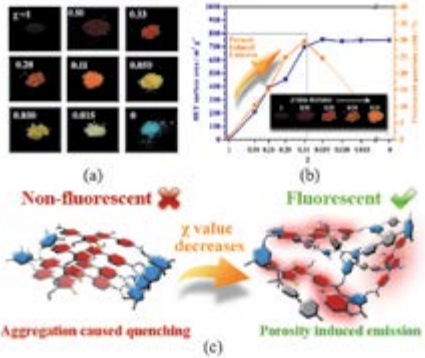


Fig.1 (a) Solid sample under a UV lamp (365 nm); (b) correlation between BET surface area and fluorescence quantum yield of POPs; (c) illustration for "porosity induced emission"

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Large Area Mesoporous Silica Thin Films with Vertically-Oriented Nanochannels on Flat Substrates

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Abstract

Mesoporous silica thin films (MSTFs) with vertically-oriented nanochannels were synthesized in a decane-CTAB-ethanol-TEOS ammonia solution. By controlling the synthetic temperature and ammonia concentration, large area and uniform MSTFs with adjustable film thickness (20 – 100 nm) can be obtained. Among these parameters, decane plays the most important role on inducing well-ordered and perpendicular mesostructures by forming a symmetrically confined space for silica condensation [1]. To support this idea, decane solution was postponed adding into the synthetic solution until forming mesoporous silica nanoparticles (MSNs) which indicates the condensation of silica and CTAB. We found that postponed the addition of decane can still induced vertical channels before forming MSNs (5 min after adding TEOS), but parallel-oriented channels was obtained after the critical time (Figure 1). In addition, MSTFs synthesized with different amount of decane were systematically studied by grazing incidence small-angle X-ray scattering (GISAXS). Both the pore size and domain size of MSTFs increased while increased the amount of decane (Figure 2). Decane not only serves as a pore-expanding reagent but also assists the self-assembly of mesochannels on substrates. High-quality MSTFs on centimeter wide substrates were expected for a variety of useful applications such as host-guest chemistry and biosensing.

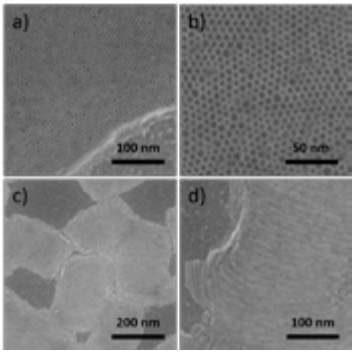


Figure 1. Representative SEM images of MSTF synthesized with addition of decane (a)(b) before and (c)(d) after formation of MSNs.

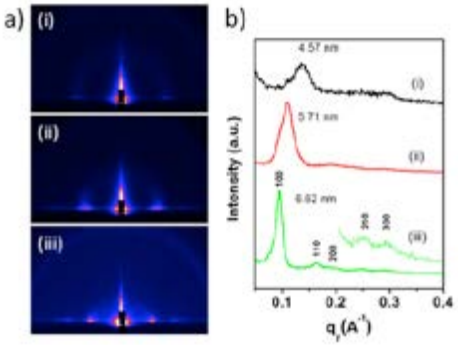


Figure 2. (a) GISAXS patterns and (b) corresponding *in-plane* 1-D linecuts from three MSTFs with addition of increasing amounts of decane.

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CO_2 Adsorption on Fluorinated SiC-derived Carbon

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Abstract

There have been numerous recent studies of adsorption in carbide derived carbons (CDCs) because of their unique characteristics such as tuneability of their pore structure, high surface area and pore volume, which makes them attractive in application; however, there is a little reported on their functionalization and surface modification, and its effect on their hydrophilic/hydrophobic and adsorption properties. Recently, Farmahini et al. [1] have theoretically investigated the effect of fluorination of CDCs, using atomistic models of fluorine-doped CDC. They have shown an apparent dual effect of fluorination, demonstrating that while fluorination generates more hydrophilic carbon surfaces, they act as more hydrophobic structures due to increased energy barriers in the disordered structure of nanoporous CDC. They have demonstrated that fluorination gives rise to reduction of pore volume, surface area, and CO_2 uptake. Here, the characterization and CO_2 capture performance of fluorinated CDCs has been investigated experimentally to obtain a comprehensive understanding of the microstructure of the CDCs. Fluorine doped CDCs are prepared at three different levels of fluorination (SiCDC-LF, SiCDC-MF, SiCDC-HF). It has been observed that increasing fluorination level from LF to HF leads to a decrease of surface area and pore volume even under mild fluorination conditions. It is shown that increasing fluorination level also narrows the range of the CDC's pore size distribution (PSD) slightly (Fig. 1). We find that for low level of fluorination (LF), there is little effect on the ultra-microporosity, recently shown to exist in the virgin CDC based on the PSD determined using CO_2 adsorption [2, 3]; however higher levels of fluorination significantly decrease the ultra-microporosity. This leads to significant decrease of CO_2 adsorption capacity. From the comparison of kinetic uptake curves of CO_2 on both virgin and fluorinated samples, we find that CO_2 uptake at high level of fluorination proceeds somewhat slower compared to that at low levels of fluorination, indicating reduction in adsorption rates. This is most likely due to dominant effect of reduction in transport coefficient arising from reduced pore volume, overshadowing any reduction in energy barrier arising from weaker interactions for the fluorinated samples.

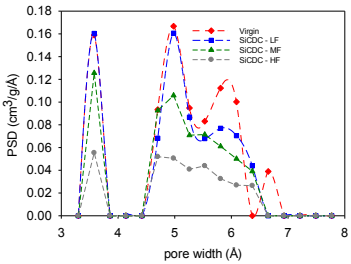


Figure 1. CO_2 – based pore size distribution.

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A Resol-Assisted Co-Assembly Approach to Crystalline Mesoporous Niobia Spheres

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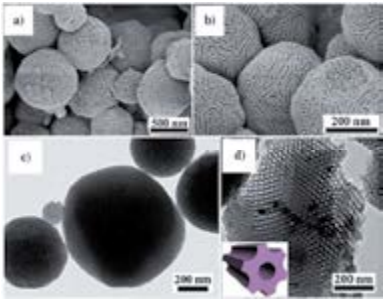
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Abstract

As an important transition-metal oxide, niobium oxide is attracting more and more attention owing to its unique catalytic and electronic properties and applications in catalysis, sensing, *etc*. Design and synthesis of ordered mesoporous niobium oxides are important to improve their application performances, because the uniform and well-connected mesopores can facilitate the diffusion of guest molecules within frameworks and the high surface areas can offer abundant accessible active sites. Solvent-evaporation-induced self-assembly (EISA) has been employed to synthesize various ordered mesoporous metal oxides by using various amphiphilic organic molecules as the template, and it usually only leads to film-like or monolithic mesoporous materials in previous studies.

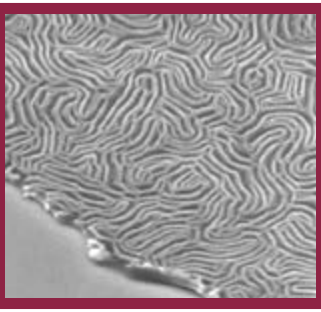


Inspired by the unique properties of resol, we herein demonstrate a facile resol-assisted solvent evaporation induced self-assembly (RA-EISA) to synthesize large-pore mesoporous niobia spheres with a 2D hexagonal mesostructure for the first time by using a high molecular weight poly(ethylene oxide)-block-Polystyrene (PEO-*b*-PS) copolymer as a structure-directing agent, resol and $NbCl_5$ as the precursors. The as-synthesized large-pore mesoporous niobia spheres were demonstrated as an excellent carrier in immobilization of hemoglobin (Hb) for application as a novel biosensor.

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Nitrogen-doped Mesoporous TiO_2 for Phenol Degradation

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Abstract

Mesoporous CN-doped TiO_2 material was prepared using tetrabutyl titanate (TBT), urea, polyaniline (PANi) and carbon tetrachloride (CCl_4) as precursors in a two-step process. Initially, the mesoporous TiO_2 was prepared using TBT and CCl_4 and calcined at 600 ^oC for 2 h. Later, the doping step was achieved by mixing and stirring the mesoporous TiO_2 with PANi and CCl_4 (as carbon and nitrogen sources, respectively) and carbonizing this mixture after washing and drying at 550 ^oC for 5 h. The thermal stability of the as-prepared mesoporous material was checked using thermal gravimetric analysis (TGA). Furthermore, the prepared mesoporous materials was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), Fourier Transform infrared (FT-IR) spectroscopy, and CHN analysis. X-Ray photoelectron spectroscopy (XPS) results revealed that oxygen sites in the TiO_2 lattice were substituted by carbon atoms and formed a C-Ti-O-C. In addition, the XPS results revealed that the nitrogen content is around 2.4 %. The high photocatalytic activity of the as-prepared was confirmed towards the phenol degradation under UV illumination in a short period of time (30 min).

Mesoporous Silica of SBA-15 Type as A Support for Acidic and Basic Functionalities

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Abstract

The desired physicochemical properties of silica materials may be achieved by surface functionalization processes. In general, there are two different procedures that may be used to incorporate acidic (sulfonic) or basic (amino) moieties into or onto the silica matrix, namely "one-pot" synthesis and post-functionalization (i.e. "grafting"). Ordered mesoporous silicas functionalized with sulfonic or amino groups may find a wide range of applications e.g., in catalysis and adsorption [e.g., 1, 2]. Therefore, our studies were focused on the obtaining of amino- or sulfonic-modified ordered mesoporous silicas of SBA-15 type, which may be applied in acid-base catalytic reactions.

Mesoporous silica materials bearing sulfonic or amino groups were synthesized by one-pot and post-functionalization techniques. Tetraethyl orthosilicate (TEOS, Sigma-Aldrich) and triblock copolymer Pluronic F-127 (BASF) were used as a silica source and a structure directing agent, respectively. N-(vinylbenzyl)-2-aminoethyl-3-aminopropyltrimethoxysilane (Z-6032 Silane, Dow Corning) and (3-mercaptopropyl)trimethoxysilane (ABCR) were applied as precursors of amino and sulfonic groups. HCl/EtOH-based extraction procedure was recognized as the most effective in the template removal from silica matrix.

Small-angle XRD measurements and TEM analysis confirmed mesoporosity and hexagonal pore ordering in the obtained materials. Low-temperature N_2 sorption analysis revealed that synthesized materials possess well-developed surface areas and quite narrow pore size distributions. Moreover, sorption isotherms and hysteresis loops were of type IV and H1, respectively, proving mesoporous character of synthesized SBA-15 samples. FT-IR and elemental analysis confirmed the presence of amino and sulfonic groups grafted onto the silica matrix. Additionally, incorporation of acidic and basic functionalities onto silica matrix, stemming from mercapto- and amino-siloxanes, was established on the basis of thermogravimetric (DTG/DTA) measurements.

Preliminary catalytic test revealed that synthesized materials may be promising catalysts in Friedel-Crafts alkylation of anisole with benzyl alcohol and in Knoevenagel condensation between benzaldehyde and ethyl acetoacetate, resulting in 95% selectivity in the latter reaction.

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Hybrid Ordered Mesoporous Silicas Containing Amino Groups as Catalysts in Knoevenagel Condensation

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Abstract

Surface functionalization of materials is carried out to obtain the desired physicochemical properties. Silica mesoporous materials may be modified simultaneously by organic and amino groups when appropriate aminoorganosilanes are applied during the synthesis. Organic moieties provide hydrophobic character, while amino groups can act as basic centers giving rise to catalytic activity [1]. "One-pot" technique, where the compounds containing desired functional groups are incorporated during synthesis and post-synthetic modifications of the surface silanol groups are common methods to prepare functionalized mesoporous silicas [2].

Our studies were focused on obtaining hybrid ordered mesoporous silicas containing amino groups and on applying them as catalysts in the Knoevenagel condensation. We have synthesized mesoporous materials of SBA-15 and SBA-16 types in the purely siliceous form, as well as their counterparts modified with aminoorganosilanes. Two different approaches, namely co-condensation and grafting were applied during synthesis. We have attempted to receive modified ordered silica nanomaterials in a form of both powders and self-standing films that would offer catalytic activity in Knoevenagel condensation.

Tetraethyl orthosilicate was used as a silica source, whereas triblock copolymers Pluronic P123 and F127 were applied as templates in order to obtain hexagonal (SBA-15) and regular (SBA-16) structure of silica. Vinylbenzyl-(β-aminoethyl)-γ-aminopropyl-trimethoxysilane or N-(β-aminoethyl)-γ-aminopropyl-trimethoxysilane were employed during synthesis of hybrid materials.

XRD and TEM analyses confirmed mesoporosity and hexagonal or regular pore ordering in the obtained materials. Low-temperature N_2 sorption measurements revealed also that the synthesized hybrid materials possess well-developed surface area. FT-IR and elemental analysis confirmed the presence of amino groups. Moreover, hybrid ordered mesoporous silica materials with amino groups, which were synthesized during our studies, may be used as catalysts in Knoevenagel condensation between benzaldehyde and ethyl acetoacetate, yielding ethyl 2-benzylidene-3-oxobutanoate with selectivity of 95%.

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Mesoporous Fullerenes with Ordered Porous Structure for Energy Storage and Conversion Applications

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Abstract

Fullerene is a new allotrope of carbon which exhibits interesting physical and chemical properties including high resistivity and superconductivity that make them available for various applications1. Although the structure of the fullerene molecules is highly attractive, the poor textural parameters, their conductivity and the cost in adding noble catalyst limit their applications in energy conversion. Creating mesoporosity in the fullerene could allow us to make materials with an extremely high surface area, uniform pore diameter and large pore volume, and a high electronic conductivity, which would increase the active electrochemical surface area. Moreover, the replacement of the noble metal catalyst is a long term thirst in finding efficient catalyst for fuel cells. In this work, we explore a new type of highly conductive electrodes for super-capacitors as well as a cost effective metal-free catalyst for direct methanol fuel cell (DMFC). For this, we used the nano-hard templating approach to synthesize mesoporous fullerene using fullerene C60 as the carbon source and highly ordered mesoporous silica SBA-15 as a nanotemplate (Figure 1). However, the main challenge involved in this fabrication was to obtain perfect pore filling of the templates with the fullerene solution to obtain a defect free well-ordered mesostructure. Therefore, the fullerene solutions are prepared by using special organic solvents wherein the fullerene is highly soluble, which also further facilitates the efficient diffusion of fullerene inside the channel of the template accessing all the adsorption sites. The cross linkage between the template and the carbon source along with the carbonisation process finally resulted in a well-ordered mesoporous fullerene with a large surface area in the range of 700 to m2/g, large pore diameter and uniform pore size. The highly ordered material was examined for its electrical conductivity and due to its crystalline nature, the conductivity reached to the range of 60 to186 Scm-1. Finally, the prepared materials have been employed as electrodes for the super-capacitor applications and oxygen reduction reaction and methanol tolerance. It was found that the mesoporous fullerene shows much higher specific capacitance than the mesoporous carbon based materials and the metal-free fullerene catalyst showed up a superior methanol tolerance. In addition, we fabricated the mesoporous fullerene C70 for the first time with a highly crystalline nature which was examined for its material property and also showed amazing performances in the methanol tolerance test that could be used in DMFCs. The detailed results will be discussed during the presentation.

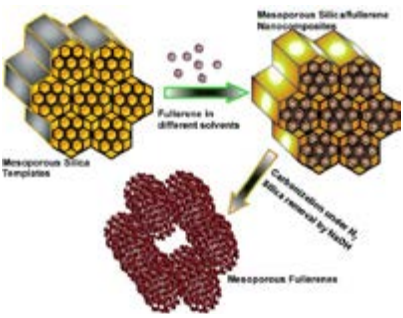


Figure 1: Schematic representation of the fabrication of Mesoporous fullerenes.

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Mesoporous Alumina Nano-wire Decorated Reduced Graphene Oxide Nanocomposites for Amine Induced CO_2 Capture

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Abstract

In recent times the graphene/ceramic composites have come up as a new class of material due to their improved mechanical, electrical and thermal properties[1, 2]. Among various ceramics, the alumina (Al_2O_3) is cheap and sustainable in harsh conditions. The disadvantages like low thermal conductivity and poor pore character of Al_2O_3 can be overcome using graphene as a filler[3] and tuning the synthetic protocol, respectively. We found that the mesoporous γ-Al_2O_3 nanowire/graphene composite can be useful as an excellent support of PEI to adsorb CO_2.

Keeping eye on the challenges, a facile synthesis of mesoporous γ-Al_2O_3/Reduced Graphene Oxide (γ-Al_2O_3/RGO) nanocomposite has been accomplished. Very fine wire like structure of γ-Al_2O_3 was observed by TEM. The surface area of the composite was found to be 327 m^2g^{-1}. The average pore size and pore volume were estimated to be 9 nm and 0.88 cm^3g^{-1}, respectively. PEI was loaded in the material through wet impregnation technique.

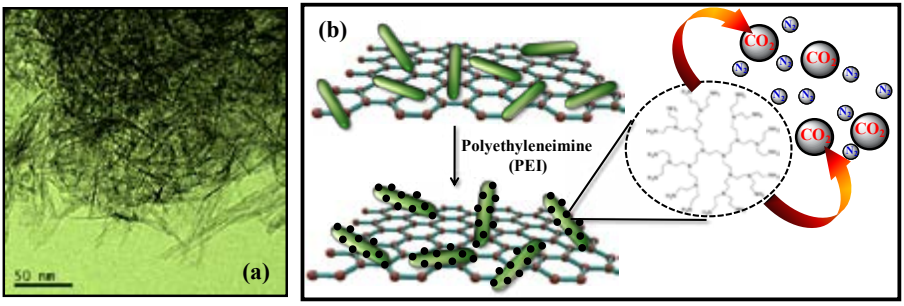


Figure: (a) TEM image showing the nanowire shaped mesoporous γ-Al_2O_3/RGO composite. (b) The schematic figure represents PEI impregnation and amine induced CO_2 adsorption.

The CO_2 adsorption capacity of this material at 75 °C was found to be 1.13 mmol g^{-1} of adsorbent with an amine efficiency of 0.22. CO_2 adsorption-desorption cycles performed by the thermogravimetric analysis (TGA) showed an excellent and stable cycling of such composite material. The presence of RGO with Al_2O_3 nanowires can efficiently restricts the overheating of the adsorbent (because CO_2 adsorption by PEI is an exothermic process), and prevents the thermal degradation of PEI. As a result, the amine efficiency is not deteriorating during repeated CO_2 adsorption-desorption cycling.

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Synthesis of Hierarchically Porous Beads with a 3D Mesopore Structure by the Co-Micelle/Emulsion Templating Method

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Abstract

The co-micelle/emulsion templating method is a recently developed technique for the synthesis of hierarchically macro/mesoporous beads [1]. This method makes use of an amphiphilic block copolymer to stabilize an oil-in-water emulsion which serves as a template for macropores. Excess block copolymer in the continuous phase forms micelles which are used as a template for the formation of mesopores similar to the formation of mesoporous materials such as SBA-15. The final material consists of beads with a hierarchical structure of macropores with mesoporous walls.

A number of applications for hierarchically macro/mesoporous materials are emerging due to the favorable properties that arise from the combination of pores on these different length scales. Specifically, the beads have potential in the separation of larger macromolecules and could also be used as a support material in bio catalysis. Previously, the beads had a 2D hexagonal mesoporous structure which has been shown to be inferior to 3D mesopore structures in terms of mass transport kinetics. Therefore, the aim of this study is to use a different block copolymer in order to obtain an interconnected 3D mesopore structure. Pluronic® F127 has been used in the past to obtain spherical mesoporous silica powders and therefore it was selected as the mesopore templating agent in this study [2]. The F127 concentration has an effect on the macropore morphology and the mesopore volume, which will in turn affect the active site capacity, strength and mass transport properties of the material, providing further tenability in the material properties.

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Hierarchical Porous $LiFePO_4$/Carbon Composite Electrodes for Lithium-Ion Batteries

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Abstract

$LiFePO_4$ is a promising cathode material for lithium-ion batteries [1]. However, the poor electronic and ionic conductivity $LiFePO_4$ hinders its industrial applications [2]. Strategies for improving the properties of $LiFePO_4$ have been reported [3-5]. Here, we describe an evaporative self-assembly method to prepare $LiFePO_4$/Carbon composite materials with a hierarchical porous structuren the presence of vegetable protein. The discharge capacity (Fig. 1a) of the $LiFePO_4$/C electrode was 168 mA h g^{-1}, which is higher than that of pristine $LiFePO_4$ (128 mA h g^{-1}). In comparison with $LiFePO_4$, the $LiFePO_4$/Carbon composite exhibited sharper and longer reduction and oxidation peaks, and lower potential difference (Fig. 1b). The $LiFePO_4$/C composite electrode delivered discharge capacities of 167 and 158 mA h g^{-1} at 0.1 C and 10 C, respectively (Fig. 1c). After 100 cycles, the material maintained a discharge capacity of 135 mA h g^{-1} at 30 C (Fig. 1c). Impedance data (Fig. 1d) showed that the $LiFePO_4$/C composite had a lower charge transfer resistance than the pristine $LiFePO_4$.

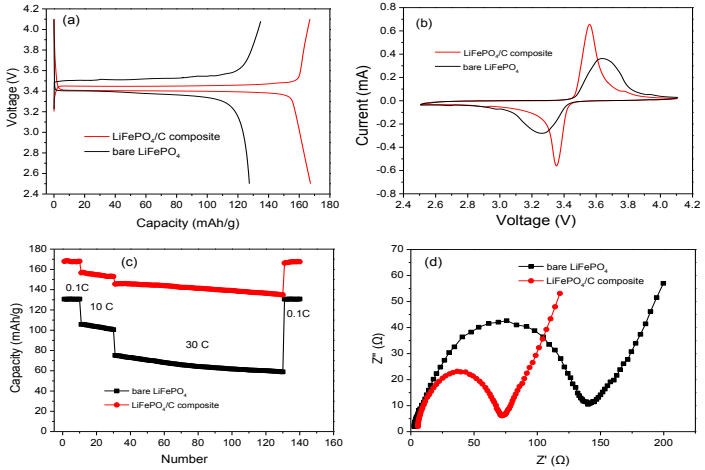


Fig. 1 Charge and discharge curves (a), cyclic voltammetry curves (b), rate performance (c) and EIS curves (d) of $LiFePO_4$/Carbon composite and pristine $LiFePO_4$.

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Random Copolymer-directed Synthesis of Highly Crystalline Sn-based InSn- and GaSn- oxide Nanosponges with Uniform Mesopores

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Abstract

Highly crystalline mesoporous Sn-based InSn- and GaSn- oxides were solvothermally synthesized using random copolymer of 4-vinylphenol and methylmethacrylate as the mesopore generating agent. The resultant InSn- and GaSn- oxides exhibited nanosponge-like morphologies, in which 4-nm thick frameworks of InSn- (and GaSn-) with the crystalline rutile structure were assembled in a disordered manner. Despite the disordered network, the mesopore diameters were quite uniform (~4 nm). In addition, as a result of the high crystallinity of the mesopore wall, the crystalline mesoporous InSn oxides obtained in this manner were much more stable than that of CTAB-directed mesoporous InSn oxides[1] against thermal sintering. The high thermal stability allowed us to anneal the mesoporous InSn oxide at high temperature to increase the electrical conductivity significantly. The mesoporous InSn oxide after annealing at 823 K exhibited much higher electrical conductivity than mesoporous SnO_2, and bulk InSn oxide. The mesoporous mixed metal oxides synthesized in the present work would be promising materials for supporting metal nanoparticle in a number of electrical devices. Furthermore, we believed that the diverse hetero-nanostructures of the mixed metal oxides synthesized through this simple method might find widespread application in a number of fields.

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A Facile One-pot Strategy of Synthesizing Pt Based–Ionic Liquid Composite Dispersed on Carbon Black as An Efficient Catalyst for Oxygen Reduction Reaction

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Abstract

The enhancement of catalyst for oxygen reduction reaction (ORR) is still a huge challenge. Recently, the incorporation of PtNi alloy with a hydrophobic, protic ionic liquid shows good electrocatalytic activity, due to the high O_2 solubility of the ionic liquid which can induce the increase of O_2 concentration at the catalyst surface. Thus, the residence time of O_2 on the catalyst surface increases, resulting in high frequency and high mass activity of ORR. However, the PtNi-ionic liquid composites in previous reports were synthesized through several complicated steps and ionic liquid just mixed with PtNi alloy led to unstable composites. Herein, we report a facile one-pot strategy of synthesizing Pt-based–ionic liquid composite dispersed on carbon black (SuperP, Fig. 1(a)) in room temperature ionic liquid, 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide, under one atmospheric pressure plasma. The PtNi-NPs with the size of 2–3 nm were stably and uniformly hybridized on the surface of carbon blacks, which were covered by the ionic liquid layer, as seen in Fig. 1(b). The obtained PtNi-ionic liquid/carbon black composite catalyst shows high ORR activity, which is better than that of commercial Pt/C catalysts. The PtNiRu-ionic liquid/carbon black catalyst (Fig. 1(c)) is also more stable than the commercial Pt/C under the same ORR condition. The results prove that the Pt-based–ionic liquid composites dispersed on carbon black push the ORR towards completion and can indeed be one of promising candidates for many electrocatalytic applications.

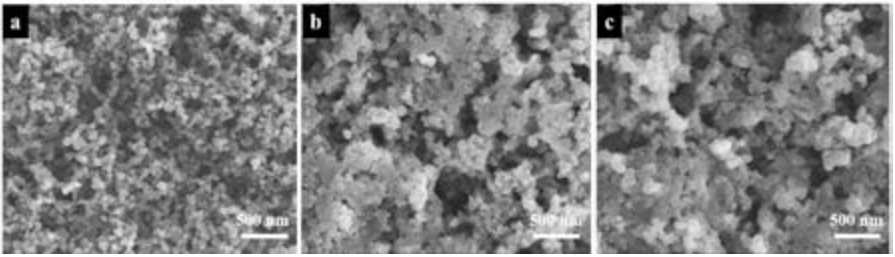


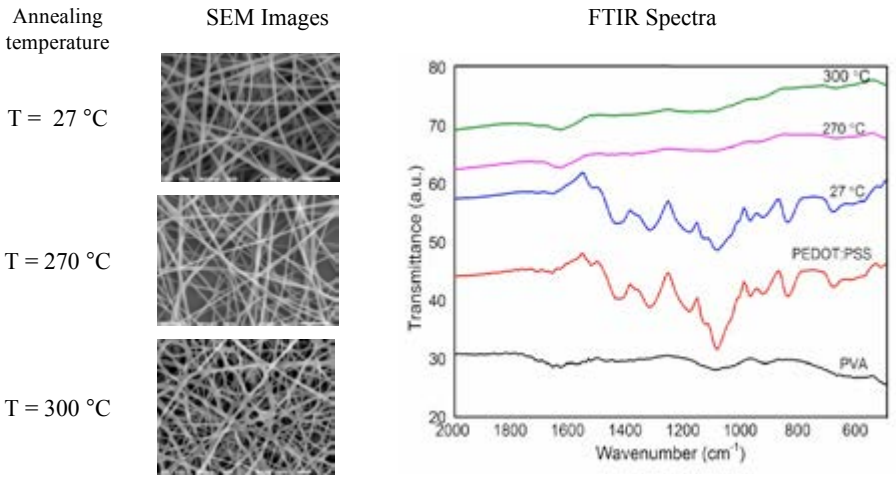
Fig. 1. SEM images of (a) pristine SuperP Carbon black, (b) PtNi-IL/SuperP composite, and (c) PtNiRu-IL/SuperP composite.

Effect of Annealing Temperature on Morphology and Composition of Electrospun PEDOT:PSS Nanofibers

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Abstract

Poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) fibers have been successfully fabricated by a simple and low cost electrospinning technique. Polyvinyl alcohol (PVA) dissolved in water (10% w/v) was added as a matrix to improve mechanical properties of the nanofiber mats. The electrospinning was performed at an applied voltage of 15 kV, an electrode distance of 12 cm, and a flowrate of 8.3 μL/min. A syringe with a stainless-steel needle (inner diameter of 0.4 mm) was used to transfer the PEDOT:PSS/PVA solution. The morphology and diameter of electrospun nanofibers were investigated by scanning electron microscopy (SEM), while the chemical compositions and molecular interactions among nanofiber blend components were determined using Fourier transform infrared (FTIR) spectroscopy. Based on the SEM images, the best nanofibers were obtained when the ratio between PEDOT:PSS and PVA was 2:3. This ratio was then choosen for high temperature annealing treatment. Based on the SEM images, the diameters of PEDOT:PSS/PVA nanofibers were in the range of 92 to 160 nm. It was observed no significant change in the fibers morphology after being annealed up to 270 ^{o}C. Thus, the PEDOT: PSS/PVA fibers are potential to be used as a buffer layer on the solar cell device and other electronic application requiring high operating temperature.



Three-dimensionally Ordered Macroporous Cerium Oxide Supported Co–Pd Alloy Nanocatalysts for Methane Combustion

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Abstract

Although most of transition metal oxides or mixed oxides perform well in the combustion of methane, the supported palladium or platinum nanoparticles have been generally regarded as the most active catalysts [1,2]. The high cost of noble metals, however, limits their wide applications. Herein, we report the alloying of Pd with Co and load them on three-dimensionally ordered macroporous (3DOM) cerium oxide via a polyvinyl alcohol-protected $NaBH_4$ reduction route, and found that the as-prepared nanocatalysts exhibited high efficiency in methane combustion.

Co–Pd alloy nanoparticles (NPs) (average size = 2.5–3.0 nm) with different Co/Pd molar ratios (4–18) were synthesized (Fig. 1A) and were uniformly anchored on the surface of 3DOM CeO_2. Among all of the samples, the 1 wt% Co_6Pd/3DOM CeO_2 sample showed the best catalytic performance for methane combustion (the temperature for achieving a methane conversion of 90% was 470 ^oC (Fig. 1B). Such a Co–Pd alloy nanocatalyst was much more stable than the supported Co catalyst during 20 h of on-stream reaction (Fig. 1C). Based on the XPS, H_2-TPR, and *in situ* DRIFT characterization results and activity data, we conclude that the super catalytic performance of 1 wt% Co_6Pd/3DOM CeO_2 was associated with the unique alloy structure and strong redox ability of CeO_2 promoted by Co–Pd alloy.

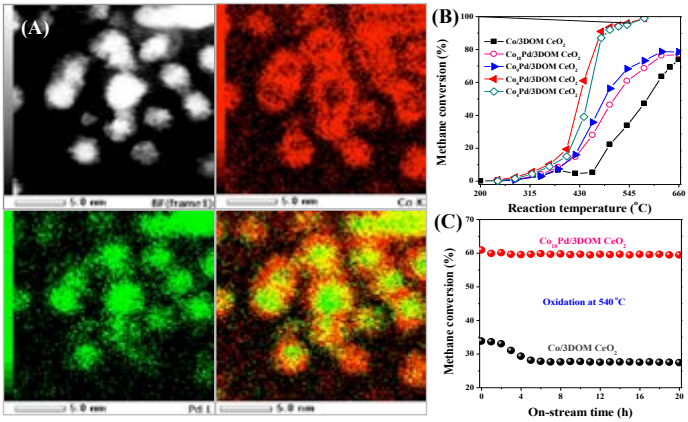


Fig. 1. (A) STEM–EDS element mapping images of Co_6Pd NPs, (B) catalytic performance of the as-prepared samples for methane combustion (condition: reactants = 2.5% CH_4 + 20% O_2 + N_2 (balance) and space velocity = 20,000 mL/(g h)), and (C) catalytic stability at space velocity = 20,000 mL/(g h).

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Au–Pt/3DOM $Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3: Highly Active Catalysts for the Oxidation of Toluene

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Abstract

Development of high-performance catalysts is the focus on heterogeneous catalysis. Supported noble metals (Au, Pd, and Pt) show excellent low-temperature activities for the oxidation of volatile organic compounds (VOCs). It was reported that Pt exhibited higher activities for the oxidation of long-chain hydrocarbons and aromatics [1]. Alloying of Au with other noble metals to form bimetallic alloy nanoparticles (NPs) is an efficient way to improve stability and performance of Au-based catalysts for toluene oxidation [2]. Due to the easy transportation and diffusion properties, three-dimensionally ordered macroporous (3DOM) metal oxides have been utilized to catalyze the combustion of VOCs. Up to now, however, there have been no works on the preparation and catalytic applications of 3DOM $Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3 (denoted as CZA) supported bi-noble metal alloy nanocatalysts for toluene combustion. Herein, we report the catalytic performance of *z*Au–*y*Pt/3DOM *x*$Ce_{0.5}Zr_{0.5}O_2$–Al_2O_3 (*z*Au–*y*Pt/3DOM CZA; *z* = 1.0, 0.5, 0.25, and 0.1 wt%; *y* = 0.5 wt%; *x* = 20 wt%).

The 3DOM CZA support with mesoporous walls was fabricated using the Pluronic F127-assisted polymethyl methacrylate (PMMA) microspheres-templating method. The *z*Au–*y*Pt/3DOM CZA catalysts were prepared via the polyvinyl alcohol (PVA)-protected $NaBH_4$ reduction route. Physicochemical properties of the catalysts were characterized by means of the ICP–AES, XRD, BET, SEM, TEM/SAED, XPS, and H_2-TPR techniques, and their catalytic activities were evaluated for toluene oxidation in a continuous flow fixed-bed quartz microreactor. The concentrations of the reactant (1000 ppm toluene) and products were determined on an online GC2010 apparatus.

It is found that the noble metal NPs with a size of 2–5 nm were uniformly dispersed on the surface of mesopore-walled 3DOM CZA. XPS and TPR investigations demonstrate that the surface adsorbed oxygen (O_{ads}) species concentration and low-temperature reducibility increased in the order of 1.0Au/3DOM CZA < 1.0Au–0.5Pt/3DOM CZA < 0.5Au–0.5Pt/3DOM CZA < 0.25Au–0.5Pt/3DOM CZA < 0.1Au–0.5Pt/3DOM CZA < 0.5Pt/3DOM CZA, coinciding with their catalytic performance sequence. The 0.5Pt/3DOM CZA catalyst performed the best, showing the $T_{50\%}$ and $T_{90\%}$ (temperatures for achieving toluene conversions of 50 and 90%) of 165 and 180 °C at a space velocity of 20,000 mL/(g h), respectively. It is concluded that the excellent catalytic performance of 0.5Pt/3DOM CZA was associated with its high O_{ads} species concentration, good low-temperature reducibility, and strong Pt NPs–3DOM CZA interaction as well as mesopore-walled 3DOM structure.

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Template Technique for Synthesis of CaO-based Sorbents

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Abstract

Emissions of large amounts of CO_2 to the atmosphere, mostly as a by-product of burning fossil fuels in man-made processes, are contributing to climate change. Among the options for reducing greenhouse gas emissions there is CO_2 capture from the large stationary sources. It was proposed in many works to use calcium-based sorbents for effective CO_2 capture from gases at high temperatures. It is well known that textural properties drastically effects to sorption/regeneration performance of sorbent during cycles under the conditions of CO_2 capture process [1]. Different methods involving direct thermal decomposition of the, Ca-containing precursors, wet chemistry, sol-gel technique and flame pyrolysis, were applied to modify porous structure of Ca-based sorbents. In mentioned cases porosity and pore size distribution are regulated by chemical nature of precursors and conditions of experiment.

In parallel with interest growing to CaO-sorbents novel template approach started emerging and developing. In general this technique consists of two steps: at first step the template particles with definite shape and size are introduced to matrix media. After that matrix material solidifies and template is deleted. Thus, template synthesis with nanocasting is a direct technique for design materials with appropriate porosity and pore size distribution [2].

We have used template approach to introduce additional porosity in CaO-based sorbents and to arrange theirs pore size distribution. The effect of synthetized sorbents porous structure on their sorption performance during repetitive carbonation/regeneration cycles was investigated.

The pore size distribution of prepaid sorbents drastically depends on the quantity and the size of introduced template, but also on the sorbent preparation conditions. The introducing of template significantly increases the rate both of sorbent carbonation and calcination reactions. of sorbent with template for more than 1 order of magnitude in comparing with the pure sample without template. In this way template approach seems to be a perspective technique to prepare the CaO-based sorbents with better carbonation/calcination performance [3] it is also a subsequent development and improvement of synthesis technique required.

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EU-1 Zeolite Prepared with Capping Agent as Upgraded Catalyst for Ethylbenzene Isomerization

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Abstract

EU-1 zeolite (with EUO topology) is one of the few zeolite-based catalysts that has found industrial application, particularly in xylene/ethylbenzene isomerization[1]. The xylenes products are, after benzenes, the most important chemical products. Recovery of *p*-xylene with simultaneous conversion of the remaining C8 aromatic cut has become a process of growing interest for the petrochemical industry, following an increase of the demand of the *p*-isomer. During the catalytic reaction EU-1 is quickly deactivated by coke deposition blocking the acid sites located in micropore channels, although the active sites on external surface remain active and relatively insensitive for deactivation. Therefore, the preparation of EU-1 catalyst with large and easily accessible external surface is of a great interest.

To reach this goal we synthesized EU-1 zeolite using capping agent. This novel approach for preparation of nanomorphic zeolites is based on the inhibition of excessive crystal growth by addition of a capping agent, which strongly binds to the substrate surface. The method was successfully applied to zeolites MFI, CHA, MOR and FAU[2].

Herein, zeolite EU-1 was prepared from a synthesis gel containing besides organic structure-directing-agent (SDA) also the capping agent (CA) of gemini-type, $C_{18}H_{37}N^{+}(Me)_2C_6H_{12}N^{+}(Me)_2C_6H_{12}\text{-}N^{+}(Me)_2C_{18}H_{37}$ (C18-N3-C18 for brevity, see **Fig. 1**). Three different amounts of capping agent were introduced to the synthetic gel to study its influence on textural properties of the final product. In comparison to bulk EU-1, its nanomorphic counterparts exhibit similar or slightly higher BET surface area, however, with distinctly increased portion of external surface area presenting now more than half of the total surface area. In this contribution we will discuss the effect of using capping agent for the synthesis of EU-1 on its textural properties and consequently its catalytic performance. The catalytic activity of nanomorphic EU-1 materials prepared with different amount of capping agent and varying in aluminium content were hence tested in the presence of a metallic phase in ethylbenzene isomerization reaction.

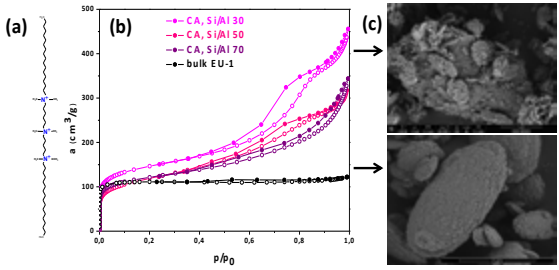


Fig. 1 The capping agent C18-N3-C18 **(a)**; Ar isotherms measured at 87 K on bulk EU-1 and nanomorphic EU-1 prepared with 1.5 mols of CA **(b)**; SEM images of bulk EU-1 and its counterpart prepared by capping **(c)**.

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Etherification of Glycerol with Methanol Catalyzed by Mesoporous Materials Containing Niobium and Aluminium

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Abstract

The role of chemistry, as one of the disciplines, is to increase efficacy in the use of the sources of raw materials. One of the renewable materials is glycerol, which is the main by-product in making biodiesel [1]. A growth of glycerol production and a decrease of its price causes that glycerol has become a promising substrate in many chemical processes [2]. In our work we carried out etherification of glycerol to compounds, which may be used in cosmetic and pharmaceutical industry, and mainly as an excellent oxygen additives for diesel fuel [2]. Mesoporous materials containing niobium and aluminium, i.e., T-MSU-X, T-SBA-16 and T-FDU-1 (T=Nb or Al) were applied as catalysts in this reaction. We studied the reaction of glycerol with methanol in absence of solvents and using heterogeneous catalysts.

A series of niobium/aluminium-incorporated MSU-X, SBA-16 and FDU-1 mesoporous molecular sieves were synthesized by using different types of templates, initial Si/T (T=Nb or Al) molar ratios or hydrothermal parameters. The nanostructure of these materials can be observed by thorough control of the synthesis parameters.

Etherification of glycerol was carried out by using microwave method of heating. The mixture of glycerol, methanol and catalyst was transferred into microwave reaction vessel and treated in the CEM MARS microwave system under stirring at 303 and 313 K for 20, 30 and 40 minutes. The reactor content, taken at specified intervals, was analysed by a Varian chromatograph GC3800. Samples were additionally analysed by GC analysis with (EI)MS-MS (Varian 4000 ion trap) detector.

This paper reports on the etherification of glycerol with methanol to 3-methyl-1,3,5-pentanetriol, 2-ethyl-1,3-dioxolane-4-methanol and monomethyl ether-1-glycerol. The reaction conditions (reacting temperature, catalyst loading) leading to maximum glycerol ethers concentration were investigated. The conversion increases with reactions time. When we want to compare the conversion between catalysts containing niobium or aluminium, one can observe higher conversion on the aluminium samples (around 60%). Etherification of glycerol on heterogeneous Al-FDU-1 catalysts yielded around 60% of the monomethyl ether-1-glycerol. One can conclude that production of glycerol ethers by etherification of glycerol with methanol catalyzed by heterogeneous acid catalysts, such as Al- and Nb-FDU-1, is feasible, whereas the adjustable acidity is necessary for high efficiency.

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Synthesis, Characteristic and Catalytic Properties of Mesoporous Materials of SBA-12-type Containing Transition Metals

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Abstract

Since their discovery in 1992, mesoporous molecular sieves offer many possibilities in transformation of various organic substances. The novel materials possess special textural properties such as: large surface area, narrow size pore distribution or uniformly ordered channels. Such inartistic properties led to a broad application in catalysis, separation, photoelectronics and nanosynthesis. The introduction of transition metals into the framework of mesoporous materials of various structural types results in the formation of selective and active catalyst for oxidation reactions that are fundamental reactions in industrial chemistry leading to obtain of fine chemicals or pharmaceuticals [1-2].

The aim of this work was synthesis, characteristic and catalytic properties of the nanoporous materials of SBA-12-type.

The synthesis of these materials involves the addition of tetraethyl orthosilicate (TEOS) to a solution of non-ionic surfactant Brij 76, distilled water and 0.1 M HCl. Tetraethyl orthosilicate and aqueous solutions of metal salts of ruthenium, tin and niobium were used as silicon and metals sources, respectively. Various physicochemical techniques, such as: X-ray diffraction (XRD), transition electron microscopy (TEM), scanning electron microscopy (SEM), N_2 physisorption, X-ray fluorescence (XRF), FTIR and UV-Vis spectroscopies were used to check the textural/structural properties of the samples and to find the localization of ruthenium, tin and niobium ions in the SBA-12 matrix.

Basing on N_2 sorption measurements and XRD analysis, it can be concluded that mesoporous materials containing ruthenium, tin and niobium SBA-12-type were synthesized. Nitrogen-physisorption isotherms showed type IV profiles according to IUPAC, which is typical of mesoporous materials. The BET surface area for all materials studied was similar, over 1000 m^2g^{-1}. Additionally, the new materials were very active and differently selective in the oxidation of cyclohexene and in the Baeyer-Villiger oxidation of citral. The results of the oxidation showed that 2-hydroxy-2,4-dimethyl-hept-6-en-3-one is the main product, followed by cyclocitral (2,6,6-trimethyl-1-cyclohexene-1-carboxaldehyde, α,β-unsaturated aldehyde) and dihydromyrcenol. The influence of metal-type and SBA-12-type synthesis parameters on catalytic activity will be presented.

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The Preparation of Activated Carbon Foam Disks from Tar Pitch and Coal Power for the Adsorption of CO_2, CH_4 and N_2

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Abstract

We prepared high surface area activated carbon foam disks with a relatively high mechanical strength from mixtures of tar pitch and coal powders, with potassium hydroxide as a chemical activator. The two primary parameters investigated in this study were the size of the coal particles (0 – 53 μm, 150 – 250 μm, 355 – 550 μm) and the amount of nitric acid used in the pitch pre-treatment. Our results show that the coal size of 0 – 53 μm produced the carbon foam disks with the highest gas adsorption capacity, which we attribute to stabilization of the pitch foaming process. The pre-treatment of the pitch was observed to be critical in the production of the carbon disks and in this study the preferred rate of nitric acid (15 M) addition was 18 mL per 100 g pitch. Equilibrium adsorption capacities of CO_2, N_2, and CH_4 on the carbons were measured by a gravimetric sorption method at pressures up to 4500 kPa.

New Catalyst for Electron Transfer Reactions Based on Galinstan

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Abstract

Galinstan, a nontoxic liquid metal alloy (Ga 68.5%, In 21.5% and Sn 10%), is a suitable alternative to mercury since it exhibits an ultralow vapor pressure at room temperature. Nevertheless, the substitution of mercury with this new material has been limited to a few applications mainly due to its facile oxidation in air. Recently however, more diverse applications including a liquid metal enabled pump[1] and photocatalysis[2] have been reported.

Here in this study, a new catalyst for electron transfer reactions based on microspheres of galinstan, synthesized via the sonication of the liquid metal, is reported for the first time. The model system of potassium ferricyanide reduction by sodium thiosulfate was chosen to illustrate the activity of this new heterogeneous catalyst. Sodium hydroxide was required to activate the surface of the galinstan microspheres (by eliminating the native oxide) and the reaction was faster when both the reaction and the catalyst are in basic medium.

The catalyst was characterized by scanning electron microscopy (SEM) (Fig. 1a) and energy dispersive X-ray spectroscopy (EDX) (Fig. 1b). EDX analysis revealed that the composition of galinstan was modified after sonication and interestingly no trace of gallium metal was detected. The catalytic reaction was monitored by time dependent UV-vis spectroscopy as illustrated in Fig. 1c. The design of catalysts based on galinstan was also extended to other charge transfer reactions such as Cr^{VI} and 4-Nitrophenol reduction, showing the diverse applicability of this material for water treatment and organic transformation reactions respectively.

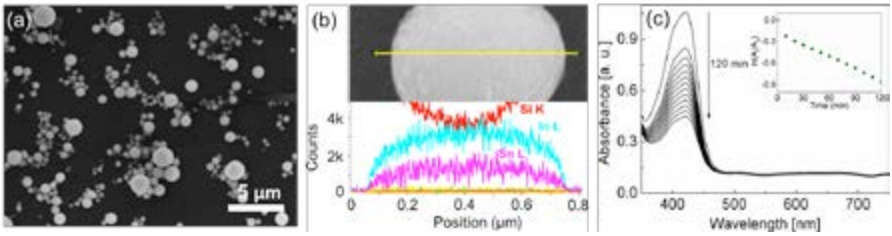


Fig. 1: (a) SEM image of galinstan microspheres after sonication in basic solution for 30 min and drop casted on Si/SiO_2 substrate, (b) an EDX profile across the microsphere shown in the high resolution SEM image and (c) successive UV-vis absorption spectra of the reduction of $Fe(CN)_6^{3-}$ in the presence of galinstan based catalyst (inset: plot of $\ln(A_t/A_0)$ *versus* time).

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Magnetically Triggered Mechanosensitive Channels for Liposomal Drug Delivery

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Abstract

Liposomal drug delivery systems (LDDS) are promising tools used for the treatment of diseases where highly toxic pharmacological agents are administered. Currently, a major challenge remains to destabilise LDDS by a specific stimulus at a target site. The bacterial mechanosensitive channel of large conductance (MscL) presents an excellent candidate biomolecule that could be employed as a remotely controlled pore-forming nanovalve for triggered drug release from LDDS. In this study, we have developed superparamagnetic nanoparticles for activation of the MscL nanovalves by magnetic field. Synthesised $CoFe_2O_4$ nanoparticles with the radius less than 10 nm were labelled by SH-groups for attachement to MscL. Activation of MscL by magnetic field with the nanoparticles attached was examined by the patch clamp technique showing that the number of activated channels under ramp pressure increased upon application of magnetic field. In addition, we have not observed any cytotoxicity of the nanoparticles in human cultured cells. Our study suggests the possibility of using magnetic nanoparticles as a specific trigger for activation of MscL nanovalves for drug release in LDDS.

Synthesis and Characterisation of Spherical Carbon Replicas for Adsorption of Volatile Organic Compounds

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Abstract

Mesoporous CMK-1 carbon, which is an exact inverse replica of MCM-48 silica template, exhibits excellent adsorption properties with respect to the elimination of various types of inorganic and organic contaminants [1,2]. In the presented work, we developed the method of synthesis suitable to produce spherical CMK-1 particles. The final carbon materials were tested as adsorbents of volatile organic compounds (VOCs). The measured adsorption capacities were compared to the values collected for activated carbon prepared from bulky poly(furfuryl alcohol) and MCM-48 silica as well.

The CMK-1 carbon replica was synthesized using the hard-templating method with poly(furfuryl alcohol) as a carbon source, which was deposited in the pore system of MCM-48 sieve by polycondensation of furfuryl alcohol performed in an aqueous suspension of silica template. The polycondensation process was carried out at various intended PFA/MCM-48 mass ratios equal to 0.75, 1.00, 1.25 or 1.50. The resulting PFA/MCM-48 composites were subjected to a thermal treatment at 650, 750, 850, 950 and 1050°C under inert atmosphere, and then the silica template was etched using a sodium hydroxide solution. To characterize the synthesized samples X-ray powder diffraction (XRD), low temperature nitrogen adsorption, scanning electron microscopy (SEM) and thermogravimetry (TG) were used. All materials were also tested as adsorbents in the elimination of methyl ethyl ketone, isopropanol, heptane and toluene vapors.

The XRD and SEM results confirmed the formation of materials characterized by the regular pore ordering and the spherical morphology. Textural parameters (surface area, pore volume and pore size distribution) determined using low temperature adsorption of nitrogen proved the highly developed surface area, narrow pore size distribution and high pore volume of the synthesized templates and replicas. The determined adsorption capacities for the CMK-1 carbon replicas confirmed their high efficiency in the removal of VOCs.

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Facile Synthesis of CMK-1 Replica by Precipitation Polycondensation of Furfuryl Alcohol in Pore System of MCM-48 Silica

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Abstract

Carbon mesoporous replicas have been recognized as prospective catalysts, because of their unique properties, i.e. high specific surface area, ordered pore arrangement as well as a presence of oxygen-containing surface functionalities. The concept of synthesis of CMK-1 replica is based on an inversed replication of pore system of MCM-48 silica template, which has a regular structure with two complex interweaved mesochannels. The known methods of CMK-1 preparation are usually multi-step and time-consuming. In the presented study, the CMK-1 carbon replica was synthesized using a new, simple approach. First, the MCM-48 silica was obtained using tetraethyl orthosilicate and cetyltrimethylammonium chloride. After removal of the surfactant by a thermal treatment at elevated temperature, the pore system of MCM-48 was filled with a carbon precursor by precipitation polycondensation of furfuryl alcohol (FA) in an aqueous slurry of mesoporous silica using HCl as a polycondensation catalyst. The optimization of the synthesis conditions was performed by preparing samples at various FA/MCM-48 mass ratios equal to 0.50; 0.75; 1.00; 1.25; 1.50; 1.75 and 2.00. The process was performed at 100°C for 6 h. Subsequently, the obtained PFA/silica composites were carbonized in the temperature range of 650-1050°C under N_2 atmosphere to eliminate the majority of non-carbon elements and reorganize the crystal structure of organic part into the turbostratic form. Finally, the silica template was removed by a treatment with HF solution.

The structural and textural properties of the synthesized materials were studied by powder X-ray diffraction (XRD) and low-temperature adsorption of N_2. The adsorption isotherms recorded for the carbon/silica composites confirmed that the carbon precursor gradually clogs the mesopores in MCM-48 with increasing PFA/MCM-48 mass ratio. Moreover, the XRD patterns collected for the samples after the HF treatment showed that the samples with higher PFA/MCM-48 mass ratios exhibit better structural ordering. The thermogravimetric analysis allowed to determine the real PFA/MCM-48 mass ratios, which were lower than expected for all studied composites, indicating an incomplete effectiveness of PFA deposition on the MCM-48 surface. X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) were applied to determine the content of oxygen-containing functionalities on the surface of synthesized CMK-1 replicas. Ultimately, transmission electron microsocopy (TEM) was used to look into the morphology of synthesized materials.

The synthesized carbon replicas were tested as catalysts in the oxidative dehydrogenation of ethylbenzene (ODH) being an alternative method of styrene production. Analyses confirmed the high activity and stability of the synthesized replicas after an inherent initial period. The initial ethylbenzene conversion at relatively low temperature of 350°C exceeded 35%, whereas selectivity to styrene achieved 98%. It is especially noteworthy that all catalysts exhibited very low selectivity to CO_x (< 2%).

This work was supported by the National Science Centre under the grant no. 2013/09/B/ST5/03419.

Low Cost Nanoporous Carbons Derived from Soft Drinks and Milk for Supercapacitors

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Abstract

To address some of the global issues such as depletion of fossil fuels, energy demand, rising atmospheric CO_2 levels, global warming and climate change, innovative, efficient and economical technologies like supercapacitors are needed for clean energy generation and storage. Supercapacitors are able to store and deliver energy at relatively high rates than the conventional batteries although the charge storage mechanism is same in both. However, the storage capacity of supercapacitors is extremely low mainly because of the poor textural parameters of the electrode materials. Recent applications using porous carbon as electrode materials for electric double-layer capacitors (EDLC) have aroused significant worldwide attention because of their porous structures and electrochemical behavior. Unfortunately, the low efficiency, high cost and lack of suitable electrode materials is a big obstacle in the commercialization of supercapacitors as an affordable energy storage device. In this work, we have developed a low cost nanoporous carbons as electrode materials with excellent textural properties from a low cost carbon precursors such as waste milk, commercial juice and coke instead of sucrose or glucose via nanohard templating approach wherein mesoporous silica SBA-15 was used as a template. The structural properties of the electrode materials were studied using XRD, HRSEM, HRTEM and Raman spectroscopy whereas the textural characteristics of the prepared electrode materials were evaluated using nitrogen adsorption-desorption technique. The prepared materials possess well-ordered structure with the surface area in the range of 1000 to 1900 m^2/g. Among the materials prepared, the nanoporous carbon prepared from coke showed the highest surface area which is higher than that of the nanoporous carbon prepared from sucrose precursors. The supercapacitance behavior of these electrode materials was investigated in aqueous solutions of sulfuric acid by cyclic voltammetry and battery cycler. Among the samples studied, CMK-3-130-coke registered the highest specific capacitance of 195 F/g which is much higher than that of the CMK-3 mesoporous carbon (143 F/g) and the mesoporous carbons prepared from milk (145 F/g) and orange juice (167 F/g). The excellent performance of the CMK-3-130-coke is mainly attributed to higher specific surface area, pore volume, and better structural order than other samples used in this study.

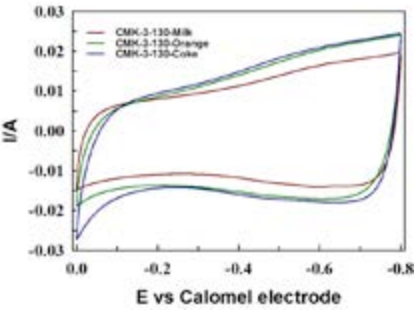


Fig.1: CV of nanoporous carbons prepared from different low cost carbon sources

Table 1: Textural parameters and the specific capacitance of nanoporous carbons prepared from different low cost carbon sources

Sample Code	BET S.A (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)	Specific capacitance (F/g)
CMK-3-130-Milk	1079.7	1.21	3.56	145
CMK-3-130-Orange	1196.4	1.42	3.48	167
CMK-3-130-Coke	1890.4	1.85	3.70	195

Nanoporous Aerogels with Super-high Thermal Stability

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Abstract

Because of ultrahigh porosity, specific surface area and low density, metal oxide aerogels have drawn great interest as catalysts, adsorbents as well as thermal insulators. However, they are usually too fragile and readily to sinter upon heat treatment, which badly limits their high-temperature applications. Herein, Robust, highly thermally stable core-shell nanoporous metal oxide aerogels are produced via a novel acetone-aniline in situ water formation method combined with novel modification techniques: supercritical modification and chemical liquid deposition. The core-shell nanostructure not only significantly reinforces the nanoparticles but also effectively inhibits the crystal growth and phase transition of metal oxide upon heat treatment, which enhances the heat resistance from approximate 400-800℃ up to 1000-1300℃. The resultant core-shell nanoporous Al_2O_3, ZrO_2 and TiO_2 aerogels have good mechanical strength and exhibit high surface areas of 139, 186 and 154m^2/g after fired at 1300, 1000 and 1000℃, respectively. We demonstrate that the core-shell ZrO_2 and TiO_2 aerogels show enhanced adsorption and photocatalytic performances, respectively, for dye after fired at 1000℃. The core-shell Al_2O_3 aerogel/mullite fiber/TiO_2 composite possesses ultra-low thermal conductivities of 0.058, 0.080 and 0.11W/mK at 800, 1000 and 1200℃, respectively. The resulting materials are promising candidates as high-temperature (400-1300℃) thermal superinsulators, adsorbents and catalysts[1-5].

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Rattle-type Magnetic Mesoporous Hollow Carbon Particles as a High-performance Adsorbant for Water Treatment

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Abstract

Di (2-ethylhexyl) phthalate (DEHP), a widely used plasticizer, has become a serious pollutant in plastic industry, which causes a range of adverse effects on the human health such as cancer and memory loss.[1] Recently, magnetic mesoporous carbon particles (MMCPs) have been proved as excellent adsorbents to remove water contaminants.[2,3] However, for applications in which large contaminant such as DEHP are dealt with, MMCPs with high mesopore volume and large pore sizes is highly desired. Herein, novel rattle-type magnetic mesoporous hollow carbon hybrid particles (Figure 1a-b) were synthesized via a simple surfactant-free method, which possesses high mesopore volume of 0.52 cm^3 g^{-1} and large pore size of 7.6 nm. The designed nanomaterial exhibited excellent fast adsorption and more effective removal capacity of DEHP of 798 mg g^{-1} (Figure 1c) compared with previously reported adsorbent materials.[4] The used adsorbent particles could be separated easily from the aqueous suspensions by an external magnetic field and could be used repeatedly after a simple regenerating treatment (Figure 1d). We also investigated the influences of the carbonization temperature and silica precursors on the structures of magnetic mesoporous hollow carbon hybrid particles as well as their performance in DEHP removal. Our designed material provides a great promising candidate adsorbent in water treatment.

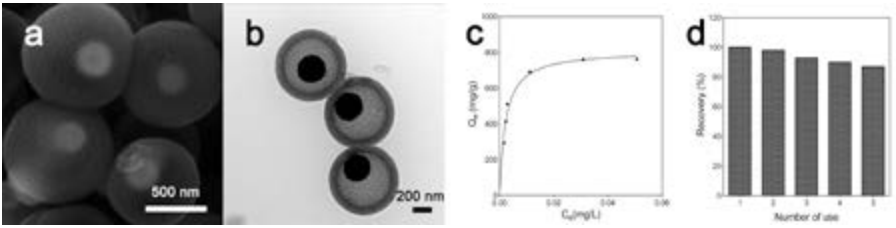


Figure 1 (a) SEM and (b) TEM images, (c) adsorption isotherm and (d) reusability over five cycles of rattle-type magnetic mesoporous hollow carbon hybrid particles.

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Study of Binary Alkaline Ratio on the Synthesis of Titania Nanostructured via Hydrothermal Method

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Abstract

The effect of alkaline binary mixture of NaOH and NH_3 in the synthesis of nanostructured TiO_2 has been studied. Powder of anatase titania as the precursor was mixed with various volume ratio of 10 M of NaOH and 15 M of NH_3. The mixture was heated in Teflon-lined autoclave at 150 ^oC for 24h. The as-synthesized TiO_2 powders were then washed with 0.1 M HCl and calcined at 300 ^oC. The calcined samples were characterized using TEM (transmission electron microscope), SEM (scanning electron microscope), XRD (X-Ray diffraction) and Raman spectroscopy.

The TEM images shows the formation of nanotube structure as high amount of NaOH applied, with diameter of about 10 nm. At volume ratio of NaOH to NH_3 of 1:3, nanosheets contributed as its main morphology. The crystallinity of TiO_2 anatase crystalline phase was enhanced as more NH_3 utilized. Raman spectroscopy will further used to determine the contributing crystalline phases for the synthesized TiO_2 at the solvent volume ratio of 1:1 and 3:1. Selected nanostructured titania will be applied as photoanode on dye-sensitized solar cells.

Surfactant-Tailored Nanosponge Zeolite with Uniform Mesopores Supporting Cobalt Nanoparticles as a High Performance Fischer-Tropsch Catalyst

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Abstract

Fischer-Tropsch (FT) synthesis is one of important catalytic process that produces liquid fuels from a mixture of H_2 and CO. In the FT synthesis process, cobalt nanoparticles (Co NPs) supported on γ-Al_2O_3 are used as catalysts due to its high CO converting activity and high yield of long-chain linear hydrocarbons with limited formation of oxygenates and aromatics. However, Co/γ-Al_2O_3 catalyst exhibited an unselective distribution of product hydrocarbon chain lengths, according to the Anderson-Schultz-Flory model. Recently, the product selectivity could be increased to a desired range of chain lengths when zeolite was used as a support for Co NPs. However, the zeolite-based catalysts exhibited much lower CO conversion, as compared to the conventional alumina-based catalysts due to low dispersion of Co NPs. Very recently, nanosponge zeolites with MFI, beta, MTW and MRE-type framework (namely, NSZ) were hydrothermally synthesized via a surfactant-directed synthesis route.[1] These zeolites were composed of disordered network of ultrathin (~ 5 nm) thick zeolitic frameworks having a sharp distribution of mesopore diameters centered at 4 nm. In this work, we investigated the NSZ as a supporting material of Co NPs for FT synthesis reaction. The highly mesoporous texture (high surface area and large pore volumes) of NSZ was suitable for supporting Co NPs with a narrow distribution of particle diameters centered at 4 nm. The Co/NSZ exhibited high stability of the Co NPs against particle growth, and there was accordingly high catalytic conversion of carbon monoxide to hydrocarbons and long catalytic lifetime in the FT synthesis reaction. The high CO conversion without significant deactivation over the Co/NSZ catalyst means that the Co NPs were supported with optimum diameters, and were stably retained in the mesopores of the NSZ sample. Additionally, the Co/NSZ exhibited high selectivity for branched hydrocarbons in the gasoline range (C_5-C_{11}), as compared to conventional alumina-based catalysts. This high selectivity could be attributed to hydroisomerization reaction in the extremely thin zeolite frameworks that provided short diffusion path lengths for branched hydrocarbons.[2] The NSZs provided new opportunities as advanced catalysts for bi-functional catalytic applications that require both high dispersion of metal nanoparticles and strong acidity of zeolite frameworks.

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Influence of the Pretreatment of Mesoporous Graphitic Carbon Nitrides on the Photocatalytic Degradation Activity of Organics

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Abstract

The extension of the used spectral range of sun light into the visible range to increase the energetic efficiency by using lower band gap materials, which work with visible light, is a challenge. Photocatalysis is a green, economical and efficient technology to use light, ideally solar light, to drive catalytic reactions, which has wide application in water/air purification, hydrogen production from water and energy conversion. Many inorganic semiconductors have been used as photocatalyst in the degradation of environmental hazardous organic pollutants and hydrogen evolution from water .Graphitic carbon nitride (g-C_3N_4) is a polymer semiconductor with a moderate band gap of *ca.* 2.7 eV, showing an intrinsic semiconductor-like absorption in the blue region of the visible spectrum. It has a high thermal and chemical stability.

Graphitic carbon nitride materials with tri-*s*-triazine based structures were prepared by thermal condensation of melamine (CNT) An amphiphilic block copolymer-F68 was used as a soft template for the synthesis of mesoporous carbon nitride. As-prepared samples were calcined under different conditions. The structural and photophysical properties of the as-prepared catalysts were characterized by XRD, elemental analysis, N_2-adsorption measurement, TEM, XPS, DSC, TOC and d UV-Vis absorption as well as time-resolved picosecond emission spectroscopy. The photocatalytic activity of the samples was in the degradation of pharmaceutical, the recalcitrant x-ray contrast agent trizoic acid and rose Bengal (RB)). The pretreatment conditions show a markedly effect on the photocatalytic activity, which are attributed to its crystallinity. Quenching experiments for the hole scavenger EDTA reveal that formed holes h+ are the active sites. The activity of samples has been compared with that of titania P25. The comparison shows that polymeric mpg-CN materials may comparatively high activity. Dissolved oxygen has nearly no impact on photocatalytic activity. However, it cannot be excluded that *in situ* at h+ formed oxygen can transferred to peroxy radicals or singlet oxygen taking part in the oxidative degradation.

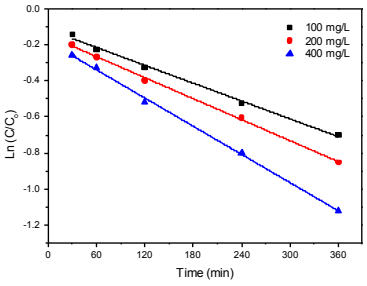


Fig.1 RB removal over different g-C3N4

Mesoporous Co_3O_4/montmorillonite Composite Catalysts for Toluene Combustion Synthesized by Hydrogel-assisted Route at Controlled pH of Co^{2+} Adsorption Step

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Abstract

In recent years, aluminosilicates-hydrogel nanocomposites have been become an object of intense research due to their improved properties compared to pure polymers. Such materials are most frequently based on montmorillonite, which is an easily available clay. As has been found, the formed montmorillonite-hydrogel nanocomposites exhibit a high efficiency in the adsorption of transition metal cations. This feature can be used in the preparation of new types of catalyst precursors. The introduction of transition metal cations into the hydrogel network, which is located between the layers of montmorillonite, and then calcination of the obtained precursor at elevated temperature, leads to partial exfoliation of the aluminosilicate structure with an exposition of metal oxide crystallites highly dispersed on the clay surface.

In the presented work, using of such approach to the synthesis of Co-containing clay catalysts, dedicated to the total oxidation of toluene, is described. The composite precursors were obtained by in situ polymerization of acrylic acid (AA) in a slurry containing a natural montmorillonite (MT). N,N'-methylenebisacrylamide (MBA) and ammonium persulfate (APS) were used as a crosslinking agent and an initiator, respectively. The amounts of AA and MT were selected to achieve the composite containing 50 wt% of poly(acrylic acid) (PAA). The formed MT-PAA composite was modified by adsorption of cobalt(II) cations from aqueous solution of $Co(NO_3)_2$ (0,01 M) at controlled pH (ranging from 3,3 to 9,0). In the final step of the synthesis, a series of MT-PAA materials containing Co^{2+} cations was calcined in order to remove the hydrogel part and to form metal oxide phase deposited on the surface of montmorillonite. The synthesized materials were characterized by XRD, XRF, TG, UV-vis-DR, DRIFT and low-temperature nitrogen adsorption.

It was found that pH conditions influenced the swelling capacity and the accessibility of free COO^- groups of the modified composites, therefore different distributions and contents of Co species were obtained depending on pH of solution used during adsorption. The calcined materials after adsorption at low pH (3,3-6,0) showed a significant increase in the BET surface area due to partial exfoliation of layered structure and the appearance of additional mesopores. Moreover, XRD and UV-vis-DR studies revealed the presence of nanometric Co_3O_4 crystallites (with a mean size of 15-22 nm) highly dispersed on the surface of such materials. The further increase in pH resulted in a loss of porosity. The catalytic tests showed the high performance of the calcined materials in the total oxidation of volatile organic compounds. The highest conversions of toluene were achieved over the Co-containing catalysts modified at pH between 5,0 and 7,0. For these catalysts the determined temperatures of 50% toluene conversion were 270-280°C. The catalytic activity of the studied materials was correlated to the distribution of crystallite sizes and their dispersion on the exfoliated clay support.

Impact of Pore Architecture in Amino-functionalized Polymer-mesoporous Silica Hybrid Materials on Their Catalytic Activity in Knoevenagel condensation

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Abstract

The most important features of ordered mesoporous silicas are: high surface area, large pore volume, ordered pore structure, uniform and tunable pore size along with chemical and thermal stability. However, the surface of these materials is rather low reactive and has to be modified in order to enhance activity in specific applications. The recent studies have suggested that the functionalization of silica surface by grafting of polymers may play an important role in designing novel polymer-silica hybrid materials. Such hybrid materials are becoming important heterogeneous catalysts used in the synthesis of fine chemicals, particularly in carbon-carbon bond forming reactions (e.g. Knoevenagel condensation, aldol condensation, Michael addition).

The main objective of the presented work was to study the influence of structural and surface properties of mesoporous silica support on the distribution of deposited polymer phase and the catalytic activity in the Knoevenagel condensation. For this purpose, three ordered mesoporous silicas with different pore architecture and pore diameter (SBA-15 with 2D, hexagonal arrangement of cylindrical mesopores, SBA-16 with 3D, cubic cage structure of spherical mesopores and MCF with 3D structure of large spherical cells connected by large windows) were synthesized. The obtained silica supports were functionalized with polyvinylamine (PVAm), polymer with a high amount of primary amino groups located along the backbone, by radical graft copolymerization. The typical process leading to obtain the silica-based hybrid materials included three stages. First, vinyltriethoxysilane (VTS), with polymerisable double bonds, was grafted on the surface of silica support. Subsequently, the polymer growth was initiated from the surface by radical copolymerization between the vinyl-modified SBA-15 particles and N-vinylformamide. Finally, poly(N-vinylformamide) grafted on the silica surface was converted to PVAm by acid-catalyzed hydrolysis followed by neutralization.

The textural and structural properties of the initial mesoporous silica supports and the hybrid materials were determined using low-temperature adsorption of nitrogen (BET) and powder X-ray diffraction (XRD). The collected results revealed that all mesoporous silicas maintained their structure after the performed modifications. Nevertheless, the functionalization influenced the textural parameters (BET surface area, pore volume and pore size distribution) of the studied silica supports. The effect of pore architecture of the pristine silica on the amount of deposited polymer phase was assessed by thermogravimetry (TG) and elemental analysis (EA). The changes in the form of deposited polymer, especially the distribution of N-containing species (amide as well as non-protonated and protonated amino groups) were determined by diffuse reflectance infrared Fourier transform (DRIFT) and X-ray photoelectron spectroscopy (XPS). The collected results showed that the formed polymeric species were successfully deposited in the mesopores. The obtained amino-functionalized polymer-silica hybrid materials appeared to be very active catalysts of the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate.

This work was supported by the National Science Centre under the grant no. 2012/07/B/ST5/00917.

Energy Efficient Synthesis of Mesoporous CN with Rod Shaped Morphology and Tunable Pore Diameters for CO_2 Adsorption

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Abstract

Carbon nitride (CN) is a fascinating material that has attracted a significant attention as the incorporation of nitrogen atoms in the carbon nanostructure can significantly influence its mechanical, conducting, and semiconducting properties. The presence of free amine and NH groups on the surface of the CN offers highly and basic catalytic properties. In order to improve the textural and semiconducting properties of the CN, Vinu et al. introduced mesoporosity in CN using a hard templating procedure involving the polymerization of carbon tetrachloride and ethylenediamine inside the nano channels of SBA-15 and the removal of template by either NaOH or HF [1]. They further demonstrated that mesoporous CNs (MCN) are good candidates for the adsorption of CO_2 as the basic surface sites favors the capture of CO_2 through a simple acid base interaction [2]. The overall energy economics of the process is too high as it involves several energy intensive steps including high temperature calcination for the mesoporous silica template and therefore unattractive from commercial standpoint. In this work, we report on the preparation of MCNs with excellent morphological control using as-synthesized mesoporous silica SBA-15 washed with ethanol prepared by "static method" which is considered as an easy, salt-free and inexpensive approach to control the morphology. Moreover, the use of the uncalcined SBA-15 as template for the fabrication of MCNs makes this process both energetically efficient and economically viable. The characterization results reveal that the prepared MCNs have well-ordered porous structure with larger pore diameter and much better morphology than that of the MCNs prepared by the calcined SBA-15. The pore diameter of the MCNs (2.8-5.9 nm) can also be controlled by using the templates with different pore diameters prepared at different synthesis temperature from 100 to 150 ^oC. The prepared samples were also used for the adsorption of CO_2 molecules. It was found that the CO_2 adsorption capacity of the MCNs prepared by ethanol washed SBA-15 (MCN-TE) is 15.4 mmol/g which is much higher than that of activated carbon and MWCNT but similar to that of the MCNs prepared by using calcined SBA-15 templates (MCN-TC) (Figure 1).

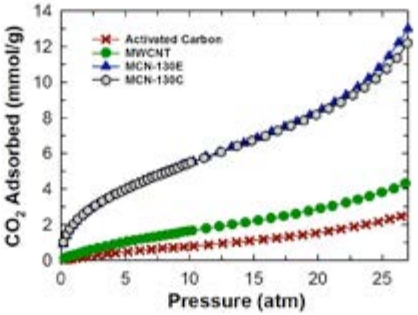


Figure 1: Comparison of CO_2 adsorption isotherms of MCN-130E and other materials.

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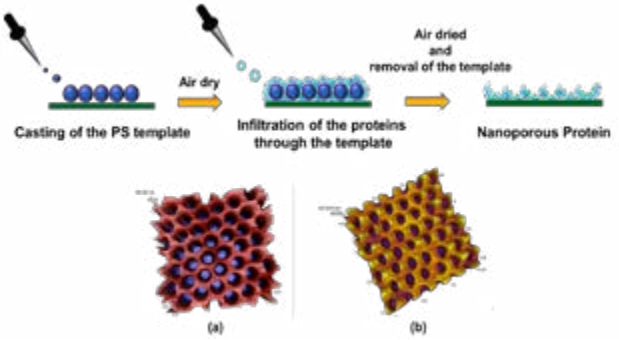
Soft-Templated Synthesis of Highly Ordered Nanoporous Heme Proteins for Selective Sensing of Toxic Vapors

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Abstract

A novel fabrication method has been developed for the creation of nanoporosity in heme protein films such as hemoglobin and myoglobin. The protein films are prepared by using a one-pot approach via soft templating technique wherein polystyrene (PS) beads with different molecular diameters are used as the structure directing agents (Scheme1). The obtained protein films are subjected to thorough physico-chemical characterization employing sophisticated techniques such as high resolution scanning electron microscopy (HRSEM), atomic force microscopy (AFM) and Fourier transform infra-red spectroscopy (FT-IR). HRSEM and AFM results reveal that the films have highly ordered nanopores that are arranged in an orderly fashion (Figure1). One of the most crucial steps in the fabrication of the highly ordered nanoporous proteins without affecting its local structure is the dissolution of the PS spheres with the proper solvent. In this case, toluene is used for the dissolution of PS spheres. FT-IR results confirm that the local structure of the proteins is maintained even after removal of the template. Moreover, the pore diameter and the thickness of the films can be finely controlled by varying the diameter of the PS spheres. The protein films were also grown on a quartz crystal microbalance (QCM) and used for sensing of organic vapours. Due to the simple basic nature of these protein films, it was found that they showed a high selectivity towards acidic vapour molecules with high levels of affinity and sensitivity. The amount of adsorption was found to decrease with increasing length of the carbon chain of the organic acids. The extent of adsorption was also found to be influenced by the concentration and the pore diameters of the nanoporous protein films. The sensing performance increased with increasing concentration of the protein used for the fabrication of the films but decreased with increasing the size of the pores of the protein films. It was also noticed that the performance of the films varied with the molecular diameter of the protein films used. Among the protein films studied, cytochrome c, which has the smallest diameter, was found to be the best films for the selective sensing for acidic organic vapors whereas myoglobin (mol wt of 17 kDa) whose molecular diameter is larger than other proteins used in this study exhibited a lesser performance in comparison to other heme proteins.

Scheme 1 Fabrication of nanoporous protein films



Hard-template Synthesis of N, S Dual-doped Microporous Carbons as A Highly Active Electrocatalyst for Oxygen Reduction

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Abstract

Carbon containing non-metal heteroatoms has attracted much attention as an electrocatalyst for oxygen reduction reaction (ORR) due to high conductivity and activity, and low cost.[1] Here, microporous carbon incorporated with nitrogen and sulfur was synthesized by hard template method using beta zeolite. 2-thiophenemethanol and acetonitrile were used as sulfur and nitrogen precursor, respectively. The carbon deposition into zeolite micropores was performed by two-step method: 1) incipient wetness of 2-thiophenemethanol, 2) chemical vapor deposition of acetonitrile at 750 °C. Template-free carbon product exhibited uniform micropore size centered at 1.2 nm and high surface area (1500 cm^2g^{-1}). The contents of nitrogen and sulfur were 3 wt.% and 1.5 wt.%, respectively, as confirmed by elements analysis. The N, S dual-doped microporous carbon showed higher activity in ORR than pure microporous carbon and nitrogen mono-doped microporous carbon. This result indicated that synergetic effect between nitrogen and sulfur reduced the energetic barrier of electron transfer from carbon surface to the absorbed oxygen.[2] We expect that this carbon could be promising alternative material to platinum-based ORR catalyst.

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Mesoporous Manganese Silicate Coated Silica Nanoparticles as Multi-Stimuli-Responsive T_1-MRI Contrast Agents and Drug Delivery Carriers

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Abstract

In this work, a novel kind of monodispersed mesoporous manganese silicate coated silica nanoparticles (MMSSNs) as a highly efficient and cytotoxicity-free T_1-weighted MRI contrast agents (CAs) and drug carriers for cancer diagnosis and chemotherapy has been constructed by a facile surfactant-free "SiO_2 sacrifice and *in situ* silicate growth" approach. It is revealed that the mesoporous structure provides a large specific surface area and abundant exposed manganese paramagnetic centers to water molecules. The MMSSNs exhibit a positive T_1-MRI signal with r_1 of 0.91 $mM^{-1}s^{-1}$ on a 3.0 T human clinical scanner. Interestingly, the MMSSNs present an efficient pH/redox-responsive T_1-MRI feature based on the significant enhancements of relaxation rate stimulated by mild acidic environment and reducing agent (GSH) both *in vitro* and *in vivo*. The r_1 values have reached 4.34 and 6.32 $mM^{-1}s^{-1}$ in the buffer solutions of pH=5.4 and 1.0 mM GSH, respectively, considerably higher than that of commercial Gd-based CAs ($r_1 \approx 3.4$ $mM^{-1}s^{-1}$), and present about 10-12.6-fold magnitude increase over those of conventional MnO-based nanoparticles (typically $r_1 < 0.5$ $mM^{-1}s^{-1}$). It indicates that such a variation of T_1-MRI signal intensity can be utilized for stimuli-responsive T_1-MRI by using MMSSNs instead of elaborately designing complicated pH-/redox-responsive chemical bonds. Furthermore, the MMSSNs behaved an efficient anti-cancer drug (DOX) storage and a pH-responsive release. Thus, the MMSSNs could be suitable for the diagnosis and chemotherapy of tumors in an intelligent and on-demand manner. To the best of our knowledge, this is the first study on the exploration of manganese silicate-based materials used as MRI CAs and drug carriers.

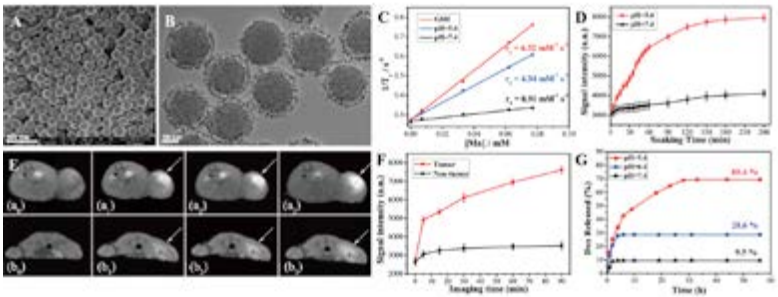


Figure 1. A) SEM and B) TEM image, C) T_1 relaxivities and D) Dynamic T_1-MRI signal intensity *in vitro*, E) T_1-MRI and F) Quantitative T_1-MRI signal intensity *in vivo* (tumor and normal tissue), G) DOX release profiles of MMSSNs.

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Smart Peptide Linker Conjugated Upconversion Nanoparticles for Targeted Cancer Imaging and Photodynamic Therapy

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Abstract

Although photodynamic therapy (PDT) has been recognized as an important strategy for tumor treatment, the development of photosensitizing drugs (PSs) has been greatly hampered by the limited penetration of irradiation light required for this therapy. Recently, near infrared (NIR) excitable upconversion nanoparticles (UCNPs) have surfaced as attractive luminescent nanomaterial candidates for imaging by guided PDT in deep-tissue due to their excellent optical properties. Under 980 nm laser excitation, PSs bound onto the surface of UCNPs can be activated by the emitted green light (~545 nm) from UCNPs. Tumor accumulation of the drug-attached UCNPs has been achieved by conjugating UCNPs with specific tumor targeting antibodies, which largely enhances treatment efficiency.

Traditional bioconjugation techniques for UCNPs rely on chemical crosslinking (e.g. EDC/NHS), which often result in low targeting efficiency due to the denaturation of the targeting antibodies. In this work, we applied an alternative bioconjugation strategy based on a smart peptide linker sequence that displays high binding affinity towards silica. The linker sequence can be genetically-fused to a protein of interest and the resulting recombinant fusion protein (Linker-Protein) exhibits strong affinity to a range of silica-based materials. This linker system has been used to produce a Linker-Antibody Binding Protein (L-ABP) that acts as an anchorage point for the orientated immobilisation of antibodies onto the surface of silica modified UCNPs (UCNPs@SiO_2) without the need for any complex surface chemical modification. To achieve the therapeutic effect of the designed nanocomposite, the photosensitizer rose bengal (RB) was encapsulated into the silica layer of the UCNPs@SiO_2, wherein green light emitted from UCNPs under NIR excitation activated the reactive oxygen species (ROS) generation from rose bengal to destroy the targeted cancer cells. The resulting "UCNPs@RB-SiO_2+L-ABP+antibody" bioconjugate is thus engineered as an integrated diagnostic and therapeutic modality for targeted cancer imaging and therapy and has been proven to detect and kill human colorectal adenocarcinoma cell line HT-29 cells *in vitro*.

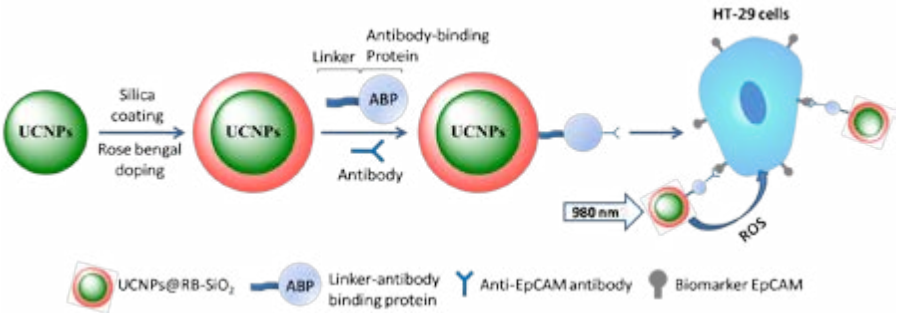


Figure 1. Illustration of preparation of UCNPs@RB-SiO_2+L-ABP+antibody nanocomposite.

A cryo-TEM Study of the Formation of Nanotubes and Helical Ribbons of Mesoporous Silica Materials

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Abstract

Chiral mesoporous silica with different handedness and morphologies can been synthesized using surfactants with a chiral head, a co-structure directing agent and a silica source.[1] The synthesis temperature determines which structure that forms. In the N-myristoyl-L-alanine (C_{14}-L-Ala) synthesis system at 0°C, nanotubes are formed in a process where ribbons, twisted ribbons and helical ribbons occur as intermediate structures.[2] Similar structural transformation has been observed in by cryogenic transmission electron microscopy (cryo-TEM) in the self-assembly process resulting in nanotubes of N-R-lauryl-lysyl-aminolauryl-lysyl-amide.[3] Sharon et al.[4] have reported a geometric-mechanical model for calculating equilibrium configurations of systems that self-assemble into these types of structures. The model is based on observations of chiral seedpods, but can be utilized on molecular self-assembled systems.

We are following the formation process of the silica nanotubes in C_{14}-L-Ala system using cryo-TEM (Figure 1) as a function of mixing/synthesis time, and are quantitatively analyzing the structures observed in relation to the model of Sharon. Our observation reveals that twisted ribbons form as threadlike objects aggregate. With time the ribbons coil up forming tubular structures, and, occasionally, the ribbons pair up resulting in a tube within a tube.

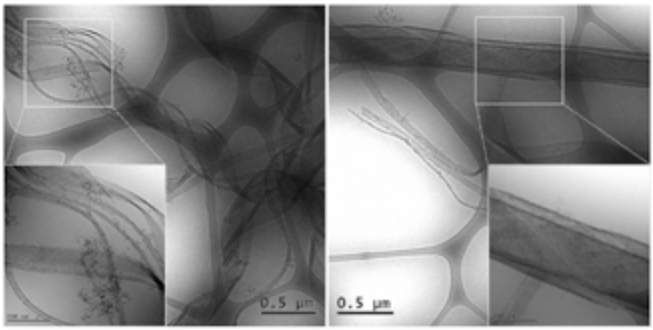


Figure 1. Cryo-TEM images of the formation of mesoporous silica nanotubes. The formation proceeds with threadlike aggregates (left image) assembling into twisted ribbons, that form helical ribbons that eventually form nanotubes. Sometimes one tube can form within another (right image).

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High Performance Mixed Matrix Membranes with Metal–organic Frameworks Decorated CNTs Fillers for CO_2 Separation

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Abstract

Membrane separation has emerged as an efficient process for various industrial applications, especially in gas separation and purification. Most of the existing polymeric membranes suffer from the limit of trade-off between permeability and selectivity, referred as Robeson upper bound. Mixed matrix membranes (MMMs) fabricated by introducing carbon nanotubes (CNTs) into polymer matrix provide promising opportunities to achieve superior gas permeance owing to the unique structure of CNTs filler. Nonetheless, the difficulty of CNT dispersion in polymer matrix and the interfacial defects are still obstacles impeding the MMMs to be prepared in for high gas selectivity.

In this work, we report a novel MMM filler derived from in-situ growth of metal–organic frameworks (MOFs) on the external surface of CNTs for gas separation. Extra amino groups and active sites were introduced to external surface of CNTs after MOF decoration. Through MOF decoration, sufficient amino groups and active sites were introduced to the external surface of CNTs. The good adhesion between the synthesized composite fillers and polymer phase was observed. Compared to pure polymeric membrane, MMMs containing the as-synthesized MOF/CNT composite displayed significantly improved CO_2 permeance (up to 150%) and CO_2/CH_4 selectivity (up to 37.5%). The combined performance of permeability and selectivity is above the Robeson upper bound.

The Influence of Different Carbon Sources on Electrochemical Performance of $Li_4Ti_5O_{12}$/C Materials

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Abstract

The rate performance is affected by low electrical conductivity (10^{-9}~10^{-13} S/cm at room temperature) of $Li_4Ti_5O_{12}$. Therefore, the commercial application of $Li_4Ti_5O_{12}$ has been limited, even though it is one of the most attractive anode materials for Li-ion batteries. It is an effective measure for improving the rate performance of $Li_4Ti_5O_{12}$ by adding conductive additives, which could enhance the inter-particle electrical conductivity of $Li_4Ti_5O_{12}$.Here, $Li_4Ti_5O_{12}$/C materials were synthesized by high-temperature solid-state method using lithium carbonate and titanium dioxide as primary starting materials. Sucrose, stearic acid, citric acid and activated carbon were used as carbon sources to increase the conductivity of lithium titanate. The best sintering conditions were 14 hours of calcination at 750 ^{o}C based on TGA-DTA analysis of the precursor and a series of experiments. The XRD patterns indicated that the synthesized product was spinel lithium titanate (Fig.1). The capacity retentions of all prepared materials were above 95.4% of their initial discharge capacity at 0.5C after 200 cycles. Rate performance of $Li_4Ti_5O_{12}$/C materials was influenced by the different carbon source. The rate performance of the $Li_4Ti_5O_{12}$/C materials coated using the stearic acid is higher than that of sucrose, citric acid and activated carbon.

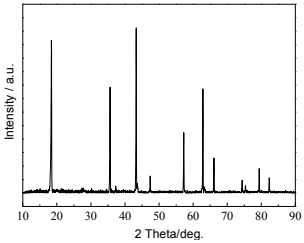


Fig. 1 X-ray diffraction pattern of $Li_4Ti_5O_{12}$/C materials.

Acknowledgements

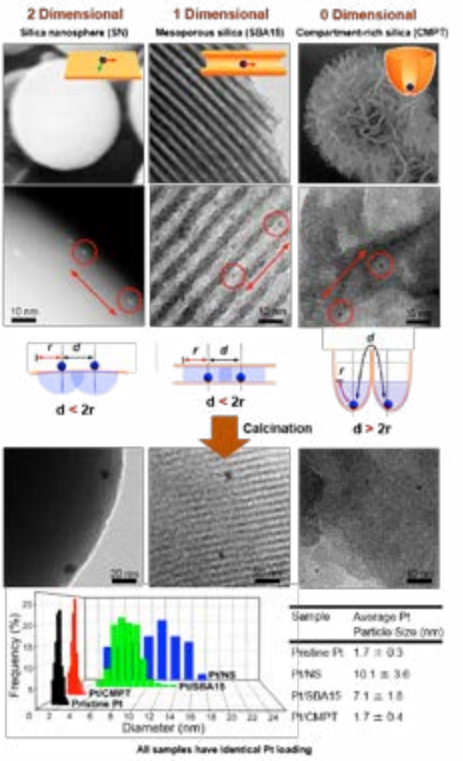
This research was supported by the National Natural Science Foundation of China (no. 51274075), the National Environmental Technology Special Project (no. 201009028) and Guangdong Province-department University-industry Collaboration Project (grant no. 2012B091100315).

Better than Mesoporous Structure: Aggregation-free Nanoparticles in Wide-Mouthed Compartments for Sustained Catalytic Performance

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Abstract

Particle aggregation is one of the most significant impediments to functional nanoparticles in many valuable applications especially catalysis. To mitigate particle aggregation, strategies have been developed focusing on steric confinement of nanoparticles by coated with a porous shell, sandwiched between a solid core and a porous shell, or encapsulated in the nanometer-sized channels of zeolites and their silica and metal-organic framework mimics. However, such confined structures passivate surface active sites of the nanoparticles and are often accompanied by decrease in mass- and/or energy transfer, giving rise to diminished catalytic activity. Herein, we report that aggregation-free nanoparticle system can be realized through a simple materials-design which maximizes the particle-to-particle traveling distance of neighboring nanoparticles. As a demonstration, platinum (Pt) nanoparticles were placed apart from each other in wide-mouthed compartments tailored on the surface of self-assembled silica nanosheets. These Pt nanoparticles retained their particle size after calcination at elevated temperatures because the compartment wall elongates the particle-to-particle traveling distance to preclude the possibility of coalescence. Moreover, the Pt nanoparticles in wide-mouthed compartments were fully accessible to the environment and exhibited much higher catalytic activity for the oxidation of carbon monoxide than the nanoparticles encapsulated in nano-channels of mesoporous supports. The proposed materials-design strategy is applicable not only to industrial catalysts operating in harsh conditions, but also opens up possibilities in developing advanced nanoparticle-based materials with sustained performance.



Polyanilne Nanoparticles Modified by Graphene for High-performance Asymmetric Supercapacitor

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Abstract

Polyanilne (PANi), one of the most important conducting polymers, has been considered as one of the most promising electrode materials for supercapacitors due to its excellent capacity for energy storage, easy synthesis, stability in air, low cost and relatively high conductivity. However, its continuous swelling and shrinkage occurring during doping/dedoping process causes poor cycling stability and hinders its practical application. In the present work, flexible wrinkle graphene was used to improve the above problem with realizing an increase on both the specific surface area and the electrical conductivity of material. From the SEM observation (see Fig. 1a), PANi nanoparticles are uniformly grown on the surfaces of graphene sheets. The BET results of PANi-graphene composite exhibits its high specific surface area of 90.89 m^2 g^{-1} and the predominance of mesopores (see Fig. 1b). The unique nanostructure indicates high energy storage capacity and fast transport and diffusion of electrolyte ions during the charge/discharge process. The asymmetric supercapacitor fabricated by PANi-graphene composite and activated carbon can be cycled reversibly in the voltage range of 0–1.6 V, and exhibits excellent cyclic durability (see Fig. 1v). Meanwhile, the device displays the maximum energy density of 29.6 Wh kg^{-1} at a power density of 555.37 W kg^{-1}(see Fig. 1d).

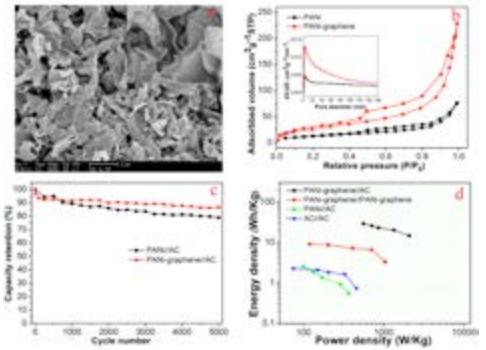


Fig. 1 (a) SEM image of PANi-graphene composite; (b) N_2 adsorption-desorption isotherms, and pore size distributions of PANi-graphene composite (the inset); (c) Cyclic performances of PANi //AC and PANi-graphene//AC; (d) Ragone plots of symmetric and asymmetric supercapacitors based on AC, PANi-graphene and PANi-graphene //AC.

Biomass-derived Mesoporous Carbons and Their Applications in Electrochemical Biosensors and Energy Storage

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Abstract

A series of biomass-derived activated carbons with high surface areas (ca. 1,500 m^2 g^{-1}) and containing desirable heteroatoms were synthesized and exploited as modified electrodes for biosensors and supercapacitors. For example, guava leaves-derived heteroatoms-containing activated carbons (GHACs) synthesized by using a facile chemical activation method using KOH as the activating agent were exploited as catalyst supports to disperse nickel oxide (NiO) nanocrystals (size ca. 2.0 nm) through a hydrothermal process. The as-synthesized GHAC/NiO nanocomposites were employed as binder-free electrodes, which exhibited superior specific capacitance (up to 461 F g^{-1} at a current density of 2.3 A g^{-1}) with remarkable cycling stability. In addition, we introduced a one-pot synthesis method for fabrication of activated carbon containing ZnO nanoparticles using sugarcane baggase as the carbon source. These novel AC-ZnO nanocomposites were employed for simultaneous electrochemical detection of ascorbic acid (AA), dopamine (DA), and uric acid (UA) as well as hazardous pollutants such as hydrogen peroxide (H_2O_2) and hydrazine (N_2H_4), revealing desirable sensitivity, selectivity, and detection limit. Moreover, heteroatoms-enriched activated carbons (HACs) were successfully prepared from banana stem. These as-synthesized HACs were further incorporated with NiO nanoparticles and used as a novel non-enzymatic glucose sensor with ultra-high sensitivity (ca. 1720 μA μM^{-1} cm^{-2}) and low detection limit (0.055 μM). Furthermore, pomegranate and orange fruit peels-derived activated carbons (PACs) modified with Pd nanoparticles were also prepared and exploited as a simple and sensitive electrochemical sensors for the trace detection of toxic metal ions (e.g., Cd^{2+}, Pb^{2+}, Cu^{2+}, and Hg^{2+}).

The Adsorption of Thiophene on Alumina with Different Pore Size

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Abstract

Adsorption is the precondition of heterogeneous catalysis reaction, and the adsorption behavior of sulfur compounds on the hydrodesulfurization catalysts depends to a large extend on the pore structure of alumina supports. In this study, γ-Al_2O_3 with different pore size (shown in Figs. 1 and 2) was successfully synthesized via cation-anion double hydrolysis method. The pore size can be tuned in the range of 3.9 to 8.5 nm. Fig. 3 demonstrates that all samples possess Lewis acid sites and the total acid amount is increased with the increase of pore size. The in situ FTIR spectra in Fig. 4 show the typical C-H stretching vibrations of thiophene adsorbed on alumina [1], and the intensities of these bands increase consistently with increasing pore size in all cases. It indicates that the larger pore size favors the adsorption of thiophene due to the less steric hindrance. Meanwhile, the more Lewis acids in the alumina can facilitate the Lewis acid-base interaction, which contributes to an increase in the adsorption amount of thiophene.

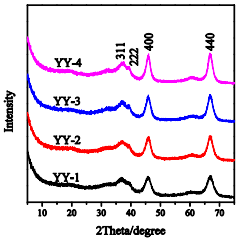


Fig. 1 XRD patterns of samples

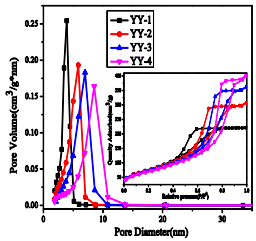


Fig. 2 Pore size distribution of alumina

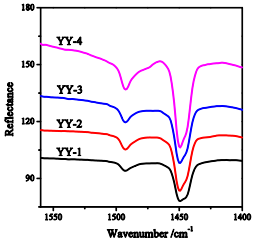


Fig. 3 Py-IR spectra of alumina

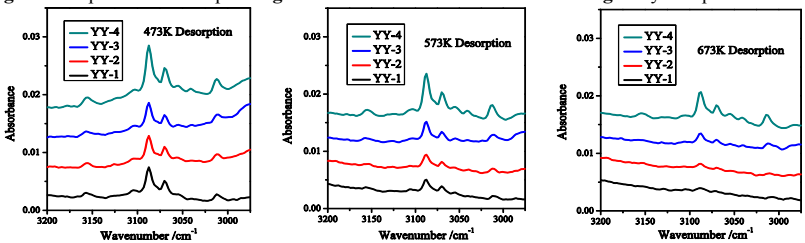


Fig. 4 In situ IR spectra recorded from the thermal desorption of thiophene adsorbed on alumina supports

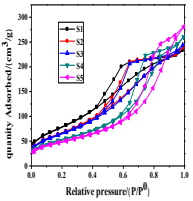
Reference and acknowledgements
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This work was financially supported by “the National Natural Science Foundation of China” (Grant No. 21376267), “the Shandong Province Natural Science Foundation of China” (Grant No. 2013ZRE28069) and “the Fundamental Research Funds for the Central Universities” (Grant No. 14CX06106A).

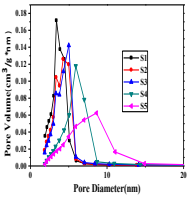
Preparation and Characterization of Mesoporous Alumina

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Abstract

Mesoporous γ-Al_2O_3 with different pore structure has been successfully synthesized under different pH values. Fig. 1 shows that all the samples are mesoporous materials with ink-bottle like pores. The mesopores could also be seen from the TEM image. When changing the pH values from 8 to 12, the crystallinity increases and the pore size also enlarges from 3.39 to 8.62 nm. This is because high pH value could facilitate nucleation process and lead to the formation of larger crystalline sizes of pseudo boehmite. FTIR spectra of pyridine adsorbed on γ-Al_2O_3 indicate that the samples possess different Lewis acid amounts. Fig. 4 demonstrates that there are only four- and six-coordinated Al atoms in the framework of alumina, which indicates that the samples are pure γ-alumina phase[1].





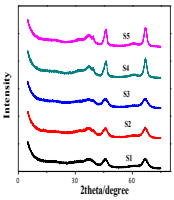
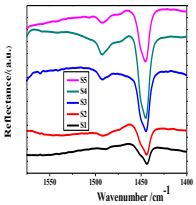
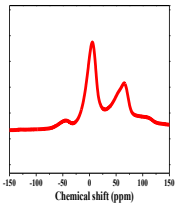


Fig.1 N_2 sorption isotherms and pore size distribution curves **Fig.2** XRD patterns





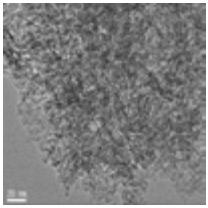


Fig.3 FTIR spectra **Fig4**. ^{27}Al MAS NMR spectra **Fig5**.TEM image

Reference and acknowledgements

[1] BAI P, SU F, WU P, et al. Copolymer-controlled homogeneous precipitation for the synthesis of porous microfibers of alumina [J]. Langmuir, 2007, 23(8): 4599-605.

This work was financially supported by "the National Natural Science Foundation of China" (Grant No. 21376267), "the Shandong Province Natural Science Foundation of China" (Grant No. 2013ZRE28069) and "the Fundamental Research Funds for the Central Universities" (Grant No. 14CX06106A).

Aging Treatment to Control the Hierarchical-pore-structured of SAPO-11 Zeolite

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Abstract

Dry gel preparation is an essential step to synthesize zeolite by dry gel method. Several aging methods (e.g. microwave treatment and ultrasonic treatment) are employed to regulate pore structure, morphology, and acid character of SAPO-11 molecular sieves. X-ray diffraction, scanning electron microscopy, N_2-adsorption, pyridine-adsorbed fourier transform infrared spectroscopy, and ^{29}Si MAS NMR were employed to investigate the effects of aging treatments on SAPO-11 products. Mesopore structure is enhanced after aging, which is formed as wedge-shaped hole. In addition, these treatments effectively affect depolymerization/ polycondensation reaction of silicon species and growth rate of different crystal planes. Hydroisomerization catalysts (Ni/ SAPO-11) with hierarchical pore structure and appropriate acid characters exhibit a higher conversion of heptane and an excellent selectivity for iso-hydrocarbon.

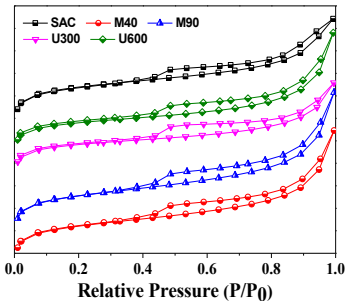


Fig. 1 N_2 adsorption- desorption isotherms of samples

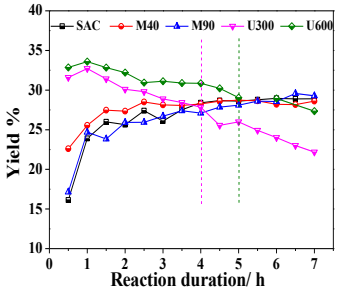


Fig. 2 Hydroisomerization performance of catalyst with different SAPO-11 support

This work was supported by the "Fundamental Research Funds for the Central Universities" (Grant No. 12CX06049A).

Preparation of Y/ZrO_2 Composite with Hierarchical Pore Structure

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Abstract

In the presence of Y zeolite seeds, Y/ZrO_2 composite material with hierarchical pore structure was synthesized by solid state reaction and in-situ crystallization method. The physical and chemical properties of the composite were characterized by powder X-ray diffraction(XRD), scanning electron microscopy(SEM), transmission electron microscopy(TEM), Fourier transform infrared(FTIR), N_2 adsorption-desorption and solid-state MAS NMR. Y zeolites with higher crystallinity are observed on the surface of ZrO_2. The micropores and mesopores are respectively shown in Y zeolite and zirconia. The composite has superior thermal stability. Considering the excellent acidic character (a desired ratio of B and L acid sites) and hierarchical pore structure of Y/ZrO_2, it will be a promising FCC catalyst in the foreseeable future.

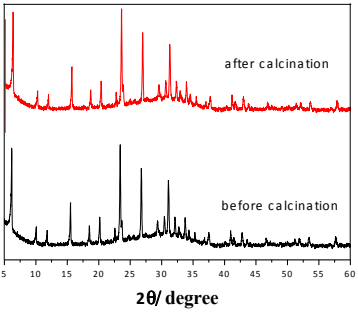


Fig. 1 XRD pattern of Y/ZrO_2 samples

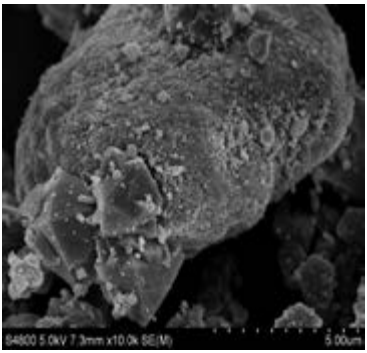


Fig. 2 SEM image of Y/ZrO_2 sample

Investigation of Low-temperature Performance of Sodium Ion Batteries Based on $Na_3V_2(PO_4)_3$/C Nanocomposite

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Abstract

Rechargeable sodium ion battery (SIB) is a sustainable and cost-effect alternative to lithium ion battery (LIB) due to cheapness and abundance of the sodium salts. The capability of electrode materials to operate in low temperature environment is an important parameter of the SIBs for the potential application. And yet, the performance of SIBs at low temperature has not been investigated in the literature. Here, carbon-coated $Na_3V_2(PO_4)_3$ (NVP@C) nanocomposite was synthesized for SIBs using a ball-milling technique and post-carbothermal reaction. The as-prepared NVP@C electrode exhibited a remarkable low-temperature performance, especially outperforming existing LIBs at high rate. As shown in Fig. 1, specific discharge capacity of the NVP@C electrodes are observed with an insignificant decline when the ambient temperature is decreased from 23 (RT) to -20 ^{o}C and the current rate is performed lower than 20 *C*. Meanwhile, the cycling capability under different rate is still maintained well at the respective temperature. At 0 ^{o}C, the capacity of *ca.* 74.6 mAg^{-1} is charged within 75 seconds at 30 *C* rate through galvanostatic charge process, accounting for *ca.* 82% of the total capacity (91.3 mAg^{-1}) charged. This excellent low-temperature performance is mainly attributed to the following three aspects: (1) nano-sized particles of NVP@C contribute a high specific surface area, leading to many active sites for Na^+ insertion/desertion reaction between electrode and electrolyte; (2) low activation energy of Na^+ interfacial reaction from liquid electrolyte to solid electrode; (3) NVP@C cathode naturally possesses the 3D diffusion structure for fast Na^+ diffusion. With such an excellent low-temperature performance, the as-prepared composite has advanced one more important step to commercialization of SIBs.

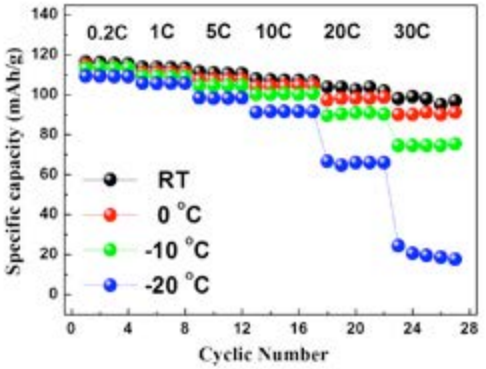


Fig. 1. Rate performance of NVP@C at 0.2 to 30 *C* discharge rates at different temperatures.

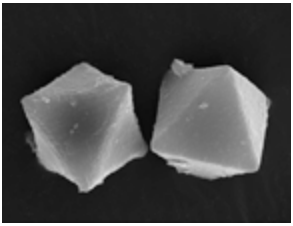
Synthesis, Characterizations and Biomedical Application of MOF-199 using Nonsurfactant Templating Method

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Abstract

Copper-based metal-organic framework (MOF-199) materials also known as $Cu_3(BTC)_2$ (copper(II)-benzene-1,3,5-tricarboxylate) with truncated and well-defined octahedral morphology were successfully synthesized using new nonsurfactant method. This new method is environmental friendly and utilized octyl alcohol as renewable template to help particle formation. Renewable template octyl alcohol was a palm oil derived fatty alcohol with eight straight carbon chain increased and enhanced the number of single octahedral particles yielded.

Varied ratios of octyl alcohol to copper salt affected the intensity of X-ray diffraction patterns and structural properties of the materials. The synthesized MOF-199 with higher ratio resulted in better crystallinity and enhanced the octahedral morphology of the materials with particle sized in the range at ca. 15-70 μm. The functional groups in the samples were disclosed using FTIR (Fourier Transform Infra-Red analysis) at a heating rate of 5°C/min. The nature of MOF-199 having high surface area, high porosity, high adsorption and flexibility provided the possibility in biomedical application by immobilizing this material.



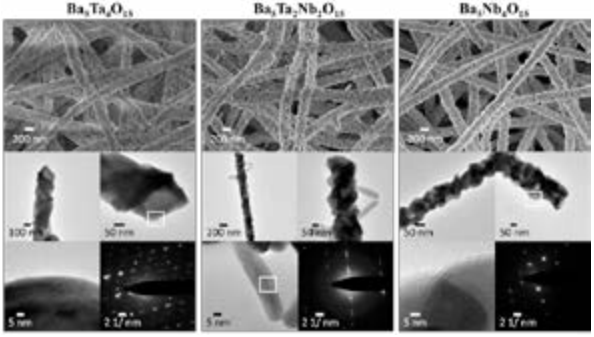
Nanostructured Layered Perovskite Nanofibers via Electrospinning for Overall Water Splitting

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Abstract

Photocatalytic water splitting induced by solar radiation on a semiconductor surface is considered as an attractive solution for sustainable solar energy conversion. However, the steps involved in the photocatalytic process are complex and certain requirements have to be complied by the photocatalyst materials, including optimum band positions with regards to the proton reduction and water oxidation potential, and optimal diffusion of photogenerated charges to the semiconductor surface.

Structuring semiconductor materials on the nanoscale to improve photocatalytic activity has gained increasing attention in recent years.[1] However, reducing the particle size of materials to values below ~10 nm (depending on the material) can increase the band gap of semiconductors absorbing less photons under the same irradiation conditions.[2] Moreover, increased surface recombination has to be inhibited by reducing surface defects. Nanofibers can therefore be of advantage compared to nanoparticulate systems, exhibiting a high aspect ratio and surface area for good photocatalytic activity, however being usually thick enough to avoid band gap increase due to quantum confinement. The formation of oxide nanofibers via electrospinning usually leads to extraordinary long isolated fibers with 50 to 500 nm thickness, and with tunable surface.[3,4] We have prepared nanofibers of the complex mixed-oxide photocatalysts $Ba_5Ta_4O_{15}$, $Ba_5Ta_2Nb_2O_{15}$ and $Ba_5Nb_4O_{15}$ via electrospinning.[5] The formation mechanism of the nanofibers was investigated in detail, indicating the intermediate formation of barium carbonate strengthening the nanofiber morphology for calcination. Superior photocatalytic activity for hydrogen generation and overall water splitting was found compared to simple powder samples, the latter upon photodeposition of a Rh-Cr_2O_3 co-catalyst system. The figure below shows the electrospun nanofibers after calcination at 900 °C, retaining their polycrystalline and nanofiber morphology.



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Mesoporous Mixed Oxide Photocatalysts by Hard-Templating

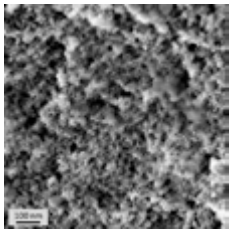
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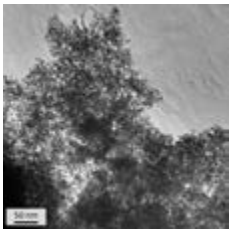
Abstract

Since the first photoelectrochemical water splitting on TiO_2 was reported by Fujishima and Honda [1] a lot of research efforts were dedicated to find efficient photocatalysts for clean hydrogen evolution and overall water splitting.[2,3] Water splitting induced by solar radiation on a semiconductor's surface is considered as an attractive solution for sustainable solar energy conversion. The challenge of current research is to develop and investigate semiconducting materials with photocatalytic activity under visible light and with high surface area.

Cesium tantalum tungstate ($CsTaWO_6$)[4,5] and barium tantalate ($Ba_5Ta_4O_{15}$)[6,7] are two promising mixed oxide photocatalysts with high potential for H_2 generation in the visible-light range. For both systems it was shown that the respective band gaps (E_g) of initially 3.6 eV ($CsTaWO_6$) or 4.4 eV ($Ba_5Ta_4O_{15}$) can be reduced by homogeneous anion doping resulting in values for E_g that enable visible-light absorption. The efficient anion doping benefits from the open structures of these two materials; $CsTaWO_6$ crystallizes in a defect-pyrochlore structure while $Ba_5Ta_4O_{15}$ exhibit a (111) layered perovskite structure. Both materials show H_2 generation under visible-light irradiation without the application of a noble metal co catalyst.

Marschall *et al*. have shown in previous studies that the photocatalytic activity of these materials is strongly affected by structural parameters like surface area and crystallinity.[5] To investigate these influences on the photocatalytic activity in more details, the hard-templating procedure is chosen as synthesis method to prepare crystalline mesoporous $CsTaWO_6$ and $Ba_5Ta_4O_{15}$ as model systems by using KIT-6 as structure matrix. The applied synthesis approach provides the opportunity to control the structural parameters, such as pore size and geometry, pore wall thickness, surface area and crystallinity, to some degree.[8] The respective mixed metal oxide is formed 'in-situ' inside the pores of the KIT-6 silica serving as structure matrix, while the synthesis of the precursor is performed by the citrate-based complexing route.[5] After various steps of infiltration with intermediate drying and calcination the silica template is removed. The figures show representative scanning (above) and transmission (below) electron microscope images of a mesoporous silica-free $CsTaWO_6$ sample.





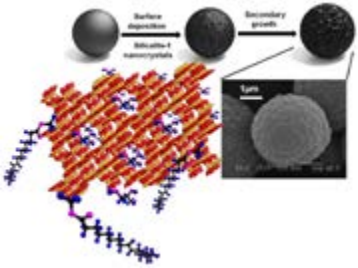
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Biodiesel Purification Using a Size-Selective Adsorbent with Microporous Zeolitic Shell and Mesoporous Silica Core

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Abstract

Free glycerol removal from crude biodiesel is of a great importance due to its negative effects on biodiesel storage and usage. Traditional purification processes suffer from a number of problems such as significant product loss. Enhancing the biodiesel purification yield, selective adsorption of free glycerol from crude biodiesel mixture might be a promising approach in biodiesel dry washing. Therefore, a core@shell architecture, consisting of high surface area, high pore volume mesoporous core templates covered with a size-selective zeolite is proposed. Various types of mesoporous silica spheres with different sizes (commercial silica gel spheres: 20-45 µm and 3 µm and HMS spheres: ~1.5 µm) were used as core templates, which subsequently covered with a polycrystalline silicalite-1 shell. Applying typical characterization techniques, complete coverage and uniformity of the shell were assured. Performing a batch-wise glycerol adsorption test, purification yield and free glycerol removal efficiency of synthesized core@shell adsorbent were evaluated and compared to those purified by using conventional adsorbents including bare mesoporous silica gel spheres, conventional zeolites and physical mixture of the constitutive building materials of the core@shell adsorbent. Although mesoporous silica gel showed slightly higher glycerol adsorption capacity, the study revealed that the mesoporous adsorbents tend to trap a significant amount of bulkier molecules, e.g. FAME in their large pore network (d_{pore}= 7nm). In contrast, microporous silicalite-1 shell with minimized effective diffusion length hindered FAME's diffusion into the mesopores by its intrinsic sieving ability, maintaining a larger number of adsorption sites for glycerol. In addition, the core@shell adsorbents benefited from large pore volume of mesoporous silica as core compartment, providing a multi-layer glycerol adsorption. This feature of the synthesized core@shell material significantly enhanced the dry washing performance in terms of purification yield and adsorption capacity, in comparison to other conventional adsorbents (remaining glycerol to FAME ratio in adsorbent improved from around 0.65 for silica gel up to 5.2 for core@shell particles).



Structural and Thermodynamic Studies on the Phase Behavior of Water in Ordered Mesoporous Host Structures with Different Pore Sizes and Different Surface Polarities

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Abstract

The first step on the way to study structural and thermodynamic behavior of water in ordered porous structures is the synthesis of the respective host. Several mesoporous silicas and organosilicas (MCM-41 and different PMOs) were synthesized using the liquid-crystal template mechanism with ionic surfactants as structure-directing agents (SDAs). To begin with the thermodynamic studies of water in these nanopores the melting and freezing points of the inner pore water were studied. This was done by differential scanning calorimetric (DSC) and cryoporometrical NMR measurements. In figure 1 the melting and freezing points of water in some MCM-41 silica and biphenyl-bridged PMO materials both with different pore diameters are shown.

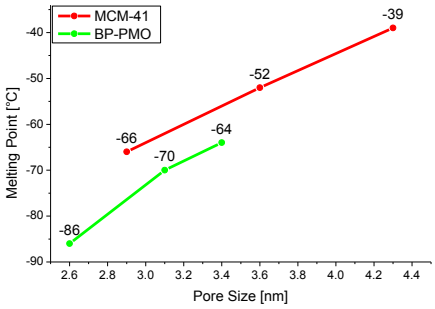


Figure 1: Melting points derived from NMR measurements of different MCM-41 silica and biphenyl-bridged PMO (BP-PMO) materials.

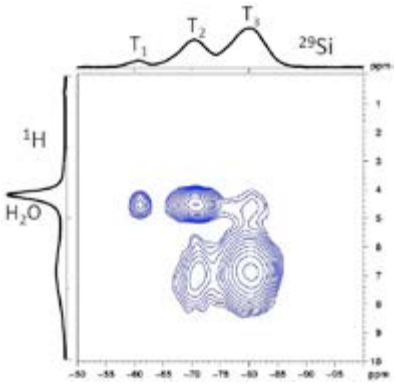


Figure 2: Solid state 2D ^{29}Si-^{1}H HETCOR-NMR measurement of a BP-PMO (pore diameter: 2.4 nm) completely filled with water at 20 °C.

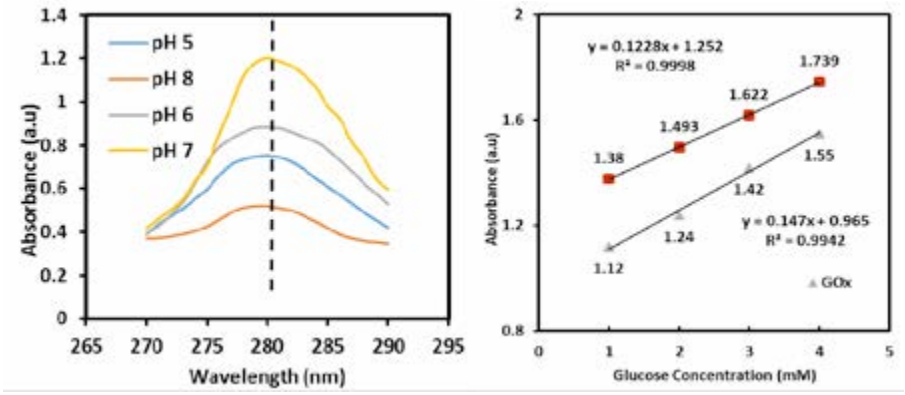
As depicted in figure 1, the melting and freezing points of the water inside the pores are strongly depending on the pore size, but also on the surface polarity of the material. The melting points of water in the BP-PMO are shifted approximately 10 °C compared to the MCM-41 materials. In figure 2 the results of a HETCOR-NMR measurement is shown where the coupling of the ^{29}Si core and the water proton can be seen. In ^{13}C-^{1}H HETCOR-NMR measurements there is no coupling of ^{13}C core and water proton visible. This indicates that the water is in closer proximity to the inorganic than to the organic part of the PMO pore wall. To determine the limits of this effect further PMOs with different sized organic moieties are currently under investigation.

MOF-199 Coordination Polymer and GOx based Non-invasive Glucose Sensing Materials Synthesized Using Straight-chain Fatty Alcohols

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Abstract

Fast and high sensitivity glucose biosensor has been developed all the time since glucose is the cause of severe diseases including diabetes resulting in metabolic disorder, kidney failure and heart attack. Metal-organic framework, MOF-199 with high porosity and stability are favorable in non-invasive glucose sensing applications. Glucose biosensor in particular was developed using glucose oxidase (GOx) enzyme as bioreceptor to enhance bionsensor's sensitivity in the limit of detection (LOD) that would synthesize the break-down of glucose into gluconic acid. In this study, copper-based metal-organic framework (MOF-199) materials with octahedral morphology synthesized using the new nonsurfactant method employing straight-chain palm oil derived fatty alcohols bearing C8 to C14 carbon chains in the backbone [1] in order to enhance enzyme loading onto single nanoparticle. MOF-199 served as templates for GOx attachment *via* electrostatic immobilization. UV-Vis analyses exhibited the successful immobilization. The glucose measurement experiment was conducted using optimum pH and temperature using different concentration of glucose (2mM-5mM) as shown in Figure 1.



(a) (b)

Figure 1. (a) UV-Vis spectra of MOF-199/GOx in different environment and (b) UV-Vis spectra of MOD-199/GOx after day 3.

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Understanding Initial Silica-surfactant Interactions in the Formation of Mesoporous Silica

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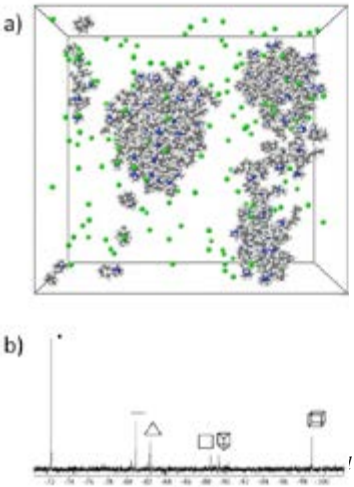
Abstract

Today a vast number of porous SiO_2-based materials can be synthetically produced, e.g. zeolites and mesoporous silica materials. Many of these materials are formed via an aqueous synthesis using a templating agent and a silica source. Despite several investigations into the formation process, using e.g. in-situ small-angle scattering[1] and ^{29}Si-NMR[2], many factors in the process remains unclear. Here we focus on the initial stages, by investigating the molecular interactions, between templating agent, silica and water.

Our main tool of investigation is near and intermediate Q-range neutron scattering combined with Empirical Potential Structure Refinement (EPSR)[3, 4], a Monte Carlo based modeling tool. The neutron data in combination with modeling provides a molecular picture of the system. An atomistic profile of a micellar solution of decyltrimethylammonium bromide (C_{10}TABr) in water, using EPSR, has already been described[5]. This surfactant is similar to the surfactants used to synthesize MCM-41. Based on this we have created a stable model system mimicking the early stages of an MCM-41 synthesis. The system contains the $C_{10}TA^+$ surfactant, see figure 1a, and small silica oligomers, determined by ^{29}Si-NMR, see figure 1b.

We have investigated the silica speciation and micelle interactions, using $C_{10}TA^+$ with different counterions (Cl^-, NO_3^-, SO_4^{2-}, Br^- and para-toluene sulphonate), to see how the silica species are influenced by the presence of micelles and their counterions.

Our results show that the silica speciation is highly affected by both the presence of the micelle and the different counterions. The effect of the silica oligomers on the size and shape of micelle will also be discussed.



simulation box with 150 surfactants in 18750 H_2O (corresponding to 0.4M), water is excluded for clarity; green: Cl ions, blue: N atoms grey: C atoms. b) ^{29}Si-NMR of an aqueous 0.4M C_{10}TACl solution with 53mM silica oligomers.

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Room Temperature Synthesis of Metal-Organic Framework (MOF-5) Using Palm Oil Derivative Template

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Abstract

In this study, metal-organic frameworks (MOF-5) were successfully synthesized at room temperature and ambient pressure using renewable templating method. The palm oil derived fatty alcohols with three different carbon chain lengths namely dodecyl alcohol (C12), tetradecyl alcohol (C14) and hexadecyl alcohol (C16) were used as template. The metal-to-linker of Zn:H_2BDC were kept at two different molar compositions of 1:0.7 and 1:0.9. X-ray diffraction analyses of dried samples exhibited three prominent peaks at ca. 2θ = 6.9˚, 9.7˚ and 13.4˚ attributable to the reflection of (200), (220) and (400) planes suggesting the successful formation of metal-organic framework. Figure 1 shows the changes in morphology of MOF-5 samples as the metal-to-linker ratios were varied from 0.7 to 0.9. As the ratios were increased, the morphology changed from faceted spherical-like morphology when Zn:H_2BDC ratio was 1:0.7 to combination of faceted and tetragonal shape form at ratio of 1:0.9. The highest Langmuir surface area and BET surface area obtained were 323 m^2/g and 245 m^2/g, respectively using dodecyl alcohol (C12).

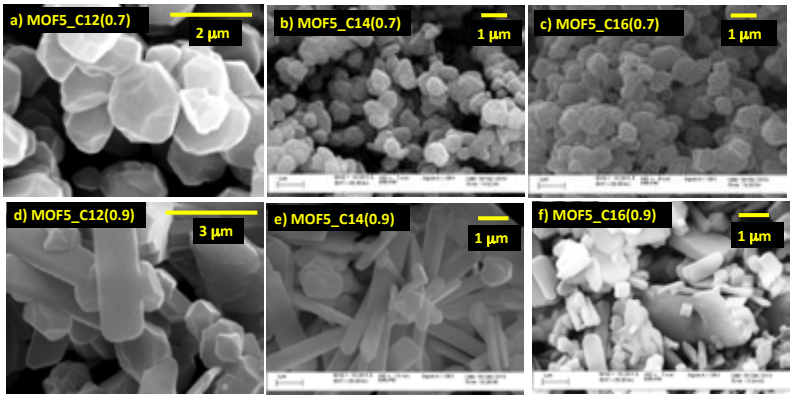


Figure 1. Morphology of MOF-5 synthesized with various length of fatty alcohol.

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Mesoporous Silica with Crystalline Meosopore Walls by Thermal Treatment with Alkali Metal Ions

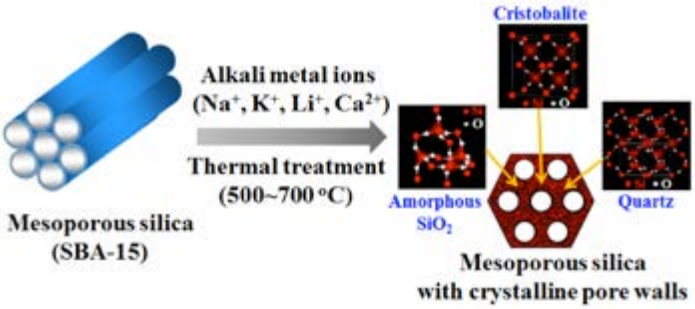
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Abstract

First, we synthesized pure mesoporous silica (SBA-15) via hydrothermal reaction process using tetraethoxy silane as silica source and triblock copolymer (P123) as template under acidic condition. Mesoporous silica materials with the crystalline walls and the extended mesopore size were produced via thermal treatment with SBA-15 using alkali metal ions (Na^+, Li^+, K^+ and Ca^{2+}) as reagent for the rearrangement of silica matrix in pore walls. Study on the effect of alkali metal ions carried out with different ratios of alkali metal ions (Si/metal ion= 2.1 to 80) and different temperature (500~700 ^oC). The crystalline SiO_2 structures (i.e. cristobalite and quartz) in pore walls were produced in the range of Si/Na=2.1 to 40 at 700 ^oC. With the increase of Na^+ amount (i.e. Si/Na=80 to 40), mesopore size was increased noteworthily from 4.8 to 98.4 nm while surface area and pore volume of the materials were decreased 201 to 34 m^2g^{-1} and 0.35 to 0.23 cm^3g^{-1}, respectively. After thermal treatment at 650 ^oC with the Si/Na=30 ratio, the crystalline SiO_2 of crystobalite structure in pore walls was formed with dual mesopore size (i.e. 11.9 and 36.4 nm), while the crystalline SiO_2 structures were not produced below 600 ^oC.

After thermal treatment at 700 ^oC of SBA-15 with Li^+, K^+ and Ca^{2+} ions (Si/metal ion=40), interestingly, the SBA-15 treated with Ca^{2+} ions exhibited crystalline SiO_2 of quartz structure with pore diameter of 7.3 nm and surface area of 450 m^2g^{-1}, whereas the SBA-15 treated with K^+ and Li^+ ions didn't have any crystalline SiO_2 structures in pore walls.

The formation of crystalline SiO_2 structures can be due to the rearrangement of silica matrix by insertion of alkali metal ions into silica matrix at high temperature.



Scheme 1. Schematic illustration for the synthesis of mesoporous silica with crystalline pore walls.

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From Silica Mesoporous Platelets Towards the Formation of An Artificial Nacre

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Abstract

Nacre is a biological material with a "brick" and "mortar" organization that is surprisingly strong and resilient. It is found for instance in mollusk's shells consisting of platelets (10-20 μm wide and 0.5 μm thick) of Aragonite with a continuous organic matrix. The physical properties of this material encourage scientists to build artificial nacre that mimics its structure and that possess innovative material properties. We are exploring a new fascinating system consisting of hard mesoporous silica platelets, functioning as "bricks", with soft responsive particles (microgel), functioning as "mortar", into novel structural organizations.

The "bricks", mesoporous silica materials, with the porosity controlled by the amphiphilic structure director, are systems extensively studied during the past 20 years. The so-called precipitation method, consisting of mixing a micellar solution and a silica precursor, results in well-defined materials with particles in the (sub-)micrometer regime. It is possible by careful control of the synthesis conditions to obtain particles with well-defined morphology, such as rods, rice shape or donuts [1]. Among the various type of possible materials, a mix of the Pluronic P104, as the amphiphilic structure director, and TMOS (tetramethoxy-orthosilicate), as the silica precursor, allows the formation of mesoporous silica platelets with a diameter of about 1 μm and a thickness of 300 nm [2].

The "mortar" is made of a microgel, poly(N-isoprylacrylamide) or PNIPAM, which has an inherent sensitivity to temperature. Indeed, colloidal microgel of PNIPAM goes from a collapsed state at temperature higher than the volume phase transition temperature T_{VPT}=32°C to a swollen state below T_{VPT} [3].

Here we present the first steps towards a new, thermo-sensitive, artificial nacre structure. By polymerizing the PNIPAM as a shell surrounding the silica platelets, it is possible to form hybrid polymer-silica materials. Such hybrid structure have specific properties that can be adjusted by the temperature, due to the PNIPAM shell, and by subjecting it to an electric field due to the core [4]. By adjusting the material concentration and by use of those external triggers, we are exploring the possibility to assemble the building-blocs into organized structures.

NH_3 Gas Sensing Performance of Nanostructured CuTCNQ Based Conductometric Devices

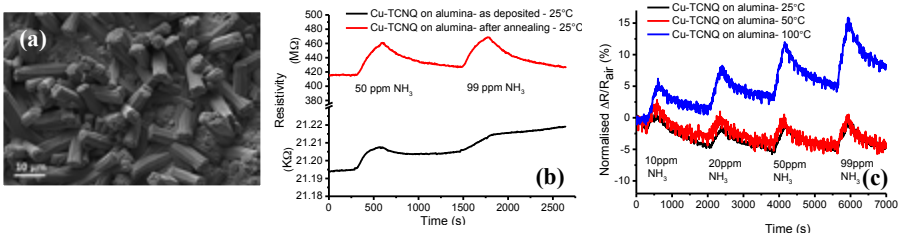
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Abstract

Organic semiconducting transition metal-TCNQ(TCNQ = 7,7',8,8' – tetracyanoquino dimethane) materials have received a great deal of attention over the past several years due to their interesting structural, electronic and optical properties [1]. Potential applications of these materials include energy and data storage [2], sensors [3] and catalysis [4]. To the best of authors' knowledge, the gas sensing properties of these materials have not yet been investigated. For the first time, we have fabricated and tested CuTCNQ nanostructured based conductometric devices towards NH_3.

A Cu thin film with thickness of 300 nm was deposited on alumina substrates via electron beam evaporation and was then immersed in solution comprising of TCNQ dissolved in acetonitrile for 1hr at room temperature (RT). The developed films were characterised by SEM, XPS, XRD and Raman spectroscopy. The SEM images revealed nanorods with surface dimensions ranging from 100 to 500 nm in width to tens of micrometres in length.

We investigated the electrical and gas sensing performance at RT of the as-deposited sensors and of the annealed films up to 200°C. The annealed sensors showed much higher sensitivity, and better recovery achieving a detection limit of 10 ppm NH_3 at RT. The annealed sensors were then tested at high temperature 50 and 100°C. As the temperature increased, the recovery time and sensitivity improved but the baseline drifted significantly. More experiments are in progress to optimise the sensing performance. In conclusion, CuTCNQ is a promising material for gas sensing applications. Other M-TCNQ materials (M= Zn, Ni, Ag) will also be tested for potential gas sensing applications.



(a) SEM of as-deposited film; Dynamic response (b) before/after annealing at 25°C (c) annealed at 25, 50, 100°C

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Mesoporous Anatase Titania Synthesized using Polyphenolic Structure-Directing Agent as Supports for Loading Pt Nanoparticles

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Abstract

Crystalline mesoporous titania (TiO_2) has attracted tremendous interests due to its high-potential applications in sensors, dye-sensitized solar cells, lithium-ion battery technologies, photocatalysis, and heterogeneous catalysis.[1, 2] The versatile applicability of TiO_2 is attributed to its high surface area, large pore volume, and uniform mesopores, which promote a facile diffusion of reactants and products as well as an increased accessibility of active sites through the mesopores. In the present work, crystalline anatase TiO_2 with a nanosponge-like morphology was solvothermally synthesized using a random copolymer of 4-vinylphenol and methylmethacrylate as a structure-directing agent. In this polymer-directed crystallization process,[3] the phenolic groups in the polymer could strongly bind to the titania precursor, leading to the formation of the crystalline nanosponge materials (**Fig. 1**). The resulting TiO_2 nanosponge possessed mesopores with a narrow distribution of diameters, which could be systematically controlled over a range of 2 nm to 12 nm by changing synthetic gel composition, calcination atmosphere (*e. g.,* O_2 or ozone), and temperature. Furthermore, the synthesis domain for highly mesoporous TiO_2 nanosponge was established over a wide range of synthetic gel compositions. The TiO_2 nanosponge supporting Pt catalyst (1 wt% Pt/TiO_2) showed high dispersion of Pt nanoparticles with average size of 1.4 nm (**Fig. 2**). In alcohol-to-aldehyde partial oxidation reaction, Pt/TiO_2 nanosponge exhibited a higher conversion of benzyl alcohol (50%, with 100% selectivity towards benzaldehyde), compared to Pt/commercial-TiO_2 catalyst (33% conversion, with 100% selectivity).

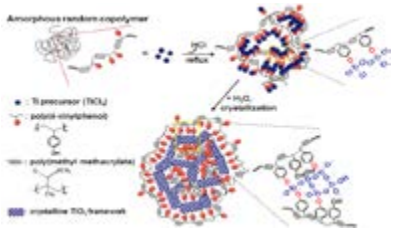


Fig. 1 Schematic illustration of the formation of TiO_2 nanosponge.

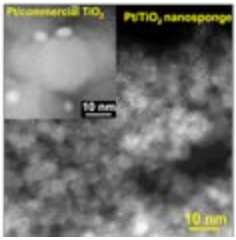


Fig. 2 STEM images of 1 wt% Pt/TiO_2.

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Periodic Mesoporous Organosilica with Different Macroscopic Morphologies

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Abstract

Tailored porous materials are of great interest in many fields of application. In addition to the chemical nature of the material certain morphologies and adjusted pore characteristics are of importance. We focus on periodic mesoporous organosilica (PMO) materials with defined properties for various applications, such as optics[1], catalysis or separation processes[2,3,4]. These PMO materials are inverse opal-, core-shell- and spherical macroscopic structures showing a uniform and periodic porosity and crystal-like orientation of the incorporated precursor molecules. Three different bis-silylated precursor, 1,4-bis(triethoxysilyl)benzene (BTEB), 1,4-(*E*)-bis(triethoxysilyl)vinyl)benzene (BTEVB), 2,5-(*E*)-bis(triethoxysilyl)vinyl)-anilin (BTEVA) were used to tune the surface chemistry of the materials.

Figure 1 shows SEM images of the three macroscopic morphologies, which were obtained with the different precursor. X-ray powder diffraction and nitrogen physisorption showed that periodic, porous materials with surface areas of approx. 400 - 1000 m^2g^{-1} and pore diameters of up to 5 nm were realized.

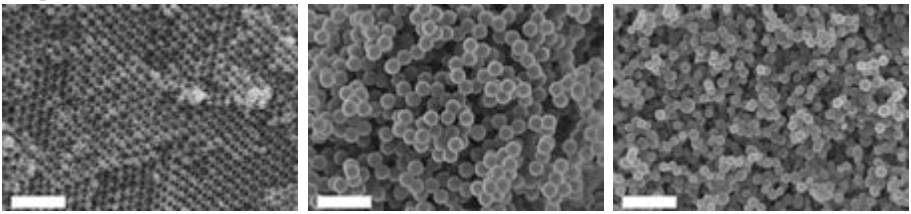


Figure 1 SEM image of phenylene-bridged organosilica materials with different morphologies **(left)** inverse opal-, **(center)** core-shell- and **(right)** spherical macroscopic structure. Scale bar in all SEM images is 2 µm.

Furthermore the obtained core-shell particles were synthesized as a mixed PMO with two different precursor (BTEB, BTEVB) coexisting in the shell of the particle, which enables Förster resonance energy transfer (FRET). Figure 2 shows the fluorescence spectroscopy of the particles containing 75 mol% BTEB and 25 mol% BTEVB.

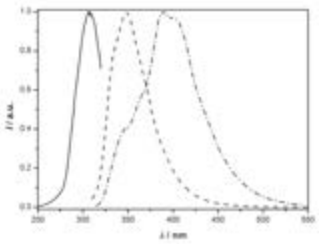


Figure 2 Fluorescence emission spectra of pure BTEB core-shell particles black dashed line and mixed core-shell particles (75 mol% BTEB and 25 mol% BTEVB in the shell) black dashed/dote line. The black solid line shows the excitation spectrum (307 nm) for these two emissions.

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Numerical Investigation on Structural Evolution and Stress in Amorphous Silicon Li ion battery Anodes

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Abstract

Silicon (Si) is widely regarded as one of the most promising anode materials for Li ion battery (LIB) due to its high theoretical specific capacity. However, the volume change (~300%) during lithiation/delithiation results in poor mechanical integrity, which impedes its commercialization. To address this issue, a better understanding of the atomistic mechanisms behind lithiation is necessary. In this work, the atomic structure and stress evolution during lithiation/delithiation was investigated on an amorphous silicon film (2.7 nm) using molecular dynamics. Steep stress gradients were observed when the lithium content in the anode is very low ($<Li_{0.5}Si$). Plastic flow and stress relaxation are dominant in higher Li concentrations. The microstructure evolution during lithiation process is associated with the break of covalent amorphous structure into small clusters, when Li concentration exceeds ~$Li_{0.5}Si$. At a low Li concentration, the sharp stress increase is due to the elastic deformation of the covalent Si lattice. The Radial Distribution Function (RDF) analysis revealed a defective amorphous structure in silicon film after a complete lithiation/delithiation cycle, which is attributed to breaking down of covalent silicon network and subsequent plastic flow. These results are believed to be able to help improve the materials selection and design of next generation Li ion battery.

Facile Synthesis of Pollen-like Mesoporous Silica Hollow Spheres for Efficient Antimicrobial Protein Delivery

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Abstract

The increasing level of antimicrobial resistance (AMR) is becoming a major threat to the global public health.[1] Extensive efforts have been devoted to the development of novel antibacterial agents as alternatives to conventional antibiotics.[2] Mesoporous silica nanoparticles have attracted much attention as nano-carriers for antibiotics delivery due to the tunable nanostructures and good biocompatibility. However, limited by the weak binding affinity between silica nanoparticles and bacteria surface, the delivery efficacy remains a great challenge.[3] Inspired by the adhesive property of spiky pollens, silica nanoparticle with rough surface is desired for efficient delivery. However the fabrication of rough silica nanoparticles currently employed expensive precursors and surfactants with sophisticated procedures.

Herein, pollen-like meosporous silica hollow spheres (R-MSHSs) with pore size of 9.3 nm and particle size of 265 nm were synthesized via a one-pot, surfactant-free, cheap and scalable approach (Fig. 1a), which showed high loading capacity of lysozyme and sustained release (Fig. 1b). Lysozyme-loaded R-MSHSs showed improved antibacterial activity compared with free lysozyme (Fig. 1c). The strong binding affinity between R-MSHSs and bacteria surface raised the local concentration of lysozyme towards bacteria cell walls where cell wall lysis can be clearly identified as shown in Fig.1d (indicated by black arrows). This work provides new understandings for the rational design of nano-carriers for antimicrobial drug delivery.

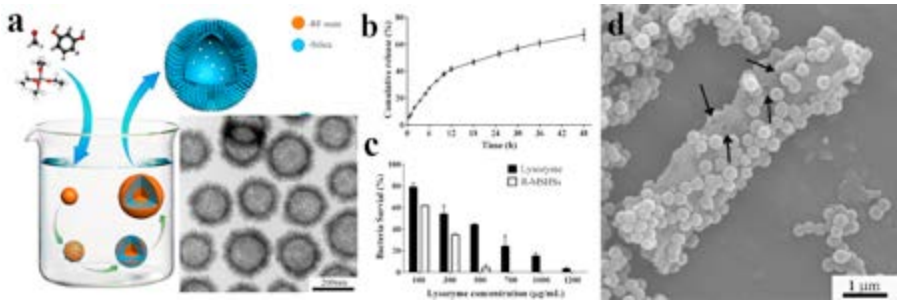


Fig. 1 Schematic illustration of the synthesis of R-MSHS and typical TEM image (a), lysozyme release profile (b), antibacterial activity of Lyz-R-MSHSs and free lysozyme (c), and SEM image (d) of Lyz-R-MSHS adhere on bacteria cell wall for lysis.

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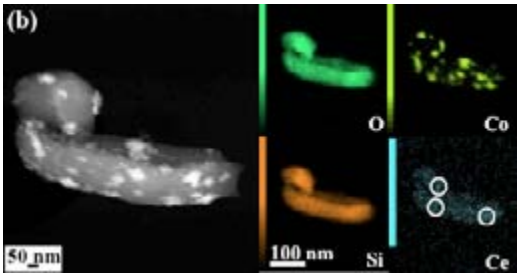
The Morphology and Catalytic Behaviour of Co_3O_4 Supported on Meosporous SBA-15

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Abstract

We have been investigating the potential of cobalt oxide supported on mesoporous silica SBA-15 as a robust heterogeneous catalyst system for the selective oxidation of organic substrates. For catalysts prepared by the 'two-solvent' method we observed the formation of cobalt oxide 'patches' which are larger in diameter that the SBA-15 channels [1]. This phenomenon is attributed to the fact that SBA-15 mesopores are interconnected by micropores that facilitate extended crystallite growth. As a result, catalysts of this type prepared with lower cobalt content exhibit higher oxidation activity (e.g., for cyclohexanol to cyclohexanone), due to the better accessibility of the reactants to more catalytic sites [2]. X-ray diffraction revealed that the cobalt oxide patches were crystalline with a spinel structure.

In recent work we synthesised analogous Ce-doped cobalt oxide composite catalysts. The liquid phase catalytic performance of the Ce-doped composites was found to be higher than either the un-doped composites or analogous Ce-composites. This is attributed to the improved dispersion of Co_3O_4 species in the Ce-doped composite, such that more active surface area becomes available for the organic substrates to access. Also, the extent to which CeO_2 covers over the surface of Co_3O_4 species appears to cause a synergistic effect and thus improve the redox properties of the catalytic system.



STEM image and elemental mapping profiles of a Ce-doped cobalt oxide on SBA-15 composite catalyst.

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Activation of Aryl Chlorides in Water under Ligand-free Suzuki Coupling by Heterogeneous Palladium Supported on Hybrid Mesoporous Carbon

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Abstract

Ligand-free heterogeneous Pd-based catalysts have attracted much attention in Palladium-catalyzed Heck and Suzuki coupling reactions because they possess great advantages in terms of recyclability.[1] Aryl chlorides, which are more economical and accessible than aryl iodides and triflates, have rarely been used as electrophiles in Pd-catalyzed Suzuki coupling due to the high activation barriers associated with the difficult oxidative insertion of Pd(0) species into the Ar-Cl bond.

Here, heterogeneous palladium catalysts supported on ordered mesoporous carbonaceous nanocomposites including carbon-silica [2], CoO-C [3,4] and quaternary ammonium phase transfer agent modified mesoporous carbonaceous resins, were applied to the water-mediated Heck or Suzuki coupling reaction using chlorobenzene as the substrate and exhibited a high yields of target products under mild reaction conditions free of phase transfer agents and ligands. For example, the heterogeneous Pd catalysts which were loaded onto quaternary ammonium phase transfer agent modified mesoporous polymers were highly active in the Heck coupling of aryl bromides and styrene to produce trans-stilbene at high yields (84%) without the need to exclude air or to use water as a solvent. The electron-rich environment stabilized by functional quaternary ammonium groups was responsible to the high activity in converting aryl bromides. Furthermore, the mesoporous Pd/CoO-C catalyst showed a high yield of biphenyl (49%) in the water-mediated Suzuki coupling reaction of chlorobenzene and phenylboronic acid. Product yields in the reaction of aryl chlorides containing electron-withdrawing groups attached to their benzene ring can reach approximately 90%. Very small Pd clusters consisting of approximately 3 atoms and Pd-O bonds formed on the interface between CoO and Pd nanoparticles. The unsaturated coordinative Pd may be responsible for the activation of chlorobenzene in the absence of any additives or ligands.

Thiol-functionalized mesoporous silica, which can trap soluble Pd species, was used to confirm the negligible leaching in solution and therefore heterogeneous reaction. These heterogeneous catalyst are stable, showing unobvious activity loss after ten catalytic runs. Additionally, uniform mesopores and the hydrophobic nature of the carbon support may also facilitate the mass transfer of the reactant molecules and enrichment inside pores.

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Carbon Templated Mesoporous Silica Membranes for Desalination

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Abstract

Sol-gel derived silica membranes for desalination offer the advantages of tunable morphology and micropore size (dp = 3–5 Å). Yet, silica membranes must overcome hydrolytic degradation of the silica structures for deployment in desalination plants. Over the last decade great improvements in silica membranes hydrostability have been reported by the introduction of organic templates into the silica matrices via sol-gel methods. The organic templates were retained in the silica matrices as the membranes were calcined in inert nitrogen gas atmosphere.

A second drawback of silica membranes relates to their preparation. Traditionally, a multilayer asymmetric configuration involves a macroporous substrate and several intermediate layers, which is imperative to achieve a high quality membrane support by gradually decreasing pore size and surface roughness. Such a preparation method is synthetically intensive and time consuming, even before the top membrane layer can be applied.

This work is the first report on the preparation of high quality silica derived membranes by the "interlayer-free" method. Hence, silica membranes can be directly coated on substrates instead of smooth interlayers which add extra costs in the production of membranes. The "interlayer-free" method was achieved by using a base catalysed sol-gel process with carbon templates, instead of the conventional acid catalysed sol-gel silica membranes. Using these membranes for desalination, extreme high salt rejection (>99.5%) were measured for a several temperatures and saline waters ranging from brackish to sea water and brine concentrations. A major finding of this work is related to salt concentration polarisation effect which greatly decreased as the content of carbon template embedded in the silica matrix increased. This has not been previously reported for silica derived membranes.

Aptamer Functionalized Fe_3O_4 Core/Mesoporous TiO_2 Shell Nanomaterials for Highly Efficient Targets Extraction from Complex Matrices

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Abstract

Adsorbents are widely employed in both fundamental and applied research areas such as separation technology, biotechnology and environmental science. Selectivity and reusability are two of the most important requirements for adsorbents. Aptamers possesses excellent properties such as perfect selectivity and easy regeneration,[1] which wed them great promise for serving as uniquely effective materials for adsorption. Mesoporous materials, with the characteristics of highly uniform channels, large surface area, narrow pore-size distribution, tunable pore sizes over a wide range, and so on, have much more application in environment protection, catalytic chemistry, engery conversion and biological technology. High porosity and large surface area to volume ratio endow mesoporous materials with great adsorption properties.[2] Herein, we have rationally designed novel aptamer functionalized Fe_3O_4 core/mesoporous TiO_2 shell nanomaterials and investigated their performance in extraction/separation of targets from aqueous solution. These aptamers-based adsorbents can selectively extract targets from complicated sample matrices containing background compounds. The TiO_2 shell can adsorb phosphate due to the classic coordination reaction between titanium ions and PO_4^{3-},[3] and the active sites for binding with phosphate was greatly increased due to the mesoporous structure of TiO_2. Besides, the adsorbents can also be easily recycled for several times without significant loss of their adsorption capacities. It was noteworthy that the adsorbents didn't affect the activity of isolated biological samples, revealing its potential for purification/separation of biomolecules. Composite adsorbents were further constructed by using aptamers-based adsorbents and porous polymer. The composite adsorbents displayed high efficiencies in separation of targets from aqueous solution. Finally, separation columns were constructed and targets in aqueous solution were efficiently separated by these columns. The aptamers-based adsorbents described here exhibited great promise for potential applications in separation technology, biotechnology and environment related areas.

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Facile Fabrication of Tunable $Ba_xNi_{3-x}(PO_4)_2$ Nanobelts for High-performance Supercapacitors

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Abstract

Supercapacitors, referred as electrochemical capacitors, have drawn intensive attention due to their superior properties such as good reversibility, high power density and long cycle life (up to over 500 000 times) compare to other energy storage systems. These advantages make them highly promising in the application of portable electronics, hybrid electric vehicles, and back-up power sources, etc. However, most of commercial supercapacitors are electrical double layer capacitors (EDLC) based on carbon materials which exhibit relatively low energy density (less than 10 Wh kg^{-1}) compared to other battery systems. One of the most effective ways to overcome this bottleneck is to develop high performance pseudocapacitive electrode materials which store electric energy through faradaic charge transfer process and therefore can provide much higher energy density. Recently, various metal phosphates have proved to be ideal faradaic electrode materials for supercapacitors. For example, Changzheng Wu et al. reported the fabrication of two-dimensional vanadyl phosphate ultrathin nanosheets. The corresponding flexible ultrathin-film pseudocapacitor exhibits excellent supercapacitive performances. [1] Moreover, Jing-He Yang et al.[2] showed that the nickel phosphate molecular sieve VSB-5 can be used for supercapacitors. The specific capacitance of VSB-5 went up to 2740 F g^{-1} at a current density of 3 A g^{-1} and no significant reduction was observed after 3000 cycles at 30 A g^{-1}. Herein, the ultra-long tunable $Ba_xNi_{3-x}(PO_4)_2$ nanobelts are firstly synthesized through a facile solution reaction under room temperature. The morphology can be rationally tuned via changing the reaction parameters. Moreover, they showed promising electrochemical performances including high specific capacity and long cycle life in supercapacitors.

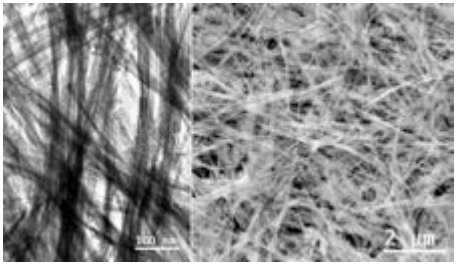


Figure 1: TEM and SEM images of $Ba_xNi_{3-x}(PO_4)_2$ nanobelts

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A Facial method to Prepare An Open Cell Structure Carbon Foam and Its promising Application in Electrochemical Energy Storage and Catalyst Supports

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Abstract

Carbon foam with a great quantity of uniformly distributed open micro-pores shows excellent potential applications because of a numerous of special features, such as light weight, high temperature tolerance, large external surface area, and superior thermal and electrical conductivity. In order to fully take advantage of its porous structure, efforts must be made to ensure an uniform open cell structure, which is a key factor should be considered when exploring an appropriate manufacturing process. In this present work, we reported a facial method to prepare functional carbon foam using sponge as the template and furfuryl alcohol as the carbon source. X-ray diffraction and scanning electron microscope characterized results demonstrated the furfuralcohol resin was carbonized completely with a highly amorphous structure as well as an uniform open cell micromorphology (see Fig.1). Further, according to the N_2 adsorption and desorption and electrical test, the obtained carbon foam has been demonstrated owning high specific area, large pore volume and good electrical conductivity. Therefore, based the abovementioned properties, such a carbon foam can be expected to exhibit a broad application prospect including high-temperature thermal insulation, high thermally conductive heat sinks, electrodes for energy storage, energy absorption material, catalyst supports and filters, etc.

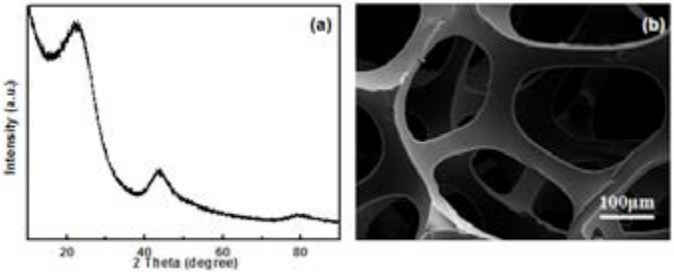


Fig. 1 (a) X-ray diffraction patterns of Carbon foam; (b) SEM image of Carbon foam.

Synthesis, Characterization and Pilot Scale of Meso-ZSM-5 Zeolite by Acid-base Composite Processing

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Abstract

Compared with conventional zeolites, meso-zeolites have received an ever-increasing attention as a promising material that could be industrialized in the near future. Both desilication and dealuminum have become widely applied preparation methods to tailor zeolites, due to an optimal combination of efficiency and simplicity. However, systematic studies on the effects of acid-base composite processing, have not yet been reported, specifically the pilot scale of meso-ZSM-5 zeolite. Therefore in this work, synthesis and characterization of meso-ZSM-5 zeolite are investigated, and acid-base composite processing has been scaled up from laboratory to pilot (50L) scale.

Desilication in 50 L scale led to a spate of mesoporous structures. After acid treatment, mesoporous specific surface area and mesoporous volume have been increased. As can be seen from TEM images, mesoporous structure is presented after alkali treatment. Through acid treatment, mesoporous channel become more obvious. All these results demonstrate that desilication is a suitable post-synthetic method to introduce intracrystalline mesoporosity in ZSM-5 zeolites and dealuminum is an effective way to remove non-framework aluminum which is caused by desilication. This phenomenon is also can be proved by silica-alumina ratio. Thus, this process is unique and important as it shows a bright prospective on large-scale fabrications and applications of meso-ZSM-5 in bulk-type industries, such as refining and petrochemistry.

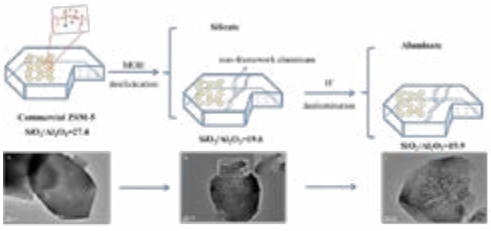


Fig 1. Schematic of mechanism, XRF data and TEM images of samples

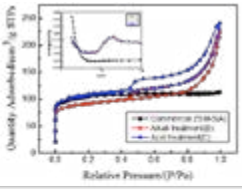


Fig.2 Nitrogen adsorption–desorption isotherm and pore size distribution of samples

Tab.1 Textural properties of samples

Samples	A	B	C
S_{BET}(m²/g)	322	279	330
S_{meso}(m²/g)	110	95	105
V_{total}(cm³/g)	0.176	0.346	0.373
V_{meso}(cm³/g)	0.063	0.247	0.253

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Soft-Templated Mesoporous $CsTaWO_6$ for Photocatalytic Hydrogen Production

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Abstract

One alternative to the limited resources of fossil fuels could be a hydrogen-based economy. A promising method to produce hydrogen is the photocatalytic splitting of water on the surface of a semiconductor.[1] Considering the potential for the water splitting reaction, one can find a minimum band gap (E_g) of 1.23 eV. Kinetic hindering causes an overpotential for both parts of the redox reaction, resulting in a minimum E_g of approx. 2 eV ($\lambda \approx 620$ nm).[2] Therefore, with photocatalytic water splitting most of the solar light could be converted into chemical energy. High crystallinity and a high surface area are required to increase the catalytic activity of a photocatalyst.[1] There are different examples of mesoporous semiconducting oxides with photocatalytic activity in literature, such as Ta_2O_5[3] and Mg–Ta oxide.[4] However, there is no example for a mesoporous quaternary oxide. Here we present a soft-templating synthesis strategy for mesoporous $CsTaWO_6$ and its photocatalytic performance. $CsTaWO_6$ is a semiconductor with a band gap of 3.6 eV[5] which can be decreased via nitrogen doping to approx. 2.3 eV.[6] In a typical synthesis, Cs_2CO_3, $TaCl_5$ and WCl_6 in a molar ratio of 1:2:2 were dissolved in a solution of EtOH, THF, Pluronic P-123 and different additives and poured into Petri dishes. The solution was dried under controlled conditions and calcined at 550 °C. The as-synthesized mesoporous $CsTaWO_6$ shows a high crystallinity at moderate calcination temperatures with an average crystallite size of approx. 20 nm. The BET surface areas measured by N_2 physisorption are up to 78 $m^2 g^{-1}$ and the pore sizes range from 5 to 10 nm, depending on the additives. Figure 1 shows TEM images of mesoporous $CsTaWO_6$. First photocatalytic measurements demonstrate an increased activity in H_2 generation up to a factor of two, compared to non-porous $CsTaWO_6$ synthesized via sol-gel citrate route.[5]

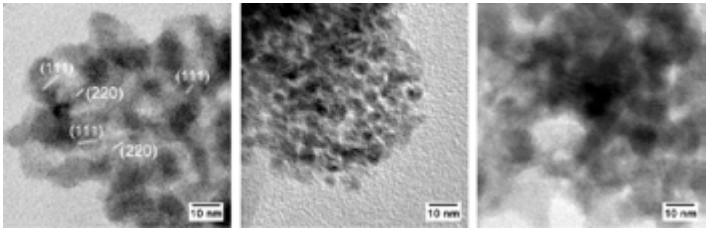


Fig. 1: TEM images of mesoporous $CsTaWO_6$ prepared with (a) no additives (b) citric acid and (c) sulfuric acid.

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Impact of Oxidative Modification on the Performance of Activated Carbon in Adsorptive Denitrogenation

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Abstract

Elimination of nitrogen-containing compounds from hydrocarbon liquids before hydrotreatment can be beneficial to the hydrotreating process. Adsorptive denitrogenation is an alternative approach to eliminate nitrogen-containing compounds from liquid hydrocarbon. Carbon-based adsorbents have attracted much attention due to the advantages of easily modifiable physical structure of pores and chemical functional bonds. A commercially available activated carbon has been oxidized by concentrated sulfuric acid, saturated ammonium persulfate solution and their mixture solution, respectively (Isotherms of different activated carbons are shown in Figure 1). Adsorption of nitrogen compounds by the commercial and modified carbons was studied using model diesel fuels (MF). Modified activated carbons can selectively adsorb indole, quinoline and carbazole even when dibenzothiophene, aromatics and/or cyclohexane coexisted in the substrate. It is also observed that the adsorption capacity for N per unit surface area was increased linearly to density of the acidic groups for adsorption of different single nitrogen compound and triple nitrogen compounds in MF (See Figure 2). The steep line for quinoline indicates that the affinity of acidic functional groups for quinoline is the greatest among the three nitrogen-containing compounds. The affinity for indole slightly higher than that for carbazole can be deduced from the slopes of fitting lines. Furthermore, the intercepts of the fitting lines represent the adsorptive capacity per unit area that is not subject to the influence of acidic groups. One may note that quinoline has the least intercept among the three nitrogen compounds, suggesting the adsorption of quinoline can be barely affected by the surface area of adsorbent. The adsorption of carbazole is the most sensitive to the surface area of adsorbent.

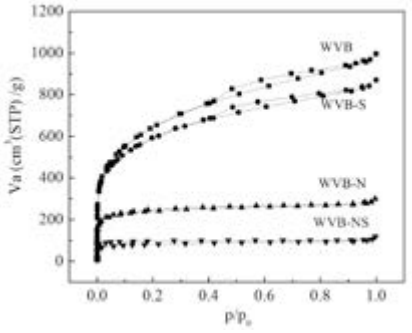


Figure 1 Isotherms of different activated carbons

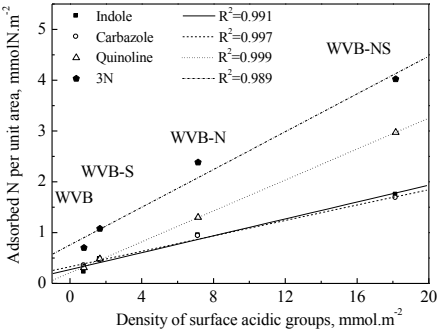


Figure 2 Capacity per unit area for nitrogen compounds as a function of the group density on carbon surface

Gold Nanoparticles Supported on Mesoporous Silica: Origin of High Activity and Role of Au NPs in Selective Oxidation of Cyclohexane

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Abstract

Gold (Au) nanoparticles (NPs) are catalytically active in many important oxidation reactions. In our previous work, a thiol-containing organosilane, mercapto-propyl-trimethoxysilane (MPTMS), was used in the synthesis of mesoporous silica supported fine Au NPs (2-4 nm) through a simple one-pot method. The resultant Au NPs exhibited an excellent catalytic activity and high stability in the solvent-free selective oxidation of cyclohexane using molecular oxygen. However, the origin of the high activity of the catalyst and the role of Au NPs in the oxidation of cyclohexane remains unclear and is still open to debate.

In this work, the origin of the high activity of Au NP_S supported on mesoporous silica was explored by correlating the catalytic performance with the structural properties of Au catalysts prepared under different conditions. The role of Au NPs in the oxidation of cyclohexane was investigated by conducting a simple control experiment and the activation of O_2 molecules by Au NPs was examined by using an O_2-temperature programmed desorption (O_2-TPD) technique. By establishing the structure-performance relationship, the origin of the high activity of mesoporous supported Au catalyst was identified to be due to the presence of low-coordinated Au (0) sites with high dispersion. Au NPs were confirmed to play a critical role in the catalytic oxidation of cyclohexane by promoting the activation of O_2 molecules and accelerating the formation of surface-active oxygen species. Based on the understanding of the catalytic mechanism of Au NPs in the oxidation of cyclohexane, the effect of reaction conditions was further investigated and optimized.

Porous Carbon-based Materials Derived from Direct Carbonization of Zeolitic Imidazolate Framework with Enhanced CO2 Uptake Capacities

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Abstract

Porous carbon materials are one of the most attractive materials due to their wide range of applications in many technically important fields.[1] Generally, porous carbon materials can be generated via various synthesis approaches and the template method has been considered as one of the most effective approaches to produce porous carbon materials with controllable architectures, narrow pore size distributions and desirable physical and chemical properties.[2] Recently, metal-organic frameworks (MOFs) have emerged as new type of templates for the generation of porous carbon materials.[3] Given that MOFs usually contain highly polymeric carbon species, it is anticipated that selected MOFs can simultaneously act as both templates and carbon precursors to produce porous carbon-based materials via direct carbonization of MOFs. Actually, several recent reports explored the generation of porous carbon materials via direct carbonization of MOFs and investigated their applications in hydrogen storage and electrochemical performance.[4] There are, however, seldom investigations on porous carbons derived from direct carbonization of zeolitic imidazolate frameworks (ZIFs), a special class of MOFs with zeolitic type structures, as CO_2 uptake adsorbents.

In this presentation, we will report our recent work on the preparation of N-doped porous carbons and composites via direct carbonization of ZIF-8 under various conditions and on the evaluation of their CO_2 uptake performances.[5] The effect of carbonization conditions on the textural properties, elemental compositions and their CO_2 uptake capacities of the ZIF-derived porous carbons are systemically addressed. The resulting N-doped porous composites (before removal of the inorganic species) and carbon materials are characterized by various techniques and their adsorption capacities for CO_2 are compared. The influence of both textural properties and surface chemistry on CO_2 capture performances of the resultant porous adsorbents is discussed.

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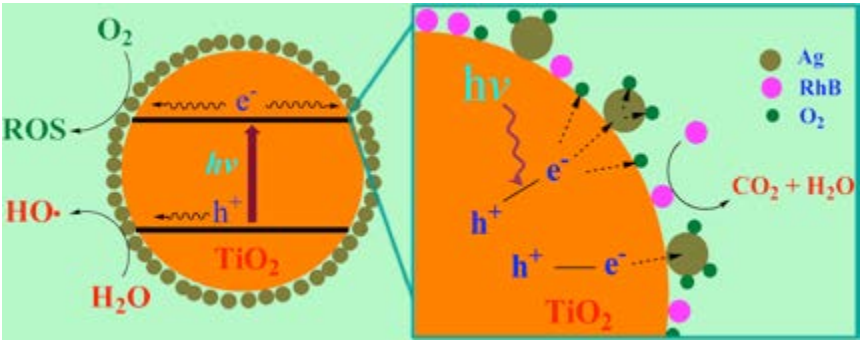
Metal Nanoparticles-Coupled Mesoporous TiO_2 with Enhanced Photocatalytic Activities

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Abstract

Many photocatalytic applications of titanium dioxide (TiO_2) undergo on the material surface.[1] We have demonstrated a method for preparing TiO_2 with a specific surface as high as 270 m^2/g.[2] Presently, the low quantum yield of excitons due to electron-hole recombination in the bulk or on the surface of TiO_2 largely limits process efficiency. Coupling metal nanoparticles (NPs) with mesoporous TiO_2 has been shown to be an effective strategy for slowing down or retarding the electron-hole recombination.[3,4]

By depositing Ag NPs on the surface of TiO_2 aggregates, the photocatalytic performance in degrading rhodamine B (RhB) and killing microorganism bacterium strain *E. coli* under UV light irradiation was greatly improved.[3] It was also found that the Ag NPs enhanced the adsorption of dissolved oxygen, promoting the production of reactive oxygen species (ROS).



Acknowledgement:
We are grateful for financial supports from Environment and Water Industry Development Council (EWI) of Singapore (project number MEWR 651/06/161) and Australian Research Council (ARC) under the ARC Future Fellow Program (FT100100879).

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Effect of Synthetic Conditions on the Properties of Pseudo-boehmite

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Abstract

The effect of synthetic conditions on the crystal structure and textual properties of pseudo-boehmite was investigated, such as synthetic temperature, pH value and the addition of sodium silicate, with using the cation-anion double hydrolysis method[1] from mixed aqueous solution of aluminum sulfate and sodium aluminate. With the assistance of characterization techniques, such as X-ray diffraction (XRD), N_2 adsorption-desorption isotherms (BET) and ^{27}Al MAS NMR, the relationship between the textural properties of the pseudo-boehmite samples and their synthetic conditions was discussed here. According to our study, an increase in synthesis temperature promoted the formation of well-crystalized pseudo-boehmite with increasing the surface area and pore volume. The pH value of the reaction system played crucial role in determining the crystal structure of the product. Pseudo-boehmite could be obtained in the pH value range from 6.0 to 9.0, while bayerite phase occurred over pH 10.0. Sodium silicate as an effective pore-expanding agent, though resulting in the decrease of crystallinity, greatly improved the pore volume (1.20 cm^3/g) and surface area (480.15 m^2/g) of pseudo-boehmite. Interestingly, pseudo-boehmite was obtained at very high pH without formation of bayerite when sodium silicate was initially added into the aluminum hydroxide colloid.

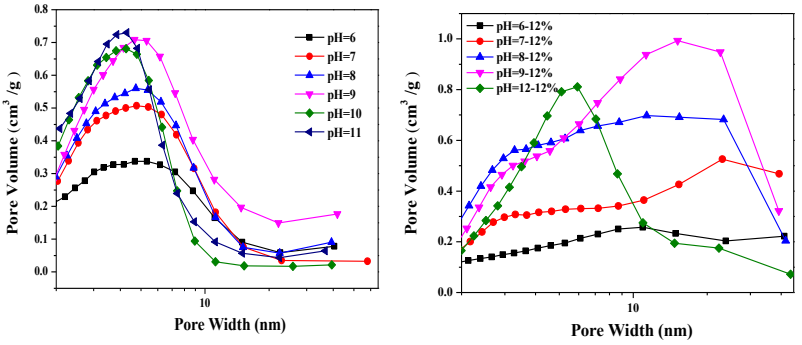


Fig.1 BJH pore size distribution for pseudo-boehmite (left) and pseudo-boehmite modified by the same amount of sodium silicate (right) prepared at different pH values

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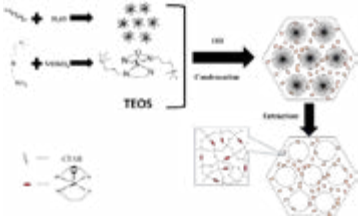
A Novel Vanadyl-bridged Organosilica Anchored in Skeleton of Mesoporous Silica for Catalytic Oxide of Styrene

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Abstract

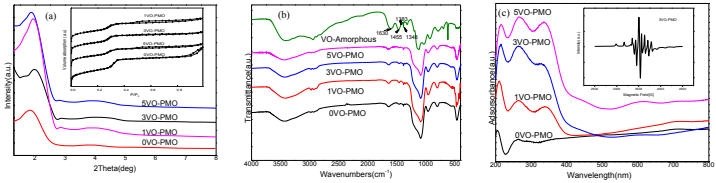
Since the discovery of periodic mesoporous organosilicas (PMO), impressive progress has been made in their application as catalysts. In-situ co-condensation of organosilica complex with appropriate silicon source can efficiently avoid channel blockage and possess homogeneous distribution of active species.

Herein, we fabricated a novel periodic mesoporous organosilica materials containing diimine moieties coordinating metal active species within network. This functional mesocomposite was synthesized by a simple and efficient one-step templating route, in which TEOS was employed as a silica, CTAB as surfactant, APATES as metal trapping agent, NaOH as mineralizing agent. The typical synthesized route was illustrated in scheme 1.



Scheme 1. Synthetic schematic of mesocomposites via direct-templating route

Typically, we obtained a VO-PMO material using VO^{2+} as the bridged metal. The characterization results such as XRD, N2 isotherms, FT-IR, UV-vis and ESR spectra demonstrated that the vanadyl active species was successful anchored inside the pore wall, and the mesoporous structure can be maintained. The prepared samples were evaluated with direct oxide of styrene as a model reaction and exhibited excellent catalytic activity.



Small-angle XRD(b), N_2 Adsorption-desorption(insert), FT-IR spectra(c), UV-vis(d) and ESR spectra(insert)

This work was supported by the National Natural Science Foundations of China (21276125, 21476108 and 20876077).

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Perovskite with Disordered Pore Systems as Highly Active Catalysts for Oxygen Evolution Reaction

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Abstract

The perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is identified as the catalyst with the highest intrinsic activity for the oxygen evolution reaction (OER) critical to many energy storage applications. However, the low specific surface area (0.5 m^2 g^{-1}) greatly constrained the catalytic performance of BSCF. We report here a facile, in-situ template method using tetraethoxysilane (TEOS) to introduce disordered pore systems into BSCF crystalline. The surface area of the BSCF prepared using a TEOS to BSCF ratio of 3.4 was increased up to 32.1 m^2 g^{-1}, which to our knowledge is the highest reported surface area in a BSCF perovskite. This sample exhibited an OER current density of 35.2 A g^{-1} at 1.63 V versus a reversible hydrogen electrode (overpotential, η=0.4 V) and this activity is 5.3 times that exhibited by non-porous BSCF (6.6 A g^{-1}). The high activity of the porous BCSF is attributed to the additional catalytic surface sites available in the pores created by the in-situ TEOS template method.

Preparation of Fe-modified Activated Carbon Fibers from Palm Fibers and Their Application for Fenton Degradation of Rhodamine B

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Abstract

Fe-modified activated carbon fibers (ACF-Fe) were successfully prepared by a two-step physical and chemical activation method and used as efficient heterogeneous catalyst for Fenton degradation of organic contaminants. X-ray diffraction and X-ray photoelectron spectroscopy analyses confirmed the existence of the Fe_3O_4 nanoparticles in the ACF-Fe catalyst. N_2 adsorption-desorption analysis showed that the specific surface area of ACF-Fe could reach 432 m^2/g and the catalyst mainly exhibited a kind of microporous structure. The catalytic activities of the ACF-Fe catalyst were evaluated by the degradation of Rhodamine B (RhB 100 mg/L) in the presence of hydrogen peroxide (H_2O_2). The catalyst exhibited very high catalytic activities for the degradation of RhB in a wide range of pH. Alkaline condition is more preferred to neutral and acidic conditions. Under the condition of pH=13, the discoloration removal of RhB was over 95% and the COD removal of RhB was over 75%. Moreover, the catalyst still showed good catalytic properties and catalytic stabilities after being recycled for five times. Finally, a possible catalytic mechanism was proposed.

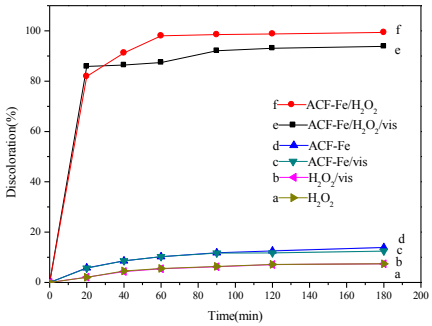


Fig. 1. Discoloration of RhB under six conditions: (a) H_2O_2 , in the dark; (b) H_2O_2/vis; (c) ACF-Fe/vis; (d) ACF-Fe, in the dark; (e) ACF -Fe/H_2O_2/vis; (f) ACF -Fe/H_2O_2, in the dark

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Self-organized Mesostructured Hollow Carbon Nanoparticles via a Surfactant-free Sequential Heterogeneous Nucleation Pathway

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Abstract

Mesostructured hollow carbon nanoparticles have widespread applications. A big challenge in materials science is surfactant-free synthesis of hollow carbon nanoparticles with tunable mesostructures. Herein we report a new surfactant-free sequential heterogeneous nucleation pathway to prepare mesostructured hollow carbon nanoparticles. This strategy relies on two polymerizable systems, i.e. resorcinol-formaldehyde and tetraethyl orthosilicate, each of which undergoes homogeneous nucleation and particle growth. By controlling the polymerization kinetics of two systems when mixed together, sequential heterogeneous nucleation can be programmed leading to monodispersed and mesostructured hollow carbon nanoparticles with large mesopores, controllable mesostructures (bi- and triple-layered) and rich morphologies (invaginated, intact and endo-invaginated spheres). For the first time, it is demonstrated that the invaginated structure shows better hemocompatibility compared to the intact one. The pristine hollow carbon nanoparticles with large pore size and high pore volume show high loading capacity of biomolecules and successfully deliver biomolecules into cells. Our strategy has paved the way for the designed synthesis of unprecedented carbon nanostructures with potential applications in drug/biomolecule delivery.

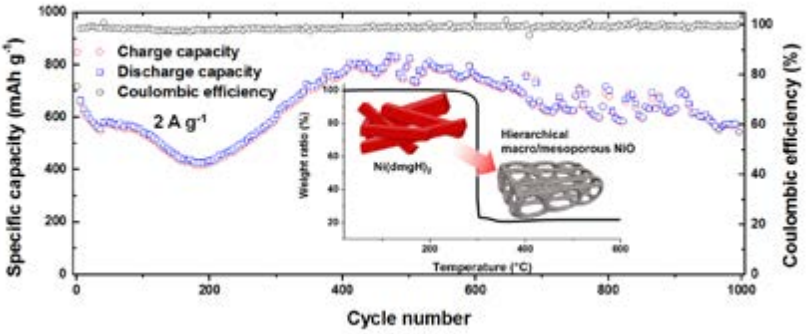


Hierarchical Macro/mesoporous NiO as Stable High Performance Anode materials for Lithium-ion batteries

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Abstract

Hierarchical macro/mesoporous nanomaterials are suggested promising electrode materials for high performance lithium-ion batteries (LIBs), because they can increase electrode/electrolyte accessibility without the cost of internal electrolyte resistance and side reactions.[1] However, the preparation of macro/mesoporous materials is challenged that often relies on expensive or sophisticatedly controlled templating methods.[2] Here we present a new type of hierarchical macro/mesoporous nickel oxide from a simple thermolysis process of nickel dimethylglyoxime complex, of which the drastic weight loss during heat treatment leads to the formation of hierarchical porous structure in crystalline NiO. The products exhibit stable high performance as anodes for LIBs, delivering remarkable discharge capacities of 911.1 mAh g^{-1} after 200 charging/discharging cycles at current dentistry of 0.5 A g^{-1}, and 558 mAh g^{-1} after 1000 cycles at 2 A g^{-1}. Such superior performance of the materials over other NiO counterparts and the further measurements confirm the advantages of such hierarchical macro/mesoporous structure.



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Proton Conductivity of SO_3H-grafted Monolithic Silica Containing Disubstituted Aromatic Scaffolds

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Abstract

The combination of specific tailored surface properties like porosity and surface areas is important for advanced functional characteristics, in particular for catalytic applications or the design of new electrode materials. Monolithic silica with bimodal porosity are considered to be suitable candidates as they offer high specific surface areas and easy tunable pore sizes which is important for well distributed active sites in diffusion proceedings. Herein we report the synthesis of monolithic silica hybrids containing disubstituted benzene units in a one pot strategy. The obtained materials were post-synthetically converted to their corresponding sulfonic acids and tested in their ability to conduct protons.

Monolithic silica hybrids were synthesized in a modified sol-gel-route after Nakanishi[1] by hydrolysis and co-condensation of 1,4-bis-(trimethoxysilyl)-benzene (*p*-BTMB) with tetramethyl orthosilicate (TMOS) following a literature procedure.[2] Materials were grafted with SO_3H units by reaction of the built in aromatic moieties with oleum at 80 °C. The degree of functionalization was determined via elemental analysis and the porosity was characterized using physisorption. The resulting proton conductivities are at least one order of magnitude higher than in comparably sulfonated hexagonal ordered benzene-PMOs[3,4], giving a first indication about the advantages of bimodal porous materials for proton conduction.

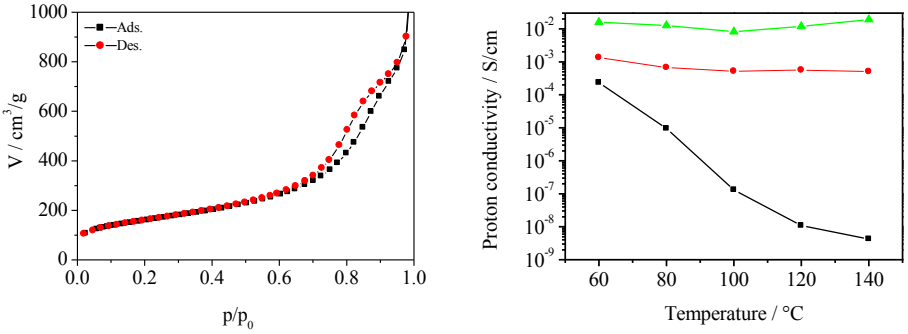


Fig.1: left: N_2 physisorption isotherms of powdered TMOS/*p*-BTMB hybrid (10 %) after grafting with sulfonic acid groups; right: proton conductivity as a function of temperature (with relative humidity conditions in the measurement of ▲ = 100 %, ● = 50 %, ■ = 0 %)

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Silanization-based Synthesis of Hierarchical Zeolite: Influence on Mesoporosity and Crystallinity

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Abstract

Nowadays, silanization-based synthesis route has been an effective pathway to prepare hierarchical zeolites. In our experiments we find that not only the types and added amount of organosilanes but also the crystallization condition are very crucial to prepare hierarchical zeolite with controllable porosity and crystallinity.

Organosilanes $(CH_3CH_2O)_3SiCH_2CH{=}CH_2$, $(CH_3CH_2O)_3SiC_6H_5$, $(CH_3CH_2O)_3Si(CH_2)_3NHC_6H_5$ and $[(CH_3O)_3Si(CH_2)_3N(CH_3)_2(CH_2)_{17}CH_3]Cl$ (TPOAC) are selected to prepare hierarchical silicalite-1 (S-1) zeolite. After different organosilanes are added into the synthesis systems of zeolite S-1, the crystallization time is controlled to obtain the product with same size. The porosity of the products are characterized systematically. It is found that the addition of different organosilanes lead to different product properties. For example, S-1-$CH_2CH{=}CH_2$ samples are similar with that of blank S-1, and no obvious mesoporosity can be observed in them. However, S-1-$(CH_2)_3NHC_6H_5$ samples show higher mesoporosity, and the mesopores ranging over 1.6-3.0 nm can be observed (Figure 1). Moreover, when the added amounts of C_6H_5 silanes are varied in 5-10 mol%, the mesoporosity of product with the same size increases with the increasing C_6H_5 silane amount. The addition of 10 mol% of C_6H_5 silane causes the creation of mesopores over 1.6-3.3 nm (Figure 1).

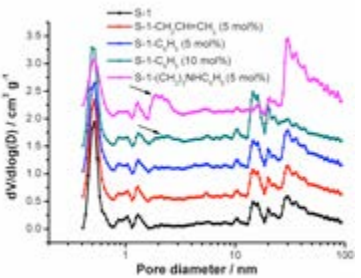


Fig. 1 Pore size distribution curves of hierarchical S-1 prepared with/without organosilanes.

It is worth noting that the modification of organosilane on zeolite is a dynamic but not static process, and the growth of zeolite accompanies with the continuous removal of organosilane, so as to gradually achieve zeolite with the increasing crystallinity. This dynamic process can be revealed by the change of morphology, crystallinity and textural properties of zeolites S-1-TPOAC with the prolonging synthesis time. As shown in Figure 2, after crystallization of S-1-TPOAC for 40 min, the as-prepared S-1-TPOAC-40 exhibits mesoporous structure with relatively low crystallinity. However, with the increase of synthesis time from 40 min to 160 min, the mesoporosity of the corresponding S-1-TPOAC-160 decreases while its crystallinity increases. As a consequence, for the silanization-based preparation of hierarchical zeolite, a balance between mesoporosity and crystallinity of as-prepared zeolite materials has to be considered. Moreover, it is possible to tailor the properties of the resulting hierarchical zeolite materials by modulating the type and amount of organosilane as well as the synthesis condition for their maximizing catalytic advantages in a desired application.

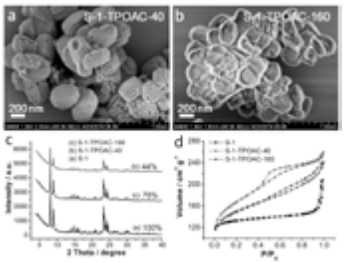


Fig. 2 FESEM images of S-1-TPOAC after crystallization for 40 min (a) and 160 min (b), as well as their XRD patterns (c) and N_2 sorption isotherms (d).

$Pd/Nb_2O_5/SiO_2$ Catalyst for Direct Hydrodeoxygenation of Biomass-related Compounds to Liquid Alkanes under Mild Conditions

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Abstract

With the diminishing of fossil fuel resources and the growing of environmental concerns, the conversion of biomass into liquid transportation fuels has attracted a lot of attention. The conversion of biomass to hydrocarbon fuels requires the removal of oxygen to improve energy density.[1] In our work, a simple Pd-loaded Nb_2O_5/SiO_2 catalyst was prepared for the hydrodeoxygenation of biomass-related compounds to alkanes under mild conditions. Niobium oxide dispersed in silica (Nb_2O_5/SiO_2) as support was prepared by sol-gel method and possesses mesoporous characteristics with pore size distributions in the range of 2-5 nm. The niobium oxide species were amorphous and well dispersed in silica. Under mild conditions (170 °C, 2.5 MPa), $Pd/10\%Nb_2O_5/SiO_2$ was effective for the hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one (aldol adduct of furfural with acetone), palmitic acid, tristearin and diphenyl ether (model compounds of microalgae oils, vegetable oils and lignin), which gave high yields (>94%) of alkanes with less C-C bond cleavage. More importantly, owing to the significant promotion effect of NbO_x species on C-O bond cleavage and the mild reaction conditions, the C-C cleavage was considerably restrained and the catalyst showed an excellent activity and stability for the hydrodeoxygenation of palmitic acid with almost no decrease in hexadecane yield (94~95%) in a 150 h time-on-stream test.



Fig. 1. Direct hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one, palmitic acid, tristearin and diphenyl ether over $Pd/10\%Nb_2O_5/SiO_2$ catalyst.

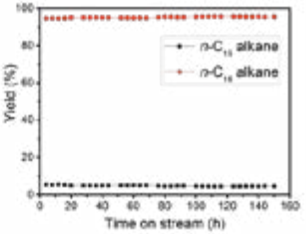


Fig.2. Products distribution in direct hydrodeoxygenation of palmitic acid in a fixed-bed reactor .

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Methyl Levulinate Production from Cellulose: the Selectivity and Mechanism

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Abstract

Recently, increasing researches are focused on the production of liquid fuels and high-quality chemicals from biomass conversion due to the deterioration of the environment and inevitable depletion of fossil resources. As one of the most popular derivatives converted from carbohydrate, methyl levulinate (ML)[1] can be widely used in agriculture, foods, medicines, cosmetics, spice industries and biofuels probably in future. In this work, we have achieved a high yield production of 55% ML from cellulose in one reactor using methanol as solvent, catalyzed by mesoporous niobium-based phosphates we synthesized before.[2] The ML was found generated through the intermediate products of methyl glucoside and 5-methoxymethyfurfural (5-MMF), different from the glucose and 5-HMF in water. Some other small molecules were also found, which generated from the break of C-C bond on intermediates. Through analyzing the results from different Brönsted/Lewis acid ratios on series of niobium-based phosphate solid acids, it was found a higher Brönsted acid ratio was benefit for the selectivity to ML, achieving the highest ML yield of 55% by the NbP-pH1 catalyst synthesized on pH=1 which containing a B/L ratio of 2.2/1. The higher Lewis acid ratio would promote the break of C-C bond and lower the conversion speed of 5-MMF to ML, leading to a low selectivity to ML, but an appropriate proportion of Lewis acid would speed up the alcoholysis of cellulose. In conclusion, we have achieved a highest yield of ML catalyzed by solid acids ever, discussed the influence on ML selectivity from acid catalyst properties, and gave out detailed mechanisms of pathway from cellulose to ML which might be very useful for the researchers in future.

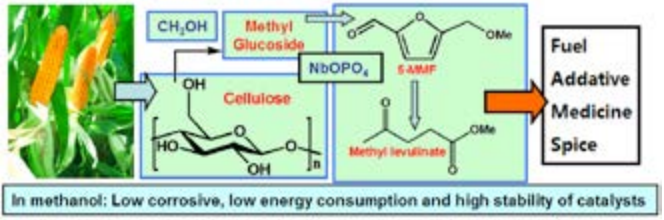


Figure 1 Reaction pathways for the acid-catalyzed conversion of cellulose to levulinate esters in alcohol

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Controlled Release of Phenazone from Ordered Mesoporous Silica Materials

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Abstract

Ordered mesoporous silica materials have attracted great attention in different scientific fields. They have found applications in catalysis, separation and adsorption processes [1-3]. Moreover, in recent years mesoporous silicas have been used for hosting and further delivery of various biomolecules and drugs. Thanks to their ordered structure, well-defined surface properties, high pore volume (0.6–1.0 cm^3/g) and surface area (600–1000 m^2/g) high drug loadings can be achieved. The advantage of a porous-media-based oral drug delivery system can be attributed to its (a) low bulk density, which allows it to float in the gastrointestinal system, and (b) ability to adhere to selective biological systems and offer a volumetric reservoir of drugs [4]. It has been reported that both small and large drug molecules can be captured into the mesopores of ordered silica in the adsorption process and released by controlled diffusion. The aim of our study was to analyse the effect of ordered mesoporous materials such as SBA-15, SBA-16 and MCM-41 modified with aluminium on the loading and release of phenazone (antipyrine) - a non-steroidal anti-inflammatory drug. Aluminium containing mesoporous materials MCM-41, SBA-15 and SBA-16 were synthesised by hydrothermal method with tetraethyl orthosilicate as the silica source and different surfactants (cetyltrimethylammonium bromide, triblock copolymers: Pluronic P123, Pluronic F127) as templates. Aluminium isopropoxide was used as precursor of metal. The Si/Al atomic ratio in the gels was 30 and 60. Structure and surface properties of the materials obtained were characterised in detail by low-temperature nitrogen sorption, X-ray diffraction, transmission electron microscopy, laser diffraction and ultraviolet-visible **spectrophotometry**. Mesoporous silica materials were used as reservoirs for the storage and controlled release of phenazone. The adsorption process was performed by solvent evaporation technique. Subsequently the release process of phenazone was examined in simulated gastric fluid by using UV spectrophotometry at the maximum absorption of 263 nm. The materials characterisation by X-ray diffraction and transmission electron microscopy confirm that all obtained silicas modified with aluminium have mesoporous ordered structures. Additionally, each sample exhibits well-developed surface area and large pore volume. It was revealed that the adsorption capacities and release of antipyrine were highly dependent on the pore size and structure of silica. Type of mesoporous materials had influence on drug diffusion rate into simulated gastric fluid. Application of aluminium modified silica enables to perform the controlled delivery of antipyrine.

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PMO-based Materials Modified with Niobium or Platinum – Synthesis and Characterization Methodology

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Abstract

Hybrid materials offer the combination of inorganic and organic properties that are potentially of interest from the commercial and scientific point of view. Up to now the PMO-related research was focused mainly on the incorporation of various organic groups in order to design materials for adsorption applications and only limited number of materials was designed for catalysis. However, it is supposed that modifications with heteroatoms should alter chemical and physical properties of these materials due to the large difference in the valence, coordination number, atomic weight and electronegativity between silicon and metallic species. It is already known that in many reactions pure silicas or organosilicas themselves are catalytically inactive. Nevertheless, when metal atoms (e.g., Au, Pd or other d-elements) are incorporated into silica frameworks, catalytically active redox centers are generated [1, 2]. Thus, our study was targeted towards design, synthesis and characterization of new inorganic-organic hybrids with potential application in catalysis.

PMO's with hexagonal ordering of pores were synthesized via typical hydrothermal method, using standard chemicals and procedures. Bis(3-trimethoxysilylpropyl)-N-methylamine or bis(3-trimethoxysilylpropyl)amine were applied during synthesis to functionalize mesoporous supports via chemical bonding. Pluronic P123 and CTABr were employed as structure-directing agents. Template removal was based on the extraction procedure with 0.1M solution of HCl in EtOH. Transition metals, namely niobium and platinum were incorporated into the siliceous matrix using "one-pot" and impregnation techniques. Ammonium tris(oxalate) complex of niobium(V) $[(NH_4)_3NbO(C_2O_4)_3(H_2O)]$ and hexachloroplatinic(IV) acid $[H_2PtCl_6 \cdot 6H_2O]$ were used as metal sources. Additionally, different procedures for metal precursors' reduction were applied.

Textural parameters, calculated on the basis of N_2 sorption measurements, show that all materials possess relatively high surface area. Sorption isotherms can be classified as a type IV, according to the IUPAC nomenclature, proving mesoporosity of synthesized silicas. Ordered mesoporous structure of the obtained materials was also confirmed in the terms of the XRD and TEM analysis. Functionalization of the mesoporous supports with selected bis(trimethoxysilyl)-based chemicals was successfully performed and confirmed by elemental analysis and FT-IR spectroscopy, whereas the presence of heteroatoms (Nb, Pt) was detected during ICP-OES and XPS measurements.

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Acknowledgement
National Science Centre is kindly acknowledged for the financial support (project no: DEC-2013/10/M/ST5/00652).

Facile Synthesis of Mesoporous Manganese Oxide Networks for Advanced Lithium-ion Batteries

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Abstract

Energy storage devices with high energy density are in great demand as they have widespread industrial applications [1-2]. Transition metal oxides (TMO) could be potential candidates due to their high conversion capacity, high intrinsic density, abundance, and non-toxicity [3]. In particular, manganese oxides (MnOx) possess a much lower reduction voltage plateau (around 0.5 V vs. Li/Li^+) due to lower electromotive force, and thus, higher energy density when coupled with specific cathodes than other TMO [3,4]. MnOx also offers much higher theoretical conversion capacity (756-1233 mAh/g) than graphitic carbon anodes. However, MnOx has poor electrochemical reversibility due to extremely low electrical conductivity and drastic chemical and structural changes that inherently accompany the conversion reactions during charge and discharge processes.

In this study, we devised a facile synthetic method in an aqueous solution containing Mn precursor and amino acids for mesoporous MnOx networks (MMN). MMN showed the BET surface area (28.6 m^2/g) and pore volume (0.2 cm^3/g) much larger than those of typical MnOx nanoaprticles (MnNP) (Figure 1a). The unique structure of MMN can facilitate Li ion diffusion/reaction kinetics and effectively accommodate mechanical stresses accompanying the electrochemical conversion reactions. Thus, MMN delivered high capacity and exhibited much enhanced cycling stability compared to MnNP as compared in Figure 1b. The details of MMN synthesis and electrochemical responses of electrode prepared with MMN are to be presented in comparison with typical MnNP and commercial graphite, for which Li-ion full cells as well as half cells were fabricated and tested.

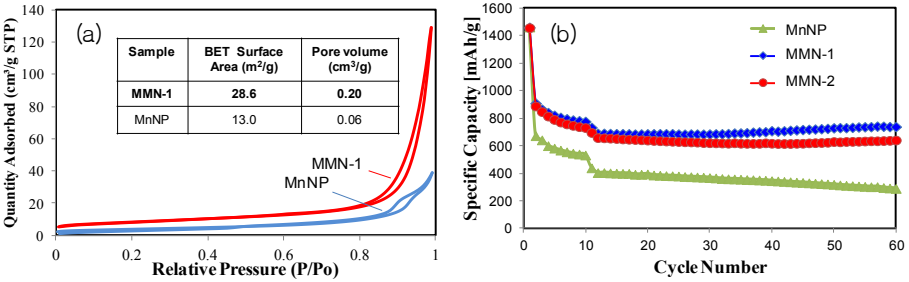


Figure 1. (a) N_2 adsorption/desorption isotherms and (b) cycling performances of MMN and MnNP samples.

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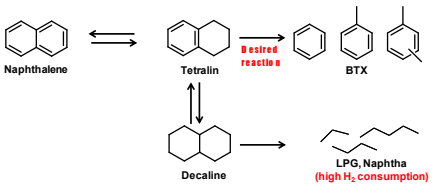
Xylene-rich BTX Production by Selective Hydroconversions of Heavy Aromatics by-Products

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Abstract

In oil refining and petrochemical plants, a large quantity of 2-ring aromatic-rich fractions, such as light cycle oil (LCO) from fluidized catalytic cracker (FCC) [1, 2], and C_{10}^+ heavy aromatics from naphtha cracking centers (NCC) [3] and para-xylene plants [4], are produced as process by-products. Due to the high aromatic hydrocarbon content, they cannot be blended in diesel pools [2] but rather are usually disposed as low-value products such as 1) a blending stock in heavy fuel oil for viscosity adjustment for LCO [1] or 2) self-use in plant fuel etc. for C_{10}^+ heavy aromatics [3,4].

In this study, we postulated a two-step catalytic process to convert the C_{10}^+ aromatics by-product from a para-xylene plant into high-value BTX (benzene, toluene and xylene) rich in xylene. To achieve a high per-pass yield of BTX with low H_2 consumption, it is important to convert the 2-ring aromatics into 1-ring aromatics in high selectivity followed by a selective hydrocracking of 1-ring aromatics into BTX as shown in scheme 1 as an example with naphthalene [4]. For this study, the C_{10}^+ aromatics by-product was hydrogenated over $Mo_2C/\gamma\text{-}Al_2O_3$ catalysts [4]. The hydrogenated product was then hydrocracked over metal/zeolite catalysts to yield BTX rich in xylene. Figure 1 shows that the C_{10}^+ aromatics by-product can be selectively converted into BTX rich in xylene with the compositon of BTX and (BTX + C9 aromatics) of 55.6 and 73.7 wt% in liquid product, respectively. The properties of hydrocracking catalysts based on metal/zeolites and hydrocracking mechanism to yield xylene-rich BTX are to be presented in detail.



Scheme 1. Selective hydroconversion of naphthalene into BTX.

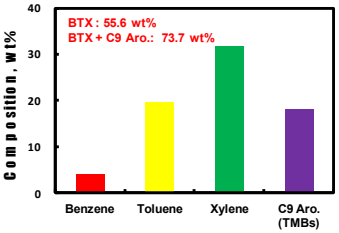


Figure 1. Aromatic products distributions obtained from the hydroconversion of C10+ aromatics by-product.

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The Advantage of VARTM Process to Fabricate Hydrophobic Silica Aerogel Blanket

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Abstract

In general, silica aerogel blankets were prepared by using ambient drying method. Silica aerogel blankets are promising materials as thermal and acoustic insulation, catalytic supports, adsorbents having easy handling and unique textural properties. But this preparation method is vulnerable to poor impregnation of silica aerogel into the blanket. To improve the degree of impregnation of silica aerogel, so-called vacuum assisted resin transfer molding(VARTM) technique was employed to prepare well-impregnation silica aerogel blankets. VARTM technique is a process where aerogel is driven by a vacuum to fill the spaces inside the blankets. To study the effects on a vacuum technique, the silica aerogel blankets were fabricated through the vacuum technique and by ambient drying method. The prepared blanket samples were characterized by thermal conduction, mechanical properties and morphological properties using scanning electron microscope.

High Performance Smart Nanoporous Hetero-Interfaces

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Abstract

High-Performance smart hetero-interfaces have recently attracted considerable interest due to unique properties, including their highly anisotropic geometry, large surface-to-volume ratio, and carrier and photon confinement.[1] Three-dimensional (3-D) nanoporous hetero-interfaces have been one of the hottest research topics in physics, chemistry, biology, and material science, due to their easily accessible pore structures and tailorable surface functionalities for applications, including energy storage and conversion, bio-tissue engineering, multi-scale drug delivery, multi-phase separation, and multi-phase catalysis.[2]

Currently, tremendous efforts are devoted to the rational synthesis of advanced porous heterostructures. Yet, if functional devices are to be made from these materials, precise control over their composition, structure, morphology, and dopant concentration must be achieved. Their fundamental properties must also be carefully investigated since the presence of a large surface and interfacial area can profoundly alter their performance.

Herein, different types of smart heterointerfaces are studied, with the aim to understand how the porosity, composition, structure, morphology, and doping of nanoporous heterostructured materials influence their performances for biomedical applications. The objective will be achieved by fabricating hetero-interfaces including 3-D porous ultralight hydrophilic and hydrophobic, porous bioinspired antenna-like structure, and porous oriented plasma gold nanopyramid arrays via an interfacial growth and self-assembly.[3-8]

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