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1. Oriented Assembly of Functional Mesoporous Materials with Multi-Level Architectures

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Functional mesoporous materials with multi-level architectures possess both unique properties of high surface area, large pore channels and volume based on mesostructures, and abundant optical, electrical, magnetic properties based on inorganic nanomaterials, showing great potential applications on catalysis, adsorption, separation, biomedicines and so on. Here we present the development and progress for the synthesis of the spherical functional mesoporous nanoparticles from "oriented assembly" strategy by interfacial control. A series of new synthesis approaches have been developed based on the oriented assembly strategy in my group, including the confined micro-emulsion self-assembly, liquid-liquid bi-phase synthesis, evaporation-driven oriented/aggregation assembly, anisotropic growth of mesoporous, and interface driven orientation arrangement, *etc.* Novel mesoporous nanospheres with one-level and multi-level architectures can be well synthesized, such as core-shell, yolk-shell, multi-shell, film structures for silica, TiO_2, carbon spheres, 3D mesoporous bouquet-posy-like TiO_2 multi-level superstructures and asymmetric Janus, single-hole hollow, nano-thermometer, hemispheres structures *etc.* The obtained functional mesoporous nanospheres with regularly multi-level architectures possess uniform and controllable mesopore channels, high surface area, large pore volume and open frameworks, showing great potential applications on catalysis, adsorption & separation, energy conversion & storage

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2. Functionalized Mesoporous Carbons for Fuel Cells and Lithium-Sulfur Batteries

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Polymer electrolyte membrane fuel cells (PEMFCs) are highly efficient at converting the chemical energy in hydrogen to electrical energy. While PEMFCs are efficient, they are expensive largely due to the high cost of the platinum catalysts typically used to facilitate the electrochemical reactions in the fuel cell. We have developed noble metal-free catalysts in the form of transition metal-containing ordered mesoporous carbons (OMCs) as low cost alternatives. In this approach nitrogen is incorporated in an Ia3d OMC matrix giving the material chelating properties for transition metal ions in porphyrin-like electrocatalytic sites active for the oxygen reduction reaction[1]. The functionalized OMC materials are typically synthesized using a silica template, which is impregnated by nitrogen-containing carbon precursors and transition metal salts followed by polymerization, carbonization and finally removal of the silica. The resulting materials are active as oxygen reduction electrocatalysts on the cathode side of the fuel cell.

By varying the synthesis variables of these catalysts and the processing conditions for depositing them in membrane electrode assemblies, we have been able to further improve their performance to an extent that may eventually challenge platinum-based fuel cell catalysts[2,3]. A major part of the further development of these catalytically active functionalized OMCs is the choice of precursors for the synthesis and understanding their influence on the atomic and mesostructure of the material. The local atomic structure of the materials has been determined with EXAFS and EPR spectroscopy and these structural features have been correlated with the materials' catalytic activity in fuel cells[4-6].

In parallel, there is a large need for new battery types with higher capacity than traditional lithium ion batteries. One interesting alternative is the lithium-sulfur (LiS) battery, but this suffers from low stability and cyclability. We have developed sulfur-functionalized OMCs and found them useful as cathodes in lithium-sulfur (LiS) batteries providing a significant stability improvement over non-functionlized carbons[7]. In addition, results will be presented from our recent development of post-synthesis modifications of OMCs, in which functional organic groups have been anchored to the carbon surface providing them with additional modes of interaction with sulfur species, resulting in improved charge-discharge cyclability of the LiS batteries[8].

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3. Sustainable hydrogen generation enabled through hydrolysis of hierarchical nanoporous aluminum in neutral water

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Although hydrogen is a very promising energy carrier for producing electricity with zero-emission upon reaction with oxygen, breakthrough in "true sustainable" hydrogen economy is hindered by two major limitations: (1) *Sustainable hydrogen production:* Steam reforming used worldwide to produce hydrogen is not a sustainable because CO_2 is co-produced during this process. (2) *Hydrogen storage:* Assuming hydrogen can be produced in a cost-effective and sustainable manner, proper storage of this hydrogen prior to usage poses another major challenge. Previously we demonstrated the use of hierarchical nanoporous Zn to produce hydrogen by hydrolysis with neutral water without the need of any catalyst or reaction promoter to activate the process.[1] Building upon this work, in this talk, I will present a new route to sustainable hydrogen generation involving: (a) The fabrication of oxide-free hierarchical bulk nanoporous Al with ultrafine ligaments in the range of 10-20 nm by dealloying; (b) Full recovery of the sacrificial element simultaneously during the dealloying; (c) Use of this hierarchical nanoporous Al to produce hydrogen with a yield of 52-80% by hydrolysis with neutral water; (d) recycling the aluminum hydroxide co-produced without CO_2 emissions.[2]

[1] J. Fu, Z. Deng, T. Lee, J.S. Corsi, Z. Wang, D. Zhang, and E. Detsi
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ACS Applied Energy Materials DOI: 10.1021/acsaem.8b00419
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Bulk Nanoporous Aluminum for On-board Hydrogen Generation by Hydrolysis
Patent Application, #18-8558-104377.000203

4. Mesoporous Materials from Self-Assembly Strategies

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The use of organic molecule self-assembly to structure direct various organic and inorganic materials into mesoporous materials is an area of intense research activity world-wide. Low cost solution assembly renders these approaches particularly interesting for applications ranging from separation and catalysis all the way to energy storage and conversion. In this talk progress in the field will be described with work by the Wiesner group at Cornell University. Examples will include the use of both, small molar mass surfactants as well as large molar mass block copolymers as structure directing agents for amorphous, polycrystalline, as well as single-crystal 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 early stage formation studies as well as theoretical and simulation work. Finally, after describing the degree of structural control achievable in various materials classes ranging from carbons and 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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5. Advancing atomic-resolution TEM of MOFs from "impossible" to "routine"

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High-resolution imaging of electron beam-sensitive crystalline materials is one of the most difficult applications of transmission electron microscopy (TEM). The challenges are manifold, including the acquisition of images with an extremely low beam dose, the time-constrained search for crystal zone axes, the precise alignment of successive images, and the accurate determination of the defocus value.

We reported that using a direct-detection electron-counting (DDEC) camera, it is possible to acquire useful high-resolution TEM images with electron dose as low as a few electrons per square angstrom to ensure that the intact structure was captured before damage occurred [1]. In this talk, we will present a suite of new methods that we recently developed to address the rest challenges mentioned above. Our methods advance the HRTEM of extremely beam-sensitive materials from “occasionally possible” to “routine”. We demonstrate the effectiveness of our methodology by capturing atomic-resolution (~ 1.5 Å) TEM images of several metal organic frameworks (MOFs) that are generally recognized as highly sensitive to electron beams. In the case of MOF UiO-66, individual metal atomic columns, various types of surface termination, and benzene rings in the organic linkers, are clearly identified. We also successfully apply our methods to other electron beam-sensitive materials, and achieve atomic-resolution TEM imaging of the organic-inorganic hybrid perovskite CH3NH3PbBr3 for the first time [2]. More recently, we applied this new technology to prove the successful encapsulation of single molecule magnets in MOF NU-1000 [3], and to investigate the evolution and transformation of various defects in MOF UiO-66 [4].

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6. SBA-15 and PMO with convenient particle morphology and tunable pore size for catalysis

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Vernonia galamensis is a native weed of Ethiopia containing high concentration of naturally epoxidized oil in its seeds, which could be used as a potential substitute for currently used epoxy oils [1]. It would be desirable to fully epoxidize VO, to obtain an oxirane value of about 10%. Epoxides are reactive intermediates that readily generate new functional groups. Due to the large size of vernonia oil (917 g/mol), ordered mesoporous materials are good candidates as catalysts for epoxidation and transesterification reactions. The aim of our work is to obtain SBA-15 and PMO with tunable pore size, convenient particle morphology to avoid diffusion problems, and surface chemistry for epoxidation reaction (incorporation of titanium) as well as immobilization of lipase for transesterification reaction. SBA-15 and PMO materials with hexagonal symmetry, surface area between 543 and 863 m2/g, high pore volume (0.57-1.32 cm3/g) and average pore diameter ranging from 5.7 to 14.1 nm have been successfully synthesized [2]. The long fibers commonly observed in SBA-15 and PMO could be avoided obtaining small crystals with plate morphology having the channels running along the short axis of the crystal [3]. Moving one step forward, Ti has been successfully incorporated in SBA-15 and PMO while maintaining good textural properties [4]. Lipase immobilization on the modified materials will yield bi-functional catalysts. Catalytic test in the epoxidation of cyclohexene for titanium and transesterification of tributyrin for lipase will be presented hoping to reach an optimum catalyst suitable for the epoxidation and transesterification of vernonia oil.

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7. Preparation of mesoporous quartz via crystallization of silica colloidal crystals

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Mesoporous silica is useful in catalysis, adsorption, optics, etc. and their properties are variable by the crystallinity, meaning the significance of the crystallinity control of mesoporous silica. We reported the preparation of mesoporous quartz by converting silica colloidal crystals to quartz by using flux, where interparticle voids are regarded as mesopores.[1] The crystallization of silica colloidal crystals will expand the possibility of mesoporous silica thanks to the optical, piezoelectric, and thermal properties of quartz. Here we report the crystallization of AlB2-type colloidal crystals to verify the versatility of this method.

The preparation is shown in Scheme 1. Silica colloidal crystals with fcc and AlB2-type structures were prepared according to previous studies.[2, 3] The diameters of nanoparticle in silica colloidal crystals were varied from 30 nm to 90 nm, and LiNO3 as a flux was introduced into the interstices. Then, the colloidal crystals were mixed with excessive furfuryl alcohol (FA), saturated with LiNO3, to introduce FA into the interstices. Subsequently, FA was polymerized and carbonized by calcination under an argon flow. The samples were further calcined at higher temperature to crystallize amorphous silica to quartz. Carbon was removed by calcination under air atmosphere to obtain mesoporous quartz.

The XRD patterns of all the samples showed the formation of quartz. The SAXS, SEM, and TEM results proved the retention of the ordered arrangements of silica nanoparticles. The N2 adsorption-desorption isotherms were type IV(a), showing the presence of mesopores. The ED patterns showed the spots assignable to quartz, and the domain size of single crystals depends on the particle size. AlB2-type silica colloidal crystals composed of nanoparticles with 30 nm and 60 nm in size were also converted to single crystalline quartz retaining the structure. These results indicate that the crystallization method is applicable to different ordered structures of silica colloidal crystals.

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8. Mesoporous Shell Nanoreactors for X-ray Nanochemistry

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Mesoporous silica shells are used as the building materials for the construction of nanoreactors that can be used to study X-ray nanochemistry, which is a new discipline of research that studies how to use nanomaterials to harvest X-rays. Several nanoreactors are made for the detection of enhancement to the X-ray effect by nanomaterials. Specifically, spherical and cylindrical nanoreactors of different sizes are made to host dosimetric reactions as well as catalytic reactions, and these reactions are used to probe the enhancement. These nanoreactors can also used as nanoscale probes to detect enhancement. They can also be used to host reactions that would otherwise be difficult to proceed in the open solution. Synthesis and applications of these nanoreactors with sealable porous walls will be discussed.

9. Designing New Functional Materials by Colloidal Nanocrystal Assembly

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The self-assembly of colloidal nanocrystals (NCs) into superstructures provides an efficient bottom-up pathway for constructing new functional materials. Among various superstructures, NC superlattices represent an entirely new class of solid-state materials with unique collective properties and wide applications. However, conventional NC superlattices are inappropriate structural motifs for energy applications due to the impeded molecular accessibility of NCs by foreign species. In pursuit of widening the range of applications of NC superlattices, it is desirable to develop new architectures that enable full access of NC constituents while simultaneously facilitating mass transport properties. Herein, I will focus on low-dimensional, hierarchical NC superlattices with rationally designed structures and mesoscale morphologies toward high-performance energy storage and conversion. I will also spend half of the time to cover NC superlattice derivatives, especially ordered graphene-like frameworks, which are emerging as a new class of mesoporous carbon materials. By exploiting the versatile surface chemistry and self-assembly behaviors of colloidal NCs, a rich array of mesoporous graphene-based materials can be designed, which show great promise as material platform for energy applications.

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10. High Troughput Screening of Vanadium Anchored by Transition Metal ion in MCM-41 like Silica for Selective C-C bond Cleavage in Diols and a-Hydroxyethers

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The development of selective and robust heterogeneous oxidation catalysts is an enabling technology for conversion of biomass-derived platform chemicals. Vanadium active sites were incorporated into the structure of mesoporous silica via an ultra-fast, one-pot synthesis method based on microwave-assisted heating. In addition, Al/Ti/Zr/Ce anchoring ions were introduced in order to minimize vanadium leaching and better control its dispersion. The supported V-(Al/Ti/Zr/Ce)-MCM-41 catalysts were applied in screening tests for aerobic C-C bond cleavage of lignin and sugar-derived polyalcohols, using the simple model substrates 1,2-diphenyl-2-methoxyethanol and meso-hydrobenzoin, respectively. Ti^{IV} ions were the best anchors to prevent V leaching, while Al^{III} and Zr^{IV} ions were the best to improve selective conversion of the substrate. The active sites in these catalysts are 2D VO_x layers stabilized on the anchors. In a screen of twelve solvents, weakly polar solvents were found to be most suitable for this reaction like the environmentally friendly ethyl acetate. The previous properties together with the high selectivity for C-C bond cleavage advocates for a heterogeneous catalytic pathway, intrinsically different from that of previously reported molecular oxovanadium(V) catalysts.[1]

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11. Easy cast-(spin)-heat method yielding monodisperse lead halide perovskite nanocrystals in the strong quantum confinement regime

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Motivated by the swift ascent of performance in lead-halide perovskite-based photovoltaic devices, a parallel branch of research started paying a close attention to their nanostructured counterparts. In particular, high quantum yields and low threshold lasing made them prone for integration in various types of light-emitting devices.

The fabrication of nanostructured perovskite has been dominated by colloidal syntheses yielding product with high purity and involving molecular ligands fulfilling three major roles: size control through electrosteric stabilization, solvent affinity for effective solubilization and surface passivation suppressing major trap states. Multistep purification, ligand exchange for device integration and sensitivity to atmospheric conditions, however, remain major limitations for commercial applications. In this project we sought to circumvent these issues by taking advantage from 1) widely documented mesoporous templates, available in various geometries and pore sizes, constitute an ideal set of nanoreactors to grow crystals; 2) the common routes to synthesize bulk lead halide perovskites which yield no side products (only solvent removal).

Until now, we focused mainly into utilizing silica matrix in order to minimize interactions between guests and hosts, thus insuring the properties are only inherent to the nanocrystals. Using self-standing templates such as MCM-41, SBA-15 and KIT-6, optical properties possess a strong dependence on the pore size, mostly due to quantum confinement effects.[1,2] We also noticed exotic phenomena related to photostability, such as a limited ion mobility and the ability to recover optical properties after exposure to strong UV light.

The hierarchical porosity (micro/meso) of SBA-15-type mesoporous films was exploited to carry efficient template-filling and growth of ultra-small nanocrystals, yielding strongly blue-shifted photoluminescent emission.

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12. Encapsulation of Pd Nanoparticle Catalysts and Aminopolymers in Hollow Silica Spheres for Efficient Semihydrogenation of Alkynes

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Semihydrogenation of alkynes to alkenes is one of the most important reactions for the synthesis of bulk and fine chemicals. Pd supported on poly(ethyleneimine) (Pd/PEI) and those supported on silica have recently been studied as catalysts, however, they still suffer from leaching of Pd NPs and PEI during catalytic cycles, resulting in a low selectivity for alkenes and decreased reusability of catalyst. In this study, we report hollow silica spheres encapsulating Pd nanoparticles (NPs) together with PEI inside the hollow cavities (Pd+PEI@HSS) act as stable catalyst for the semihydrogenation of alkynes.

Pd+PEI@HSS was synthesized by a self-assembly approach using poly(ethyleneimine) (PEI) as a template. TEM images showed that Pd+PEI@HSS is composed of dispersed hollow spheres with an average particle size of ca. 160 nm containing Pd NPs and PEI in their void spaces. The silica shell thickness was determined to be ca. 50 nm, and the average diameter of Pd NPs was determined to be ca. 9 nm. N_2 adsorption measurements verified the existence of randomly-arranged micro-pores (ca. 1 nm) in the silica shell.

In the semihydrogenation of diphenylacetylene, Pd+PEI@HSS afforded the corresponding alkene with more than 95% alkene selectivity (cis/trans = 95:5), which was far superior to those of Pd@HSS (without PEI) and unsupported Pd/PEI, demonstrating that the encapsulation of PEI inside the hollow silica drastically improves the alkene selectivity. This hybrid catalyst was also applicable to terminal alkynes, phenylacetylene, and was reusable at least 5 catalytic cycles without any significant loss of activity and selectivity because of the protective silica shell.

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13. Towards design rules for creating epitaxially connected assemblies of nanocrystals with defect free atomic precision and mesoscale order

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Recently, elegant schemes for synthesizing ordered inorganic structures by epitaxially connecting preformed semiconductor nanocrystals through oriented attachment have been developed.[1] These structures are theorized to have exotic electronic structures resulting from the dispersion of individual quantum dot electronic states into minibands. Unfortunately, when nanocrystals with surface step edges epitaxially attach, it can lead to the formation of dislocations in the nanostructure.[2] From an electronic materials perspective, it would be desirable to understand how to remove these defects since they can have deleterious effects.

In this talk, we will explore how the crystallographic attachment direction of individual rock salt PbTe nanocrystals has a large impact on the ease of dislocation removal. We use high-resolution transmission electron microscopy (HRTEM) imaging to observe the structure of dislocations that can result from imperfect attachment. In the case of PbTe, there are two commonly observed attachment facets, the {100} and {110} facets. For attachment on {100} facets, the defect that is formed has glide plane (easiest for the dislocation to move) that is noncolinear with the attachment direction, giving the dislocation a short path to the surface. Indeed, we observe using *in-situ* HRTEM that these dislocations quickly move along the glide plane to the surface yielding a perfect interface. In the case of {110} attachment, the glide plane of the dislocation is co-linear with the attachment direction meaning it must traverse the entire crystal before being removed. We believe this reveals an important design rule for preparing defect free epitaxially attached nanocrystal solids. Nanocrystals should be attached on a facet such that, if a dislocation were to form, the glide plane of that dislocation is not collinear with the attachment direction. More broadly, the geometric relationship between the atomic lattice and mesoscale structure has important implications for preparing atomically coherent mesostructured materials.

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14. Bipyridine-Periodic Mesoporous Organosilica for Heterogeneous Metal Complex Catalysis

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The use of recoverable and reusable heterogeneous metal complex catalysts, instead of homogeneous catalysts, for batch and flow-through systems is of interest in the development of environmentally friendly chemical processes. However, the intrinsic catalytic activity of metal complexes usually decreases after immobilization on conventional solid supports due to unfavorable interactions between the active sites and heterogeneous solid surface. Recently, the synthesis of a new periodic mesoporous organosilica (PMO) containing 2,2'-bipyridine (BPy) ligands within the framework (BPy-PMO) was reported.1) The BPy-PMO had a molecularly well-defined pore surface structure in which bipyridine ligands were regularly and densely arranged in the siloxane network. Heterogeneous catalysis has been reported for precious metal complexes formed on BPy-PMO such as Ir(OMe)(cod)(bpy),1,2) $[Ru(bpy)_3]Cl_2$,1) $RuCl_2(CO)_2(bpy)$,3,4) IrClCp*(bpy),5) $RhCp^*Cl_2$,6) and $Re(CO_3)Cl(bpy)$.7) However, no report has described the formation of base metal complexes, such as a Mo complex, on BPy-PMO. Here we report the immobilization of MoO_2Cl_2 on BPy-PMO-TMS and its catalysis for epoxidation of cyclooctene using tert-butyl hydroperoxide (TBHP).8) The relation between loading amount and catalytic activity, which has not been well-studied for BPy-PMO, was investigated.

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15. Synthesis and characterization of thick transparent mesoporous nanoparticle-based SiO_2 thermal barriers

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This study aims to develop a method to synthesize both transparent and thermally insulating mesoporous SiO_2 slabs. Materials that are both optically transparent and thermally insulating could reduce the energy losses of buildings through windows[1–3] and increase the thermal efficiency of solar energy conversion systems.[4,5] Silica aerogels feature extremely low thermal conductivity (<20 mW m^{-1} K^{-1}) under ambient conditions.[3] However, they are typically translucent due to scattering by their largest pores and expensive to manufacture due to costly supercritical drying process. In this study transparent and thermally insulating mesoporous slabs consisting of aggregated SiO_2 nanoparticles were synthesized using sol-gel method. The slabs were a few centimeters in diameter and several millimeters in thickness. The porosity was between 50% and 60% while the thermal conductivity ranged between 100 and 200 mW m^{-1} K^{-1}. The diameter of SiO_2 nanoparticles and the mesopore width were smaller than 20 nm to achieve high transparency and low haze. Visible light transmittance exceeded 89% and haze was less than 2.6% for a 1.5-mm thick slab.

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16. Redox-Enhanced Electrochemical Capacitors: Electrolyte Design and Device Engineering

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Research in electrochemical energy storage is converging to target systems with battery-level energy density, and capacitor-level cycling stability and power density. One approach is to utilize redox-active electrolytes that add faradaic charge storage to increase energy density of supercapacitors. Aqueous redox-active electrolytes are simple to prepare and to up-scale; and, can be synergistically optimized to fully utilize the dynamic charge/discharge and storage properties of mesoporous carbon based electrode systems.[1] However, aqueous redox-enhanced electrochemical capacitors (redox ECs) have performed relatively poorly, primarily due to the cross-diffusion of soluble redox couples, reduced cycle life, and low operating voltages. In this presentation, we show that these challenges can be met by the use of liquid-to-solid phase transitions of redox electrolyte molecules, and their reversible confinement in the pores (> 2 nm) of high-surface-area electrodes. This approach is demonstrated by the use of bromide catholyte and modified hydrophobic cations (e.g., viologens[2] and tetrabutylammonium[3]) that together induce reversible solid-state complexation of Br_2/Br_3^-. This mechanism solves the cross-diffusion issue of redox ECs without using costly ion-selective membranes, and has the added benefit of stabilizing the reactive bromine generated during charging. Furthermore, our device is simple to fabricate and uses large >10 mg carbon electrodes (BET specific surface area of 2470 m^2/g, mass loading of 12.7 mg/cm^2) to ensure that our performance metrics are practical.

Using the concepts learned from this 1st generation configuration, we created a hybrid electrochemical storage system by designing and implementing stackable bipolar pouch cells with corrosion-resistant non-metallic current collectors. The device using $ZnBr_2$ battery chemistry and tetrabutylammonium cations enables high-power aqueous electrochemical energy storage.[4] The specific energy of this system can be made competitive with that of a Pb-acid battery and has a specific power that is well within the range of commercial capacitors.

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17. Structural properties and potential applications of supramolecular templated chiral mesoporous materials

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Over the last decade we have developed the synthesis of a range of supramolecular template mesoporous materials based on the use of folic acid and guanosine monophosphate as pore templates, NFM-1 and NGM-1 respectively.[1, 2] These materials show some unique properties in comparison to other hexagonal 2d-mesostructures such as MCM-41. The self-assembly of NGM-1 and NFM-1 are synthesized relies on Hoogsteen-type hydrogen bonding to form tetramers, subsequent π-stacking interactions between adjacent tetramers promote the formation of columnar phases.[3] The structure of the supramolecular template is imprinted on to the surface of the resulting mesopores. This can be ascertained from X-ray diffraction (XRD), transmission electron microscopy and circular dichroism studies.

In this report we will present the synthesis mechanism and how the material characteristic features can be controlled. Additionally, we will present a series of carbon replica materials prepared using the supramolecular template as carbon source as well as their properties.
Our recent work shows that these materials have potential applications for the detection of biomolecules,[4] in drug delivery,[5] in chiral separation and as potential enantiomeric catalyst supports. These application areas will be reviewed.

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18. Nanoporous Materials for High Rate Energy Storage Applications

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There is an increasing need for electrochemical energy storage due to the rising use of consumer electronics, electrical vehicles, renewable energy sources, and grid storage. Unfortunately, fast charging capabilities and long cycle life remain key challenges for current lithium-ion battery technologies. Here, we explore the use of nanostructured materials synthesized using both solvothermal methods and sol-gel based polymer-templating to improve the rate capabilities and lifetimes in battery materials. We specifically consider nanocrystals based porous MoS_2 and templated porous $LiMn_2O_4$ and $LiVPO_4F$. We find that nano-structuring battery materials can increase the maximum charge and discharge rates by shortening diffusion path lengths for lithium-ions and, in some cases, allow ions to intercalate into the redox-active material in a non-diffusion controlled manner that that is termed intercalation pseudocapacitance. With MoS_2, specific capacities over 90 mAh/g were achieved in only 30 seconds of charging with lithium and almost 100 mAh/g were realized in just under 40 seconds with sodium. *Operando* X-ray diffraction indicates that the key to the fast kinetics lies in suppression of the standard ion-intercalation driven phase transitions that produce sluggish intercalation kinetic in bulk materials. Similar results were observed in nanostructured $LiMn_2O_4$, and for this system, we were also able to examine how the rate capability varied with crystallite size. *Operando* X-ray diffraction showed that fast charging, small domain size $LiMn_2O_4$ does not exhibit a phase transition features, while slower charging, larger domain size $LiMn_2O_4$ shows a clear first order intercalation induced phase transition. Finally, mesoporous $LiVPO_4F$ (LVPF) was synthesized and was able to attain 100 mAh/g in 2 minutes charge and showed 99% capacity retention after 1000 cycles. This exceptional rate capability and stability is not observed only in mesoporous LVPF due to reduced diffusion path lengths and improved electrolyte penetration. These three systems exemplify the promise of mesoporous materials for next generation electrochemical energy storage.

19. Properties of Water confined in Periodic Mesoporous Organosilicas: Nanoimprinting the local structure

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The confinement of liquids in porous media greatly influences their physical properties, in particular, when the pore size approaches the molecular length scale. Several mechanisms, such as the pure geometrical restriction and the liquid-solid interaction at the interface contribute to the confinement effects, however, their roles for the drastic changes in the thermodynamic and dynamic behaviors of the liquids are not clearly understood. Especially, water molecules adsorbed on the surface and restricted within the pores are interesting in the scope of biochemistry, catalysis, and energy storage. The influence of the pore size on the melting and freezing points of confined water has been studied extensively. It is known that the properties of water in confined spaces with extents of a few nanometers will be altered and that for example the freezing/melting point can be shifted to temperatures below 220 K or completely suppressed [1]. In contrast, fewer studies have been made concerning the effects of the surface polarity on the properties of spatially confined water, which may be due to the lack of highly defined porous substances.

Periodic mesoporous organosilicas (PMOs) fill this gap perfectly because they combine the highly ordered pore structure of the well-established M41S-phases with the variety of surface chemistry within the pores. PMOs are synthesized using only bis-silylated precursors of the form $(R'O)_3Si\text{-}R\text{-}Si(OR')_3$ where R is an organic bridging group which can be altered according to the desired surface properties. Furthermore, PMOs with an aromatic bridging group may exhibit a molecular-scale periodicity within the pore walls. This allows a periodically alternating surface chemistry along the pore channel, caused by arrays of silica and aromatic organic groups.

Here, we show that the molecular mobility of water confined in periodic mesoporous organosilicas (PMOs) is influenced by the polarity of the organic moiety. Multidimensional solid-state NMR spectroscopy directly probes the spatial arrangement of water inside the pores, showing that water interacts either with only the silicate layer or with both silicate and organic layers depending on the alternating surface polarity. A modulated and a uniform pore filling mode are proposed for different types of PMOs [2]. Our study gives a molecular-level picture of the adsorbate-surface interaction, which helps understanding various confinement effects and provides a new design concept of the pore structures with the desired properties.

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20. Ordered Mesoporous Ti^{3+}-$Li_4Ti_5O_{12}$ Nanocrystal Frameworks Surrounded by 3D Conductive Carbon Networks for High-Performance Lithium Ion Battery Anodes

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Rational designed and controllable synthesis of $Li_4Ti_5O_{12}$ based materials on nano- and micro-scale is necessary for high-performance lithium-ion batteries.[1,2] Herein, a novel material with ordered mesoporous Ti^{3+} doped $Li_4Ti_5O_{12}$ (Ti^{3+}-$Li_4Ti_5O_{12}$) nanocrystal frameworks surrounded by 3D conductive carbon networks is reported by using F127 as the structure-directing agent, titanium citrate and lithium nitrate as $Li_4Ti_5O_{12}$ precursors, ethanol and deionized water as solvent. The as-made ordered mesoporous Ti^{3+}-$Li_4Ti_5O_{12}$-carbon composites present a high specific surface area (134 $m^2\ g^{-1}$), a high pore volume (0.12 $cm^3\ g^{-1}$), a uniform pore size (~3.9 nm), and small Ti^{3+}-$Li_4Ti_5O_{12}$ nanocrystals (6−10 nm) conformably encapsulated in 3D conductive carbon networks. XPS spectra reveal the presence of Ti^{3+} and Ti^{4+} together. Owning to the high contact surface area, shortened lithium-ion diffusion distance, and sufficient conductivity, the mesoporous Ti^{3+}-$Li_4Ti_5O_{12}$-carbon composites show superb rate capability and cycling stability as an anode material for lithium-ion batteries. A high specific capacity of 153.3 mAh g^{-1} can be achieved at 2 C with no noticeable (less than 6 %) capacity loss after 1000 cycles. We believe that the mesoporous Ti^{3+}-$Li_4Ti_5O_{12}$-carbon composites are expected to be applied as a high-performance electrode material for next generation lithium ion batteries.

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21. Large Area Perpendicular Nanochanneled Mesoporous Silica Thin Film

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Large area perpendicular nano-channeled mesoporous silica thin film(MSTF) would be very desirable in applications such as membrane separation, masks for electronic nanocomposites, and sensors. Perpendicular orientation in such mesostructures with defect-free ordering on large length scales(wafer size) still remains a major research challenge. We develop a general approach to grow large area continuous vertical mesoporous thin films on various flat surfaces, such as silicon, glass and polystyrene, via facile co-assembly process. Introduction of long-chain alkane, i.e. decane, into CTAB-EtOH-TEOS aqueous solution can align growth orientation of mesochannels perpendicular to substrates. Upon an addition of decane, pore diameters expand (5.7±0.5 nm) gradually and vertical hexagonal mesophases grow continuously over wafer size area on substrates.

We also successfully grow highly ordered mesoporous zeolitic thin films (MZTFs) by using zeolite seed as silica source. The resulting thin film possesses high thermal and hydrothermal stability. The ultrathin films (10-20nm) were layer-by-layer deposited via an introduction of beta-zeolite seeds at 40-50ºC, resulting formation of uniform packing of reticular mesochannels with controlled shapes and well-defined pore sizes (6.7±1.06 nm). The zeolite films were characterized in both top-view and cross-sectional SEM/HRSEM/HRTEM microscopies as well as GIXRD/GISAXS scattering techniques.

After surface functionalization of the thin film, large amount of $AuCl_4^-$ ions can be adsorbed and chemical reduced on top of the MSTF. A hexagonal 2-D array of gold nanoparticles, in wafer size, can be produced. Strong SERS effect was demonstrated on the two-dimensional gold nanoparticle array. The SERS effect is due to large amount of hot spots developed in the narrow gap(~ 1 nm) in the array.

22. Nanoporous Metals, Sn and SbSn, for Energy Storage Applications

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Anodes that undergo alloying reactions with lithium and sodium are attractive substitutes for graphite in LIBs and SIBs owing to their high capacities. However, alloy-type anodes suffer from short lifetimes due to drastic volume changes during lithiation or sodiation. It is well-recognized that intermetallics and surface coatings can help to accommodate these volume changes. Intermetallics reduce the strain of these alloying anodes during ion intercalation by spreading out the intercalation voltages and allowing one of the components to act as the buffer at all times, and surface coatings improve the mechanical stability of the overall structure by physically restraining the volume expansion during charge and discharge. Here we synthesize nanoporous tin (NP-Sn) and antimony tin (NP-SbSn) through selective etching and combine these materials with Al2O3 and LiAlSiOx coatings to study the deleterious effects of volume change in nanoporous alloying-type anodes under transmission X-ray microscopy (TXM). Operando TXM shows that NP-Sn and NP-SbSn expand by 40 and 60% during lithiation, which is significantly less than in bulk Sn (130%). More importantly, the pore system in NP-SbSn stayed completely intact while some degree of fracturing was observed in NP-Sn, suggesting that NP-SbSn is more mechanically stable allowing for longer cycle life especially with high-strain intercalant such as Na+. Less volume expansion was indeed observed during operando TXM and the porous structure were also better preserved throughout cycling. Overall, these nanoporous metals appear to be promising solutions to combat volume expansion due to their well-maintained structures and open pores throughout cycling, allowing for good electrolyte penetration and uniform lithiation and sodiation of these electrode materials.

23. Mesoporous Liquids: Challenges and Opportunities

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Functional materials using or in the presence of ionic liquids represents a burgeoning direction in materials chemistry. Ionic liquids are a family of non-conventional molten salts that can act as both functional materials and solvents. They offer many advantages, such as negligible vapor pressures, wide liquidus ranges, good thermal stability, tunable solubility of both organic and inorganic molecules, and ion conductivity. The unique solvation environment of these ionic liquids provides new reaction and separation media for controlling many energy-related processes. We have recently developed a class of ionic liquids with intrinsic mesoporosities based on nanoscopic building blocks.[1,2] Challenges and opportunities in synthesizing and using these porous ionic liquids in energy-related applications will be discussed.

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24. Enabling Pseudocapacitive and Battery-Like Charge Storage in Manganese Oxide-Coated Porous Carbon Nanofoam Paper

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Birnessite manganese oxide (MnO*x*) is a well-established active material for electrochemical energy storage in which charge can be stored both within the interlayers of the layered structure and at the surface/sub-surface of the oxide. The performance of birnessite MnO*x* is further amplified when expressed as a thin ~10 nm coating on a supporting mesoporous carbon nanofoam (MnO*x*@CNF) architecture by electroless deposition. The MnO*x*@CNF paper electrode retains sufficient surface area (262 m^2 g^{-1}) and hierarchical pore sizes (10–80 nm range) in which high mass loadings of up to 50 wt.% of MnO*x* are present. When pairing MnO*x*@CNF with a zinc negative electrode a new charge-storage process can be tapped when cycling in a neutral-pH Zn^2–containing electrolyte; an arrangement defined “rechargeable zinc-ion battery”. In our study, we extend the functionality of such batteries by adding Na^+ to the Zn^{2+}-containing electrolyte and enable pseudocapacitance, a high-rate charge-storage mechanism. The cells reported in this study comprising a mixed Na^+:Zn^{2+} aqueous electrolyte and a nanoarchitectured MnO*x*@CNF cathode paired with a zinc foil anode (Zn||MnO*x*) exhibit high specific capacity at moderate C-rates

(1C; 300 mAh g^{-1}) and modest capacity at more challenging C-rates (20C; 100 mAh g^{-1}). The fundamental charge-storage mechanisms of the redox-active nanostructured MnO*x* are further investigated by a fleet of electroanalytical and *ex situ* materials characterization techniques. The results suggest that a number of electrochemical processes are at play for the combined pseudocapacitive and battery-like processes of MnO*x* cycled in the mixed Na^+:Zn^{2+} electrolyte.

25. Boron-rich Clusters as Molecular Cross-linkers for Hierarchical Hybrid Materials

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Cross-linking is important for materials to form rigid networks with improved thermal/mechanical properties. However, there exist a limited number of cross-linkers that are capable of generating rigid 3-dimensional networks and leading to significant changes of properties. Our group has recently developed a “molecular cross-linking” approach whereby we incorporate molecular boron clusters in the network of metal oxides using a simple solution-based synthesis.[1] This new approach is enabled by the inherent robustness of the boron-cluster molecular building block, which is compatible with harsh oxidizing and thermal conditions required for the synthesis of metal oxides. The combined comprehensive structural characterization of this material validates a hybrid molecular boron oxide that consists of a cross-linked network of intact boron clusters within which are embedded TiO_2 nanocrystals (~10 nm) in the anatase phase. The unique structure of the hybrid material displayed substantially improved electrochemical and photocatalytic property, evidenced by fast electron-transfer rates, low resistivity and photocatalysis under visible light conditions.

Furthermore, we explored the possibility of cross-linking boron-rich clusters with organic monomers to form densely cross-linked polymeric materials. The reaction between B_{12}-based clusters and diisocyanates produced a highly cross-linked polyurethane gel with a mesoporous architecture. It shows an interesting swelling/deswelling property as a function of its environment. Given the mesoporous and stimuli-responsive nature of the polymer gel, it can be potentially used for bio-medical applications. Moreover, co-condensation between B_{12}-based clusters and diboronic acids created a new type of 3-dimensional polymeric networks with spherical morphologies. These materials are expected to have significantly improved thermal/mechanical properties due to the covalently cross-linked nature. The successful modification of the materials ranging from inorganic metal oxides to organic polymeric materials demonstrates the value of molecular cross-linking as a new and previously unattainable strategy to induce change in the properties of materials for diverse applications.

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26. Multifunctional Mesoporous Silica Nanoparticles Controlled by Nanomachines for Biomedical Targeting, Imaging and Drug Delivery

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The subjects of this talk are multifunctional nanoparticles controlled by nanomachines for targeting, imaging and drug delivery in cells and in vivo. The nanoparticles are designed to 1) trap therapeutic molecules inside of nanocarriers, 2) carry therapeutics to the site of the disease with no leakage, 3) release a high local concentration of drugs, 4) release only on command – either autonomous or external, and 5) kill the cancer or infectious organism. The most important functionality is the ability to trap molecules in the pores and release them in response to desired specific stimuli. Two types of external stimuli will be discussed: light and oscillating magnetic fields. Activation by internal biological stimuli such as pH changes, redox potential changes and enzymes will also be presented. Molecular machines based on molecules that undergo large amplitude motion when attached to mesoporous silica - impellers, snap-tops and valves – will be described. Derivatized azobenzene molecules, attached to the interior pore walls function as impellers that can move other molecules through the pores. Nanoparticles containing anticancer drugs in the mesopores are taken up by cancer cells, and optical stimulation of the impellers drives out the toxic molecules and kills the cells. Snap-tops with cleavable stoppers release cargo molecules when the stopper is removed from the pore entrance. Nanovalves consisting of rotaxanes and pseudorotaxanes placed at pore entrances can trap and release molecules from the pores in response to stimuli. Activation of these nanodevices by the five types of stimuli in solution, in living cells, and in animal models will be discussed. Applications to treatments of cancers (including pancreatic and breast) and of intracellular infectious diseases (including tuberculosis and tularemia) will be presented.

27. Precision Nanomaterials from Persistent Micelle Templates

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Few aspects are as prevalent and important to energy conversion and storage as the dimension control of porous nanomaterial architectures. The study of nanostructure-dependent electrochemical behavior, however, has been broadly limited by access to well-defined nanomaterials with independent control over the pore and wall dimensions. This historic limitation is partially due to reliance upon dynamic self-assembly processes that are subject to the “tyranny of the equilibrium.” We have developed a kinetically controlled approach as a new nanofabrication tool kit. Kinetic control is historically difficult to reproduce, a challenge that we address with switchable micelle entrapment to yield reproducible and homogeneous nanomaterial series that follow model predictions. This approach enables seamless access from meso-to-macroporous materials with unprecedented ~2 Å precision of tuning, commensurate with the underlying atomic dimensions. This precision and independent control of architectures also opens new opportunities for nano-optimized devices.

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28. Mesoporous organosilica catalysts for reactions in hot liquid water

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Mesoporous silicas have been widely investigated as supports for catalytically active sites in selective transformations of large, biomass-derived molecules, including the biopolymers (hemi)cellulose and lignin. The utility of these materials depends on their stability under the required reaction conditions, which for biomass usually involves liquid phase reactions with a significant aqueous component at elevated temperatures. These conditions lead to structural collapse as well as leaching of the active sites into the reaction medium.[1] The latter may not be evident in a batch reactor experiment, since the catalytic reaction can continue in the solution phase. In a flow reactor, leaching of propylsulfonic acid groups was obvious, since the active sites are irreversibly lost (and are detected in the reactor effluent).[2] This process was slowed by adding unfunctionalized silica at the end of the catalyst bed to trap and recondense the soluble organosilanes. Additional stability was imparted by making the support much more hydrophobic, through the incorporation of a high concentration of ethylene or phenylene bridges into the silica framework.

Recently, we pioneered the use of operando solid-state NMR techniques to assess the solution environment inside porous solids, with a particular focus on aqueous-organic cosolvent systems.[3] The NMR spectrum provides distinct chemical shifts and relaxation times for confined molecules and molecules present in the bulk solution phase, allowing quantitative analysis of the pore solution. Initial results show that the composition of the solvent in the pores differs from the nominal solution composition.[4] This phenomenon affects the partitioning of dissolved molecules and thereby alters catalytic activity and selectivity. The insight is leading to the design of mesoporous organosilica materials to promote adsorption of reactants and desorption of products.

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29. High throughput screening of complex metal oxides and identification of mesostructure for improving oxygen evolution electrocatalysis

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Optimization of heterogeneous catalysts increasingly pushes research to complex materials in high-order composition spaces. The challenges for deploying computational screening and/or traditional experimental approaches for catalyst searches in these high dimensional spaces motivates the use of high throughput techniques. We have coupled inkjet printing-based deposition of metal oxides containing any combination of 1, 2, 3 or 4 metals (cations) with automated electrochemical screening to evaluate composition-activity trends in high order composition spaces. Through development of new data science techniques, we identify that select Ni-Fe-Co-Ce oxides exhibit unique electrochemical behavior and catalytic activity for the oxygen evolution reaction. The ensuing nanocharacterization and in situ characterization by the groups of Junko Yano, Walter Drisdell and Christian Kisielowski reveals that the unique catalytic properties emanate from an emergent mesostructure in the high order composition space, providing an important example of using high throughput synthesis, characterization and analysis to identify functional mesostructures.

30. Direct Access to Functional Porous Materials for Energy Conversion and Storage: From Ordered to Hierarchical Structures

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In recent decades, considerable research effort has been devoted globally to the development of new and renewable energy devices. For this, functional porous materials have attracted much attention as electrode materials due to their interconnected pores, controllable pore sizes and structures, and controllable pore wall chemical compositions. Compared with hard templated method, block copolymer self-assembly allows a one-pot simple process rather than tedious multistep procedures to prepare ordered mesoporous materials. Hierarchically porous oxide materials have immense potential for application in catalysis, separation and energy devices. However, these materials have been synthesized using multiple templates and the associated complicated steps hampered widespread application of such materials. Our research group developed a simple one-pot strategy for the synthesis of inorganic oxide materials with multiscale porosity. Mesoporous inorganic particles and hollow spheres are of increasing interest for a broad range of applications, but synthesis approaches typically are material specific, complex, or lack control over desired meso- and macrostructures. Our research group reported how combining mesoscale block copolymer (BCP) directed inorganic materials self-assembly and macroscale spinodal decomposition can be employed in multicomponent BCP/hydrophilic inorganic precursor blends with homopolymers to control their structure. The designed porous materials developed by our group have been employed as high performance electrode materials for anion exchange membrane fuel cells (AEMFC), hybrid supercapacitors, Li-S battery, and Li-O2 battery.

31. Tailoring Porosity, Crystallinity and Surface Properties of Alumina-Based Mixed Metal Oxides

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Fabrication of alumina-based metal oxide catalysts with high specific surface area, well-developed porosity, high crystallinity and tailored surface properties is a challenging task because crystallization occurring during thermal treatments promotes sintering, which is accompanied by partial or even total collapse of porous structure.

Alumina-based mixed metal oxides can be synthesized by using the evaporation-induced self-assembly strategy (EISA) with considerably high surface areas and porosity [1,2]. However, incorporation of several catalytically active metal oxides needed for achieving the desired surface properties is challenging due to the complexity of hydrolysis-condensation processes of various metal oxide precursors. Moreover, the EISA strategy provides materials with low degree of crystallinity [1-4].

The strategies suitable for synthesis of ceramic catalysts with desired degree of porosity and crystallinity are currently practically unavailable. Therefore, this talk covers three aspects: shows new possibilities of EISA to create mixed metal oxides with controlled porosity and surface properties; demonstrates how the surface properties can affect their catalytic activity and stability; and proposes a novel synthetic strategy for the development of these oxides with high porosity, crystallinity and stability at relatively low temperatures. The latter is possible via a new defect-induced strategy [5]. Moreover, this study provides fundamental understanding of the mesophase formation through thermal activation, and shows how the mesophase stability can be improved to achieve ceramic catalysts with well-defined features.

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32. Thermally Reduced Gold Nanoparticles Confined by Ordered Mesoporous Carbon as an Efficient Catalyst for Selective Hydrogenation of Nitroaromatics

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Gold nanocatalysts represent a new generation of catalysts for the selective oxidation and reduction using molecular O_2 and H_2, showing great potentials for green chemistry. Activated carbons are one of the most frequently used supports in industry. However, activated carbon has been seldom used for gold deposition[1]. Here a coordination-assisted self-assembly approach is adopted for the intercalation of thermally reduced gold nanoparticles inside ordered mesoporous carbon frameworks (Au/OMC).

An almost complete conversion of benzyl alcohol to benzoic acid is achieved within 60 min over the Au/OMC catalyst with gold nanoparticles approximately 9.0 nm under 90 ºC and 1 MPa, using potassium hydroxide as a base[2]. A reduction of gold particle size from 9.0 to 3.4 nm in the catalyst leads to an increased TOF value. The electronic modification of the d-orbitals of small particles is extremely important for chemisorption of O_2[3].

Interestingly, thermally reduced Au/OMC nanocatalyst with gold nanoparticles is highly active and selective to convert nitroaromatics containing multiple functional groups to corresponding amines using H_2 as a reducing agent, showing higher TOF values compared to commercial Au/TiO_2 with similar nanoparticle sizes[4]. By comparison, the commercial Au/C catalyst is inert under the same reaction conditions. Trapping by the SH-functionalized SBA-15 solids confirms the negligible gold leaching and the heterogeneous active centers for thermally reduced Au/OMC. 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. The simultaneous thermal reduction of gold nanoparticles and pyrolysis of the matrix facilitate the modification of carbon atoms on the gold surface and the involvement of gold inside the carbon matrix. The carbon modified gold surface reduces the H_2 dissociation barrier which is the rate determining step, changes the adsorption configuration of nitroaromatics, and can therefore significantly improve the hydrogenation activity and selectivity. The intercalation of gold nanoparticles inside ordered mesoporous carbon significantly enhances the stability in reuse.

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33. A confined monomicelle assembly method for controlled coating single-layered mesoporous TiO_2 shells

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Mesoporous core-shell nanostructures have recently been receiving extensive research interests due to the combined functionalities or pristine properties of cores and shells, improved stabilities as well as high surface area for molecules accommodation. However, despite of Si-based core-shell mesostructures, the implementation of controlled coating mesoporous materials comprised of crystalline nanocrystals still remains exciting challenges. Here, we demonstrate a general confined interfacial monomicelle self-assembly method for coating ordered mesoporous TiO_2 shells with single-layered mesopores on various surfaces. Through using triblock copolymer Pluronic F127 as a template to create mesopores, glycerol as a confined solvent to monitor condensation of titania oligomers, a monolayered TiO_2 mesostructure can be heterogeneously assembled on the solid-liquid interface. The coated TiO_2 layers have a high surface area (119 $m^2\ g^{-1}$), mean mesopore size (9.8 nm) and crystalline anatase mesopore walls. Moreover, the thickness of TiO_2 shells can be precisely controlled at 1, 2, 3, 4 and 5 layers of mesopores, and the pore size also can be manipulated from 5.5 to 21.5 nm by changing the adding amount of swelling agent. Additionally, the single-layered mesoporous TiO_2 shells are able to be coated on a variety of surfaces, including silica, metal oxides, metal sulfides, polymer, and carbon nanomaterials.

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34. Transformation of biomass-derived feedstocks into liquid biofuels by using mesoporous catalysts

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Biomass is the most widely used renewable energy source in the world today. One of the directions in which biomass is used is the production of biofuels.[1] It is an extremely important task to produce fuels from renewable energy sources - mainly due to the depletion of non-renewable energy sources and due to environmental protection.[2]

One of the most interesting methods of converting biomass to biofuels is its initial pyrolysis and then catalytic hydrodeoxygenation (HDO).[3] As a result of biomass pyrolysis a bio-oil is formed – mixture of more than 300 compounds derived from the depolymerization and fragmentation reactions of biomass components.[4] HDO process is one of the promising path leading to obtaining high-quality hydrocarbon fuels from the bio-oil intermediate. This process is carried out under elevated temperature, hydrogen pressure and in the presence of suitable catalyst. Generally the laboratory tests are carried out on lignin model compounds, which are identical to those contained in biomaterial, such as; anisole, phenol, guaiacol, 4-methylanisole or 1,3-dimethoxybenzene.[5]

A very important issue in the HDO process is the choice of the catalyst. Ordered mesoporous silica materials, especially: MCM-41, SBA-15, SBA-16 with transitional metal atoms deposited on the surface are well-evaluated in this process. Unique properties of these materials, such us: highly ordered structure, high surface area and pore volume and the possibility of surface modification, make them promising catalysts in many reactions.[6]

Therefore, our studies were focused on the obtaining of mesoporous silicas of SBA-16 type modified with transition metal atoms and their use as catalyst in HDO process of model compounds. HDO of model compounds were performed in a high-pressure reactor. A 2^2 factorial design investigation to optimize HDO reaction was carried out varying the reaction temperature (90-130°C) and hydrogen pressure (25-60 bar). Additionally, ^1H NMR spectra signals were used to monitor the reaction system. Our work demonstrated that nanocatalysts are efficient for the HDO reaction of model substrates.

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35. Block-Copolymer-Templated Mesostructured Mixed-Metal Oxides: From Thin-Film Ferroelectrics to Tunable Magnetic Materials

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Mesoporous oxides – whether in the form of films or powders – have been receiving much attention in recent years owing to their potential for various (next-generation) applications. However, especially the preparation of more complex mixed-metal oxides that are structurally and compositionally well-defined is challenging. This is due in part to the fact that both nucleation and growth of the crystalline phase are difficult to control.

Here, we describe the evaporation-induced self-assembly (or micelle templating) synthesis of high-quality cubic mesoporous mixed-metal oxides with spinel and perovskite structures and their characterization using state of the art imaging, diffraction, and spectroscopic methods. Besides the structure-property relations of r.t. thin-film ferroelectrics,[1] we demonstrate that the general idea of combining nanomagnetism and electrochemical energy storage concepts can be applied to block-copolymer-templated oxide thin films. Using such sol-gel type materials as the working electrode in secondary lithium-ion cells or double-layer capacitors and carefully controlling the cutoff potentials allows tuning the magnetism in a virtually fully reversible manner without compromising the lattice and pore structure.[2-5] These results are exciting and indicate that both techniques hold potential for application in micromagnetic actuation and spintronics.

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36. Compositions, structures, and properties of mesoporous-Fe,N-doped carbon materials for oxygen reduction reaction electrocatalysts

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Mesoporous-Fe,N-doped carbon materials exhibit high and accessible surface areas, high conductivities, and high electrocatalytic activities for oxygen reduction reactions, making them attractive as inexpensive alternatives to precious-metal/C fuel cell catalysts. The synthesis conditions, precursor compositions, and choice of templating material (e.g., salt-mixture or mesoporous-SBA-15 silica) influence the types, quantities, and distributions of Fe and N heteroatom environments, which strongly affect macroscopic oxygen reduction activities. However, it has been challenging to measure and correlate local Fe or N heteroatom environments and their distributions in graphitic carbon materials with macroscopic electrocatalytic properties. This has been due, in part, to their paramagnetic and/or conductive characters, complicated distributions of disordered and ordered regions, and heterogeneous material compositions. Here, we report detailed new insights on the local atomic environments and distributions of N and Fe heteroatoms in high N content (~28 wt%) materials prepared with different templates, which influence the surface chemistry, and thus the electrocatalytic properties. Atomic-level insights are provided by solid-state ^{13}C and ^{15}N nuclear magnetic resonance (NMR) spectroscopy, and supported by nitrogen sorption, X-ray photoelectron spectroscopy, Raman spectroscopy, ^{57}Fe Mossbauer spectroscopy, X-ray diffraction, and electrocatalytic reaction analyses. Notably, low-temperature solid-state NMR measurements of materials synthesized with ^{13}C,^{15}N-enriched precursors yield increased NMR signal sensitivity that enables powerful 2D ^{13}C{^{15}N} NMR correlation methods. The 2D ^{13}C{^{15}N} NMR spectra resolve and correlate signals from ^{15}N heteroatom sites and directly bonded ^{13}C atoms within the mesoporous carbon materials. The NMR results and analyses establish the types, atomic environments, and distributions of ^{15}N heteroatoms in the graphitic carbon, which, until now, have been infeasible to distinguish by scattering or other spectroscopic techniques. These analyses identify specific ^{15}N and ^{57}Fe heteroatom environments that correlate with increased ORR activity, providing useful new insights for the design of highly effective and stable electrocatalysts for applications in energy storage and conversion.

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37. Organic Hydrogels as Porogenic Matrices for Mesoporous Metal Oxide Films

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Mesoporous metal oxides are frequently synthesized by using either supramolecular structure directors ('soft templates') or rigid matrices as porogens ('hard templates', so-called nanocasting). Both methods have their individual advantages and disadvantages. For example, utilization of soft templates is a straightforward method that allows the preparation of mesoporous thin films by evaporation-induced self-assembly (EISA). However, this method is applicable only to a limited choice of metal oxides and the solution-based synthesis is restricted to low temperature; annealing at high temperature for increased stability can only be accomplished post-synthetically. The nanocasting method, on the other hand, is a more universal approach.[1] The metal oxides are synthesized in the pores of a silica or carbon matrix under solvent-free conditions, which allows high-temperatures and yields products with high crystallinity. This method, however, is not well suited for the preparation of thin films.

We present the synthesis of mesoporous metal oxides by utilization of poly(dimethylacrylamide) hydrogels as porogenic matrices.[2-4] The hydrogels are prepared by photo-induced cross-linking of respective polymers. Swelling the hydrogels in metal salt solutions and subsequent calcination yields metal oxides with uniform mesopores of ca. 4 nm. This approach is halfway between 'soft' and 'hard templating'. The hydrogel forms a continuous network that takes up the inorganic precursor species with no risk of phase-separation, similar to a hard matrix. At the same time, the swollen hydrogel is a highly flexible phase; the (cross-linked) polymer strands are more or less loosely arranged and displaceable, like a soft matrix. Furthermore, the hydrogels can be anchored to substrate surfaces by covalent bonding which facilitates preparation of films with thicknesses in the μm and sub-μm range.

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38. Functionalized mesoporous silica synthesized using amphiphilic polyoxometalates: extending the catalytic applications of polyoxometalates

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$P_2W_{18}O_{62}{}^{10-}$[1], a traditional polyoxometalate (POM), is widely used as a photocatalyst[2] and catalyst[3] for organic synthesis. However, the high solubility of $P_2W_{18}O_{62}{}^{10-}$ in polar solvents limits its application due to recycling problems. This disadvantage may be solved by grafting POMs within proper supports, which is a good method to extend the catalytic application of POM. Therefore, here we have explored the possibility to encapsulate POMs in mesoporous silica/titanium dioxide via a direct templating route to ensure both good dispersion and high accessibility of the POM within the mesopores. Based on this aim, we grafted double hydrocarbon tails onto a POM moiety as a headgroup which renders the final product $2C_n$-POM (n=12, 14, 16) amphiphilic. Conductivity[4] has been applied to determine the CMCs of the $2C_n$-POM (n=12, 14, 16). Micelle formation and the monolayers at the water/air interface have been studied by small angle neutron scattering (SANS) and X-ray reflectivity respectively. SANS patterns suggest that $2C_{12}$-POM forms ellipsoidal micelles in water, and that these ellipsoidal micelles become less elongated as the concentration increases. However, even though $2C_{16}$-POM has a very similar packing parameter, $2C_{16}$-POM instead forms spherical micelles at all concentrations in water. Thus tail volume effects appear to dominate over the headgroup interactions when determining the packing parameter that describe the micelle shapes. These surfactants have been used to template silica, to obtain mesoporous silica with an even distribution of the POMs on the surface of channels. The structures and properties of mesoporous silica prepared with pure POM surfactants with varied tail lengths and those made using mixtures of the POM amphiphile with a nonionic surfactant will be compared.

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39. Towards the Precise Design of Organic Functions in Non-silica-based Hybrid Mesoporous Materials

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According to well-investigated knowledge on the chemistry of silicate, periodic mesoporous organosilicas (PMOs) have so far been synthesized using amphiphilic organic molecules from a wide variety of silsesquioxanes for the design of organic functions. In contrast, non-silica-based hybrid mesoporous materials have hardly been developed so adequately. In 2003, we firstly proposed a new strategy to synthesize non-siliceous hybrid mesoporous materials from the reactions between metal sources and diphosphonic acids.[1] This synthetic strategy have only been applied to the preparation from diphosphonic acids bridged by simple alkyl groups (*1st step*), but we have recently (in 2017) succeeded in obtaining aluminum organophosphonate (AOP) type mesoporous materials containing several aromatic groups (*2nd step*) by tuning the reactivity of bisphosphonates to metal sources.[1.] Continuous reactivity control is possible by changing the ratio of -OH/-OEt in the same bisphosphonate molecules ranging from $P_2(OEt)_4$ to $P_2(OH)_4$. Here, we'd like to introduce usefulness of our improved method for obtaining a variety of supramolecular mediated AOP type mesoporous materials, which give use further development of non-silica-based hybrid mesoporous materials almost like PMO type ones.

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40. Mesoporous Silica Supported-Pd Catalysts for the Production of H-FAME as a New Type of Biodiesel Fuel for High-Blend Fuels

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The commercial palm oil-derived biodiesel fuel (shortly termed palm BDF) as a sustainable transportation fuel with low carbon footprint is synthesized by alkali-catalyzed transesterification of palm oil with methanol and subsequent processing steps for separation and purification. In the Association of South-East Asian Nations (ASEAN), the palm BDF has been widely blended with petro-diesel up to 7-20%, Thailand, Malaysia and Indonesia especially. However, the high blend fuels (petro-diesel blended with a concentration of fatty acid methyl ester in excess of 5%) formulated by blending petro-diesel with the palm BDF are harmful to the engine and exhaust systems of vehicles. It is due to that the palm BDF with ca. 8-10 wt% of polyunsaturated fatty acid methyl esters (poly-FAME) and little amounts of impurities is degraded significantly over time. Herein, we showed that partial hydrogenation of palm BDF over supported Pd catalysts to produce partially hydrogenated fatty acid methyl esters (H-FAME) with enhanced stability could be carried out under mild reaction conditions. The poly-FAME molecules were selectively hydrogenated to their monounsaturated counterparts (mono-FAME) over the metallic Pd nanoparticles as the catalytically active sites. Because the metallic Pd particles were finely impregnated into the mesoporous structure, the 1wt%Pd/SBA-15 catalyst, with its higher Pd dispersion and well-ordered pore channels, demonstrated higher activity and tolerance to impurities in the synthesis of H-FAME than the commercial 1wt%Pd/γ-Al_2O_3 catalyst, which had low Pd dispersion and irregular pores. The B20 fuels formulated by blending petrol-diesel with H-FAME showed good stability and almost no degradation after the accelerated oxidation test. In addition, the combination of adsorption and wintering posttreatments further reduced the monoglycerides (MG) and steryl glucosides (SG) contents of the palm H-FAMEs to ca. 0.1 wt% and 10 ppm, respectively, and also decreased the concentrations of metal and inorganic species. It is therefore suggested that the resulting high-stability, high-purity palm H-FAME is a promising BDF source with excellent safety and security for use in high blend fuels.

41. Selective Manipulation in Bimodal Mesoporous CMK-5 Carbon

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CMK-5 carbon exhibits two distinct mesopore systems. It consists of periodically arranged, linear cylindrical tubes of amorphous carbon. The voids between adjacent tubes form a continuous system of mesopores (inter-tubular pores), whereas the interior of the hollow tubes constitutes another mode of mesopores (intra-tubular pores). The two pore systems can be addressed independently during/after synthesis of CMK-5. It is possible to load only one of the two pore systems with a guest species or to functionalize the pore walls of only one type of pores.[1]

Selective deposition of guest species (*e.g.* sulfur or SnO_2) within the intra-tubular pores has a significant influence on the powder XRD diffractogram in the low-angle region. Material simulations were performed to obtain deeper insight into the selective guest species deposition. The synthesized composite materials show promising properties for application as electrode materials in lithium-ion batteries.[2] Furthermore, a selective surface functionalization is possible by a similar synthetic approach. Oxygen-containing functionalities at the pore walls were created by oxidative treatment with acidic persulfate solution.[3] This leads to increased polarity, as investigated by water vapor physisorption analysis. The other (inter-tubular) pore system remains unpolar, resulting in a bifunctional material with potential impact on the application in catalysis or sorption. Materials are characterized by a variety of techniques, including N_2 and H_2O physisorption analysis, electron microscopy, and low-angle X-ray diffraction, including an in-depth study by theoretical simulation of low-angle X-ray data.[1-3]

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42. TBA

43. Mesoporous materials built of MFI zeolite frameworks: surfactant-directed synthesis, pore characterization, and application as a catalyst support

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Recently, our group developed a synthesis route to hierarhical zeolite with a nanosponge-like morphology using multiammonium-type surfactants as a meso/micro dual structure-directing agent.[1,2] The zeolite nanosponge was composed with disordered networks of ultrathin zeolite nanolayers, and possessed a narrow distribution of mesopore diameters. However, because the mesopore arrangement was disordered, it was difficult to determine the detailed structures of the pores, such as mesopore shapes, interconnection, and connectivity to micropores.

Herein, we investigated the mesopore structure of zeolite nanosponges using three-dimensional transmission electron microscopy tomography after supporting platinum on zeolite nanosponges.[3] The resultant tomograms showed disordered and three-dimensionally interconnected networks of Pt nanowires, which corresponded to the shape of the surfactant-directed mesopores. In addition, argon adsorption and solvent washing experiments revealed that the mesopores were connected to zeolitic micropores within the framework, to form a hierarchically porous system.

Furthermore, we demonstrate the use of zeolite nanosponges as supports for preparing high-performance metal catalysts. When we supported metals on zeolite nanosponge, the metals were highly dispersed on the mesoporous surface in the form of tiny nanoparticles. As a result, 2 wt% Ni/zeolite nanosponge could exhibit high catalytic performance in n-dodecane hydroisomerization, which was comparable to those of Pt-based catalysts.[4] When the metal loading was increased to a very large extent (> 30 wt%), the metals were supported in the form of nanowire networks along the zeolite mesopores. Although tightly filled in the mesopores, the metal surfaces were still readily accessible for reactants through zeolitic micropores on the mesopore wall. As a result, 30-wt% Co/zeolite nanosponge exhibited 20-fold higher activity for Fischer-Tropsch reaction, compared with solely mesoporous MCM-41-supported counterpart.[5]

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44. Porous Silicon Nanoparticles for Medical Applications

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The use of porous silicon nanoparticles for peptide-targeted delivery of therapeutic payloads and for luminescence imaging will be described. One area where there are clearly unmet therapeutic needs is in the treatment of antibiotic resistant bacterial infections, and the deployment of porous silicon nanoparticles to meet this challenge will be described. Porous Si nanoparticles can be simultaneously loaded and sealed using aqueous solutions of the desired therapeutic (siRNA or small molecule antibiotics will be used as examples) in the presence of calcium or magnesium ions. The resulting core-shell nanostructures consist of a drug-loaded nanoparticle core infiltrated with a biodegradable shell of calcium or magnesium silicate. Attachment of functional peptides impart targeting and cell penetration properties to the constructs that show improved gene silencing and therapeutic outcomes in vivo. The intrinsic photoluminescence that derives from quantum confinement in the silicon skeleton provides a built-in luminescent probe that can be used for in vivo and in vitro imaging and self-reporting drug delivery in these systems.

45. Polymeric Micelle Assembly' for Synthesis of Mesoporous Metallic Materials

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Recently, we have focused on the polymeric micelles as stable and rigid templates for obtaining mesoporous materials with ultra large pore sizes. 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. Our 'polymeric micelle assembly' approach is highly useful for preparation of novel mesoporous materials which are not easily obtained by general synthetic approaches.

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. 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 favors 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.

Other mesoporous metals with different metallic frameworks can be produced by using surfactant-based synthesis with electrochemical methods. Owing to their metallic frameworks, mesoporous metals with high electroconductivity and high surface areas hold promise for a wide range of electrochemical applications. In this presentation, we would like to develop new mesoporous/nanoporous materials as well.

Selected references: *Nature Communications*, **8**, 15717 (2017); *Nature Communications*, **8**, 15581 (2017); *Nature Chemistry*, **8**, 638 (2016); *Nature Communications*, **6**, 6608 (2015); *Nature Communications*, **4**, 1632 (2013).

46. Metamaterials Made by Polymer Self-Assembly

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Metamaterials derive interesting properties from typically periodic structures that are smaller than a characteristic length scale they are probed by. For example, highly periodic 10-nm lattices in plasmonic metals can give rise to the unusual propagation of light across them, including, possibly, a negative refractive index. In this context, the self-assembly in block-copolymers is interesting, since it produces periodic arrays on a length scale that can give rise to metamaterial properties. In my talk, I will give an overview over the replication of block-copolymer self assemblies into metals and the optical an mechanical properties of the resulting metamaterials. Particular challenges in optical metamaterials include the control over the polymer self-assmbly process, electronic losses in the material, and the interplay of plasmonic surface and bulk effects. I will discuss these challenges and the provide recent progress towards the manufacture of bulk metamaterials generated by polymer self-assembled morphologies.

47. Designed Porous Carbons for Selective Gas Separations

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The discovery of selective soild adsorbents for sorting of molecules with similar sizes by adsorption technique would be a fundamental breakthrough for gas separation in chemical industry. Porous carbon materials have been widely used as adsorbents in gas separation because of their intrinsically good chemical-, thermal- and moisture-resistant properties. For practical application, in a dynamic flow situation, the adsorption capacity of the porous carbons is determined largely by the adsorption kinetics, which is closely related to size, depth, shape and connectivity of the pores.[1]

In this presentation, porous carbons with multiple-length-scale porosity and nitrogen-containing framework have been prepared by controlling the gelation and phase separation processes, which show outstanding CO_2 capture and separation capacities.[2,3] Moving forward in design of porous carbon materials with nanometer-scale skeleton, we have synthesized porous carbon nanosheets *via* a solution-chemistry using graphene oxides as the shape-directing agent and amino acid and ionic liquid as the bridging molecules, whose thickness can be precisely controlled over the nanometer length scale. Recently, we further developed a thermoregulated phase transition assisted synthesis of carbon nanoplates with over ~80% sp^2 carbon, unimodal ultramicropore and controllable thickness. [4] Thin structure allows orientated growth of carbon crystallites, and stacking of crystallites in nearly parallel orientation manner are responsible for single-sized micropores. When used for gas separation from CH_4, carbon nanoplates exhibit high uptakes (5.2, 5.3 and 5.1 mmol g^{-1}) and selectivities (7, 71 and 386) for CO_2, C_2H_6 and C_3H_8 under ambient conditions. The dynamic adsorption capacities are close to equilibrium uptakes of single components, further demonstrating superiority of carbon nanoplates in terms of selectivity and sorption kinetics.

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48. Mesoporous Organosilica Nanoparticles for Cancer Immunotherapy

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Cancer immunotherapy is a strategy that uses the innate force of immune system to fight against tumours, which is regarded as an effective methodology for safer cancer treatment than conventional cancer therapy using anticancer drug molecules. Development of potent and safe adjuvants for generating robust and long-lasting adaptive antitumor immunity remains one of the key challenges. Innovative nanomaterials including mesoporous silica nanoparticles have been used as both delivery vehicles and adjuvants in cancer vaccines. Nevertheless, the plain chemistry of bare silica has limited its performance. Introducing molecularly dispersed organic functional groups in the framework of mesoporous organosilica nanoparticles (MONs) for drug/gene delivery applications is also a well-known strategy. However, the potential of MONs as immunoadjuvants in cancer immunotherapy has received little attention.

Our systematic studies have provided fundamentally new understandings in the relationship of the composition of MONs and their performance in cancer immunotherapy when used as both antigen carriers and immunoadjuvants. In this presentation, we will introduce how the choice of various bridge groups impacts on their functions and the final antitumor performance.[1] The applications of MONs as multi-functional delievery platforms will also be introduced.[2]

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49. Using Ultraporous, Mesoscale Electrocatalytic Platforms to Deconvolve the Effects of Stoichiometry, Order/Disorder, and Architectural Expression on Oxygen Reduction and Evolution Activity

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The design platform around which our team creates high-activity electrocatalysts entails the use of mesoporous nanoarchitectures, which are built using covalently bonded catalytic nanoparticles co-continuous with a mesoporous void. These intermingled structural networks give the catalyst designer extra dimensions of control when tailoring electrocatalysts to the demands inherent to reducing and evolving oxygen (ORR and OER, respectively). Even the free volume within the architecture can be adjusted from >85% (aerogel) to 40–70% (ambigel) to 20–40% (ambigel). In the OER-functional nickel-ferrite ($\mathrm{Ni}_y\mathrm{Fe}_{1-y}\mathrm{O}x$) ambigel-vs-aerogel series, we find that the emphasis in literature studies on stoichiometry only (the Ni-to-Fe ratio) limits the ability to tune catalytic activity [1]. A single variable does not serve as a definitive predictor of catalytic performance, whether that variable is surface area, crystallite size, Ni-to-Fe stoichiometry, or single-phase purity. Significant interplay occurs between all four—not surprising in light of the mechanistic complexity inherent to cycling molecular oxygen electrochemically, but an indication that much remains to be done to design the optimal catalytic nanoscale interphase [2]. After fundamental electroanalytical assessments of ORR and OER activity, we then test technologically relevant air-breathing electrode structures in order to evaluate the activity and stability of their nanoarchitectured electrocatalysts contained therein [3]. Our ultimate goal is to prototype a rechargeable zinc–air battery that pairs NRL's rechargeable, dendrite-suppressing zinc sponge anode with a "trifunctional" air cathode that reduces oxygen, provides pulse power, and evolves oxygen.

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50. Formation of Mesoporous Silica: Interactions between Silica Oligomers & Cationic Micelles

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The interaction between silica oligomers with cationic micelles under alkaline conditions is the initiating step in the original micelle templated silica synthesis,[1] but this interaction has been difficult to study in detail due to the wide range of different size scales involved, and the fact that reacting systems can be difficult to probe for such detailed information on the necessary time scales. To obtain some insights into these initial interactions and the role of surfactant counterions, and water which compete with silica anions to bind the surfactant, we have selected a non-reacting alkaline solution based on a cubic silsesquioxane species ($\mathrm{Si}_8\mathrm{O}_{20}^{8-}$, with tetramethylammonium counterions) and decyltrimethylammonium bromide (C_{10}TAB) cationic micelles. We have used ^{29}Si NMR, and wide angle neutron scattering with empirical potential structural refinement (EPSR) modelling[2] to attempt to better understand the interactions between silica oligomers, water and surfactant molecules in these systems.

Our work shows that the presence of the surfactant micelles affects the speciation of the silica species in these solutions, favouring the cubic double-four-ring (D4R) Si-O-Si species, compared to solutions without the surfactant present. However notably, the total concentration of the silica salt has a stronger effect on this speciation than the presence of the surfactant. The silica species are not noticeably enriched around the micelle surfaces, however, surfactant monomers bind preferentially to silica monomers rather than to the oligomeric silica species. The C_{10}TAB micelles themselves shrink in the presence of the silica and become less well ordered. These observations may suggest that the first steps of mesoporous silica formation involve surfactant binding to monomeric silica that results in charge neutralisation allowing coacervation of mixed, but disordered, silica-surfactant particles, rather than silica anions coating surfactant micelles. The influence of different surfactant counterions, which compete with silica to bind the quaternary ammonium cation has also been probed.

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51. Nanoporous silica nanoparticles embedded in nanoporous platinum: A novel drug delivery material for neuronal electrodes

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Many neuronal electrodes use the noble metal platinum for the stimulation of nerve cells or the registration of neuronal signals. A typical example is the cochlea implant employed to overcome certain cases of deafness. The cochlea electrode uses platinum contacts to stimulate spiral ganglion neurons, the nerve cells of the inner ear. As for many implants, an implant-associated drug delivery device would be highly desirable also for the cochlea implant. It could be used to deliver drugs which, for example, suppress immune reactions versus the implant, combat implant-associated infections, improve healing of the operation site or induce regenerative processes. For middle-ear prostheses, we were able to show that a thin coating of nanoporous silica can act as an efficient drug delivery device. Due to its large pore volume, nanoporous silica can store large amounts of drug; its surface properties can be varied widely using silanazation reactions for modification. However, nanoporous silica alone cannot be used as a coating on neuronal electrodes because it is not electrically conducting.[1-3]

Therefore, we have constructed nanoporous platinum coatings for the storage of drugs to be released after implantation. However, platinum as an inert metal is difficult to modify chemically so that it is difficult to regulate the amount of drug to be stored and the release behavior. Therefore, we proceeded to derive a composite drug delivery coating containing nanoporous silica nanoparticles embedded in a matrix of nanoporous platinum. The preparation process involves several steps. This novel material combines the advantages of nanoporous silica with the electrical conductivity of the platinum host material.

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52. Transparent, monolithic, silica ambigels for low thermal conductivity coatings on single pane windows

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According to the US Department of Energy, HVAC systems in commercial and residential buildings accounted for 14% of primary US energy consumption in 2013 and 3.9 quads of that energy flows out through windows in cold weather.[1] Currently, state-of-the-art windows consist of expensive double- or triple-pane systems in which the gaps between the panes are filled with inert gas or vacuum that require complete reinstallation of the window system. This underscores the need for a low-cost, highly-transparent insulation material which can be retrofitted to preexisting windows and provide adequate thermal insulation in one single pane.

Sol-gel derived silica ambigels provide a cost-effective solution for manufacturing of thick, monolithic, transparent window insulation material. The key component of ambigel synthesis is the method of drying. In contrast to aerogels, which use expensive supercritical drying (typically CO_2) techniques, and xerogels, which are dried in polar solvents, ambigels utilize a high vapor pressure, nonpolar drying solvent that can minimize the surface tension on the silica surface to avoid cracking and pore collapse.[2] The tetraethylortholicate (TEOS) based, acid-catalyzed ambigel in the study is ambiently dried in cyclohexane, achieving a monolithic, crack-free gel with 52% porosity. The pore size distribution of the ambigel, from N_2 porosimetry, is between 2 and 9nm with transmittance and haze values above 95 and below 3%, respectively. A chemically identical aerogel that is dried in supercritical CO_2 is made for comparison. The thermal conductivity of the aerogel and ambigel are 0.095 ± 0.02 and 0.21 ± 0.03 W m^{-1} K^{-1} respectively, as measured by Time-Domain Thermoreflectance (TDTR). This ambient drying technique eliminates the need for expensive supercritical drying and results in a pore size distribution that is small and narrow enough to avoid scattering interaction with visible light.

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53. Biocompatible Periodic Mesoporous Ionosilica Nanoparticles: Application to Drug Delivery

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Ionosilicas recently emerged as a new family of functional organosilicas. These materials are defined as silica based materials containing covalently anchored ionic groups, and are synthesized via sol-gel reactions starting from ionic precursors.[1] Ionosilicas combine high porosity, regular architecture on the mesoscopic scale with an unmatched chemical versatility, induced by the high number of incorporated ionic sites and the high variability of possible anion-cation combinations. In analogy to ionic liquids, which are considered as *'designer solvents'*, ionosilicas can be regarded as *'designer materials'*.[2]

Here, we present the first synthesis of ionosilica nanoparticles and their application in drug delivery.[3] Periodic mesoporous ionosilica nanoparticles with ammonium walls were synthesized *via* a modified Stöber method. These original nano-objects were obtained exclusively from a silylated ammonium precursor and display highly uniform particle size centered at 90 nm together with high specific surface area up to 1000 m^2/g and regular pore arrangement. The average pore size is of approximately 1.9 nm. Both in vitro and in vivo cytotoxicity investigations of the ionosilica nanoparticles displayed high biocompatibility. The nanoparticles are efficiently endocytosed by macrophages. This feature allows the use of ionosilica nanoparticles as drug carrier vehicles. We showed that the nanoparticles can be loaded with diclofenac, an anionic anti-inflammatory drug. The diclofenac loaded nanoparticles are efficient in inhibiting lipopolysaccharide (LPS) induced inflammation.

In summary, our results show the high potential of novel hydrophilic ionosilica nanoparticles in drug delivery. Our results open new possibilities for the efficient vectorization of anionic pharmaceuticals.

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54. Single-micelle-templated Nanoparticles

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The use of individual surfactant micelles to template nanoparticles with single mesopores (single-micelle-templated nanoparticles) has been nearly unexplored until recently. In 2012, we reported that synthesis procedures used for block-copolymer-templated ordered mesoporous materials can be modified by decreasing the ratio of the framework precursor and Pluronic block copolymer (PEO-PPO-PEO) to afford single-micelle-templated nanospheres and nanotubes. It was suggested that a limited amount of the framework precursor condenses around poly(ethylene oxide) (PEO) blocks of the surfactant forming the framework, while still preserving "free" PEO segments on the periphery of the nanoparticle, and thus stabilizing them from consolidation. While this approach can readily afford nanospheres, the synthesis of nanotubes is more challenging. Block copolymer surfactants with long PEO blocks, which work best to provide the environment for the framework formation and still afford the particle stabilization due to "free" PEO segments on the outside, typically promote the spherical micelle formation. Very recently, we demonstrated that judiciously selected pairs of Pluronics, combined with an appropriate swelling agent, are excellent templates for silica nanotubes. Suitable combinations include Pluronic with long PEO blocks (Pluronic F127) and the other with a similar PPO block size, but with higher PPO content (and thus with much shorter PEO blocks). We hypothesize that the presence of long PEO blocks allows one to generate single-micelle-templated nanoparticles, while the "dilution" of long PEO blocks of one surfactant with shorter PEO blocks of the other one reduces the crowding in the PEO envelope, decreasing the driving force to form a highsurface-curvature (spherical) morphology. The combination of the latter with an increased PPO content and the resulting enhanced uptake of the swelling agent promotes the cylindrical micelle geometry and allows one to readily generate nanotubes with tunable inner diameter. The use of the single-micelle-templated approach for silica and other compositions will be presented.

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55. Polyelectrolyte-Surfactant Complex Templating: A General Approach for Hierarchically Mesoporous Materials

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Hierarchically porous materials have been of growing interest, because of their potential applications in catalysis and biomedical systems. We have developed a general method to fabricate hierarchically mesoporous single meso-crystal silica by using polyelectrolyte-surfactant complex as the template. [1]

Ionic self-assembly of polyelectrolyte and oppositely charged surfactants can form highly ordered mesomorphous liquid crystalline phases, and during the assembly between inorganic precursors and the surfactants (the origin of ordered mesopores), the polyelectrolyte chains were extruded and phase-separated from the mesomorphous complex and served as template for interstitial nanopores. Interestingly and importantly, the presence of a large amount of secondary nanopores did not disturb the single-crystal mesostructure of the silica, giving rise to hierarchically porous single meso-crystals, which would possess both the functions of crystal-like regularity and high diffusion efficiency of hierarchical pores. This method has also been applied to fabricate hierarchically porous carbon and titanium phosphonate. [2]

The hierarchically porous silica acted as catalysts,[1] functional support of drugs or template for functional polymer materials.[3]

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56. Functionally active membrane protein molecules incorporated in mesostructured silica films

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Surfactant-directed mesostructured silicas are suitable abiotic host materials for the incorporation of functionally active membrane proteins in transparent and mechanically stable films. Such host materials overcome challenges presented by the compatibility of membrane protein molecules with the aqueous acidic or alkaline conditions typically used to synthesize mesostructured oxide materials. For example, judicious choices of surfactant, solvent, silica precursor species, and synthesis conditions enable the light-responsive transmembrane protein proteorhodopsin to be stabilized in solution and subsequently co-assembled into silica−surfactant composites with high loadings. Small-angle X-ray scattering, electron paramagnetic resonance spectroscopy, and transient UV−visible spectroscopy analyses establish that the proteorhodopsin molecules in mesostructured silica films exhibit native-like dynamics, as well as enhanced thermal stability compared to surfactant or lipid environments. The light absorbance properties and light-activated conformational changes of the proteorhodopsin guest molecules in mesostructured silica films are consistent with those associated with the native H^+-pumping mechanism of these biomolecules, which have potential applications for solar-to-electrochemical energy conversion. The synthetic approach is expected to be general, as demonstrated also for the incorporation of functionally active cytochrome c , a peripheral membrane protein enzyme involved in electron transport, into mesostructured silica−cationic surfactant films.

57. Plasmonic Metal/$Mo_xW_{1-x}O_{3-y}$ for visible-light-enhanced H_2 production from ammonia borane

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Plasmonic nanostructures with unique localized surface plasmon resonance (LSPR) properties are significant candidates to harvest solar light, which involve conventional noble metals and doped semiconductors (e.g., MoO_{3-x},[1] $Cu_{2-x}S$). Our group previously reported a well-crystallized dual-plasmonic $Mo_xW_{1-x}O_{3-y}$, which shows stronger LSPRs and shorter absorption peak position than single plasmonic MoO_{3-x} and WO_{3-x}. It was demonstrated that such strong LSPR was generated from crystal vacancies, mainly including mutual doping and oxygen vacancies. However, the photocatalytic performance of H_2 evolution from NH_3BH_3 using $Mo_xW_{1-x}O_{3-y}$ does not improve much compared with plasmonic MoO_{3-x} or WO_{3-x}.[2] Herein, we report a solution-processed route to synthesize plasmonic Pd/$Mo_xW_{1-x}O_{3-y}$ hybrid by coupling a plasmonic heavily doped semiconductor $Mo_xW_{1-x}O_{3-y}$ and metal nanoparticles (NPs). The synthesized Pd/$Mo_xW_{1-x}O_{3-y}$ hybrid, having Pd NPs anchored on a plasmonic $Mo_xW_{1-x}O_{3-y}$ support, exhibited strong visible light absorption with an LSPR peak at around 700 nm. Furthermore, it is interesting that only W^{5+} ions of W species exist in Pd/$Mo_xW_{1-x}O_{3-y}$ after reduction by $NaBH_4$, which is extremely difficult to obtain. More importantly, such a Pd/$Mo_xW_{1-x}O_{3-y}$ hybrid displayed a dramatic plasmon-enhanced photocatalytic performance in the hydrolysis of NH_3BH_3 solution under visible light irradiation, which mainly results from the synergetic effect between Pd NPs and emerging W^{5+} ions in $Mo_xW_{1-x}O_{3-y}$.

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58. Amorphous Photocatalytic Titanium Dioxide Porous Matrix for Purple Membrane Encapsulation and Hydrogen Production

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We developed an amorphous sol-gel derived photocatalytic titanium dioxide (or titania) gel matrix for entrapment of bacteriorhodopsin, a visible-light absorbing membrane protein, in the form of its native purple membrane. Sol-gel synthesis procedure to produce amorphous titania gel monoliths was optimized to ensure least amount of alcohol was present in the pores to avoid denaturation of the protein or disruption of its membrane structure. Spectroscopic techniques were used to investigate the stability and functionality of bacteriorhodopsin encapsulated in the gel matrix. The encapsulated protein in the gel had a similar absorption behavior with increasing temperature as the protein in solution demonstrating retention of secondary structure. Förster resonance energy transfer between tryptophan residues and titania sol nanoparticles suggested there is less than 10 nm separation between bacteriorhodopsin and titania. This proximity suggests that electron transfer can occur from the co-retinal in the protein to titania conduction band when the assembly is irradiated under white light. This electron is then involved in a chain of hydroxyl producing reactions to split water for hydrogen production. In our preliminary results, incorporation of 5 µM bacteriorhodopsin in titania gel along with Platinum nanoparticles as reduction catalyst increased the hydrogen production by 52% compared to when no protein was present under white light. These results lay the groundwork for development of amorphous titania based photocatalytic materials using environment-friendly dyes for renewable energy production.

59. Insights on Carbon Activation Toward Advanced Nanoporous Carbon

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The global market of activated carbon is at the scale of 1.7 million tons in 2017. It is the single most manufactured nanostructured carbon material. Carbon activation in nature is the preferential removal of the certain local segments of the carbon structure. Despite the scale of this industry, the fundamental carbon activation mechanisms have remained elusive. Herein, we have paid attention to carbon activation in terms of new synthetic approaches and the structure-property correlations of conventional activation methods. We have explored two new carbon activation routes: (1) Gaseous NH_3 reacts with cellulose-derived carbon at annealing conditions, which results in fine microporosity and N-doping of the final products.[1] (2) By employing a minimal flow rate of the inert atmosphere, the carbonization of cellulose experiences a self-activation process, where no additional activation agent is necessary to form a porous carbon with very large specific surface area.[2] As for the activation mechanism, we found that the structural heterogeneity of a precursor carbon is the premise to generate ample nanoporosity. We attempted to elucidate the high-temperature CO_2 reactivity of carbon structural sites inside nongraphitizable carbon, also known as hard carbon.[3] Via a suite of characterization tools, including neutron total scattering and the associated pair distribution function, we found that hard carbon activation by CO_2 increases the extent of graphenization of hard carbon as a result of the removal of the less graphenic layers that contain more vacancies. Guided by this mechanism, we designed a bimodal mesoporous carbon by a one-step activation reaction.

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60. Nanostructured materials for electrochemical energy conversion: porosity vs. functionality

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Nanostructuring is considered one of the key routes towards the improvement of the efficiency of energy conversion and energy storage systems. In my research I focus on developing the ways to fabricate nanostructured electrode materials demonstrating maximum efficiency in various electrochemical, photoelectrochemical and photovoltaic applications, as well as understanding and controlling the processes influencing charge transfer and charge transport properties of the nanoscaled materials. This work involves the development of synthesis strategies for the fabrication of semiconducting and conducting metal oxide nanocrystals, and assembly of these nanocrystals into functional interconnected hierarchical networks providing charge transfer junctions with high interface area and a continuous pathway for the charge transport. The investigated systems comprise titania nanomorphologies for energy conversion and storage, novel morphologies of transparent conducting oxides for their use as transparent electrodes in optoelectrochemical and photoelectrochemical devices, and ultrasmall metal oxide nanoparticles for electrochemical energy storage and electrocatalysis. Chemical synthesis strategies I use for the fabrication of nanomaterials often provide unique possibilities compared to physical preparation methods. In chemical routes, the formation of nanomaterials is usually controlled kinetically rather than thermodynamically, which enables obtaining metastable and non-stoichiometric phases unachievable by traditional physical pathways.

I will address critical issues controlling the performance of nanostructured materials in electrochemical applications brought by dramatically increasing role of the interface-related processes as well as diminishing crystal size on the electron and ion transport properties.

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61. Conversion-Type Electrodes and Ceramic Separators for Next Generation Li-Ion Batteries

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Energy density and cost of Li-ion batteries (LIBs) based on conventional intercalation compounds are closely approaching their limits.[1] The reliance of conventional cathodes on the use of toxic metals additionally endangers health and safety of miners in developing countries. Conversion-type active materials offer an opportunity to double energy stored in LIBs, reduce their cost by the same factor, and improve cell safety.[2] These materials may be produced from safer, cheaper and globally available resources and contribute to accelerated adoption of electric transportation. Formation of effective nanocomposites is likely a necessity for the successful commercialization of conversion-type electrodes. I will discuss approaches taken by our laboratory to address current challenges of such materials.[3-10] Conventional polymer separators for LIBs suffer from limited mechanical strength and low thermal stability, which may lead to thermal runaway and cell explosion. I will discuss our studies on the low-cost formation of flexible, binder-free, nonwoven separator composed of alumina nanowires that overcomes the known limitations.[11]

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62. Conjugated Polymer Nanofibers and Their Applications

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Polyaniline, a conducting polymer known for its ease of processing and readily switchable optoelectronic properties upon doping/de-doping, touts itself as an ideal material for a wide range of applications. In its one dimensional regime, polyaniline nanofibers can be produced using interfacial polymerization or rapid mixing of aniline, oxidant and acid.[1] These methods are template-free and readily scalable leading to stable colloids.[2] The suppression of secondary growth that results in agglomerated conventional polyaniline is critical to forming nanofibers.[3] Polyaniline nanofibers can be used as chemiresistors,[1] mechanical actuators (artificial muscles),[6] catalysts[7] and non-volatile memory devices.[8] Recently, polyaniline has drawn our attention with its superior performance as filtration membranes.[9] The use of functionalized polyaniline nanofibers can lead to low fouling and even chlorine tolerant membranes.[10,11] Furthermore, blending in carbon nanotubes or sulfonated self-doped polyaniline significantly improves hydrophilicity, further enhancing fouling resistance. Another way to tune flux and selectivity of the membrane is to apply flash welding and the addition of carbon nanotubes which takes advantage of the polyaniline nanofibers' high photothermal conversion efficiency.[12,13]

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63. Nanoscaled Mesoporous Materials: Designed Synthesis and Applications

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Significant research efforts in recent years have been devoted to the development of nanoparticles with mesostructures for applications in diverse fields.[1] Their nanoscaled size, high surface area and large porosity make mesoporous nanoparticles useful in adsorption, catalysis, energy storage, controlled drug release and cellular delivery.[2] The composition and structure of the nanoparticles are key to the achievable properties. Among mesoporous nanoparticles, mesoporous silica nanoparticles, mesoporous metal oxides, mesoporous carbons have been extensively synthesized by a well-controllable sol-gel process. Compared with bulk materials, which are above a micrometer in size, nanometer-sized mesoporous particles not only have the advantages mentioned above, but additional properties, such as fast mass transport, effective adhesion to substrates, and good suspension in solution. For example, mesoporous carbon nanomaterials are a large class of new materials, and have great potential applications in advanced electrodes for energy conversion and storage, catalysis and nanomedicinal therapy.[3] On the consideration of the preparation methods for mesoporous nanomaterials, we are planning to develop new low cost strategies to directly synthesize nanomaterials with certain mesoporous structure. Meanwhile we will investigate the formation mechanisms and the relationship of the pore structures and properties of the obtained functionalized mesoporous materials. Thus, in our group, we not only focus on the synthesis of mesoporous nanomaterials but also provide some references and guidances to their practical applications in energy conversion and storage, catalysis and nanomedicinal therapy.

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POSTER SESSION I

1. Preparation of the Cs-Ru/SBA-15 Nanocomposite Materials for Sustainable Ammonia Synthesis

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Ammonia has recently attracted significant attention as a potential medium of energy carrier and fuel because of its high hydrogen content (17.6 wt%) and nearly no emissions of carbon dioxide, toxic gas and particulate matter to the atmosphere after burning. However, the conventional ammonia synthesis is an energy inefficient process, which largely releases CO_2 gas into the atmosphere and therefore causes global warming. To improve energy efficient and to reduce the impacts of ammonia synthesis on environments, new catalytic strategies are required to synthesize ammonia sustainably by an environmental friendly and energy-efficient. The pioneer studies had shown that the Ru catalysts were able to catalyze the ammonia synthesis under relatively mild reaction conditions, in comparison to the conventional Fe-based catalysts. It is special noted that the Ru-catalyzed ammonia synthesis can be performed in short warm-up and shutting-down periods, that is an opportunity to be a sustainable CO_2-free process using hydrogen synthesized from electrolysis of water by the renewable electricity with high variability generated from solar cell, wind power and biomass.

In this study, the Cs-Ru/SBA-15 nanocomposite materials with various Ru loadings of 2 or 10 wt% and a Cs/Ru molar ratio of 2.5 were prepared by wet impregnation method and calcined in a N_2 atmosphere, followed by using in CO_2-free ammonia synthesis under mild conditions (400-500 ºC, < 1 MPa). The Ru particles were determined by a pulse chemisorption method using CO as a probe molecule. The results showed that the Ru particle sizes of the Cs-Ru/SBA-15 catalysts were around 12-18 nm, disporprotional to the Ru loadings. For the CO_2-free ammonia synthesis, the activity of the Cs-Ru/SBA-15 as a function of the reaction temperature in ammonia synthesis gave a volcano curve, which was a consequence of the equilibrium between the formation and decomposition of ammonia. The maximum activity appeared at a reaction temperature of 430-460 ºC, which were netatively related to the Ru loading and Ru sizes. Notably, our results clealry showed that the Cs-Ru/SBA-15 catalysts are able to catalzye ammonia synthesis under mild conditions, in comparison to the conventional Fe-based catalysts.

2. A cone-shaped fluidic nanogenerator for harvesting electricity using mesoporous MWCNT bundles

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Water energy is one of the promising solutions to the energy crisis. To conventionally generate electricity, heavy and complex facilities are required. In ths work, we developed a mesoporous multi-walled carbon nanotube bundle-based cone-shaped fluidic nanogenerator (CFN) that can simultaneously generate high output power and excellent water evaporation rate. The electric powers are generated by interactions of ions and surface charges on interfaces of fluid water and nanotubes. In addition, this power generation can be accumulated by 3D conical structure of nanotubes and strongly enhanced by solar-evaporation.

The developed CFN displayed the outstanding photothermal conversion efficiency of ~80% and output power of 13.2 and 8.2 mWm-2 under one sun illumination and dark condition, respectively. The output powers increase with a water-containing NaCl with different concentrations, different cation, and anion radius. The highest output power was reached to 505.7 and 252.4 mWm-2 under one sun illumination and self-evaporation, respectively in a water-containing KCl 0.6M. Accordingly, the water evaporation rate is slightly decreased due to the deposition of salt on the cone's surface. For example, in a water-containing NaBr 0.6M, the water evaporation rates of 1.5 and 0.6 kg·m-2·h-1 in under one sun and self-evaporation, respectively. The new concept is not only applied for carbon-based on CFN such as carbon black, carbon nanotubes, graphene, but also have potentials for the porous materials with hydrophilicity properties such as cellulose fiber, etc. Furthermore, it can guide the design of advanced energy harvesting that can persistently generate both high electricity and excellent water evaporation in all weather and all times of the day.

3. Synthesis of SBA-15 under variable conditions to obtain large pore short channels

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The structure of SBA-15 can be tuned in a fairly wide range of pore sizes [1]. SBA-15 particles are commonly thick packed long fibers. This morphology hinders the accessibility to the channels. In the use of SBA-15 as a support for biomolecules, short channels and small particle size are desirable to alleviate diffusion limitations [2]. There are reports on the synthesis of SBA-15 yielding hexagonal plates with channels as short as 400nm [3]. The use of Pluronic PE10400 ($EO_{27}PO_{62}EO_{27}$) facilitates the formation of micelles that do not grow in long rods as P123 ($EO_{20}PO_{70}EO_{20}$). On the other hand, the use of different silica sources may help controlling the hydrolysis rate allowing tuning the assembling process. In this scenario, our aim is to obtain small channel SBA-15 with large pores using expanders [4]. Different surfactants, expanders, and silica sources have been tried to achieve our goal. Various synthesis conditions have been studied including different surfactant, expander and acid ratios as well as mixing and hydrothermal treatments. All the samples were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), N_2 adsorption/desorption isotherms, and scanning (SEM) and transmission (TEM) electron microscopy. SBA-15 with hexagonal symmetry, surface area between 488 and 673 m^2/g, high pore volume (0.63-1.45 cm^3/g) and average pore diameter ranging from 5.1 to 16.6 nm have been successfully synthesized. The best result has been obtained using P10400 as surfactant, TIPB (1,3,5-triisopropylbenzene) as expander and corn as silica source. There is more than 93% silica in corn waste that could be reutilized leading to a more sustainable material [5]. In this case, SiO_2 was extracted from different waste parts of corn such as stem, leaves and cobs. In order to reproduce these results, similar materials have been obtained using commercial SiO_2 (Aerosil). Hexagonal short plates were formed with highly crystalline SBA-15 structure and pore size of 12 nm.

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4. Towards understanding the effect of the protein corona on drug release from different mesoporous silica particles

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A pharmaceutical drug needs to be present in a soluble form in the gastrointestinal tract in order to permeate across the intestinal wall.[1] Low oral systemic absorption (bioavailability) remains a big challenge in drug development.[2] Mesoporous silica particles have been considered as a possible formulation aid to overcome the bioavailability problems satbilizing amorphous forms of poorly soluble drugs.[3] The effect of the biological protein corona on the drug release profile from mesoporous silica may play a critical role *in vivo.* As mesoporous particles travel through the gastrointestinal tract they will encounter different protein and enzymatic environments causing changes to their surface evaluate how different pore size and structures of mesoporous particles may be affected by the formation of a *gastrointestinal* corona and their ability to release poorly soluble drugs.[4]

Using the poorly soluble hormone testosterone as drug we have evaluated the effect of a modelled protein corona, formed by incubating the drug loaded particles in fetal bovine serum, on drug release under simulated gastric an intestine fluid. We will show detailed material characterisation, including proteomics data on the incubated particles, as well as kinetic drug release studies conducted under sink conditions for mesoporous material MCM-41 and AMS-6, with 2d and 3d pore networks respectively. Our data suggests that protein corona has an effect on drug release from mesoporous particles and it changes with time (proteomics data). In vivo assays and the use of further drugs may allow to ascertain if protein adsorption on to mesoporous particles can be a tool to further design drug delivery vehicles based on porous silica.

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5. Synthesis of Mesoporous MFI Zeolite by Dry-Gel Conversion using a Structure-Directing Surfactant

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Recently, mesoporous zeolites have been synthesized in a form of ultrathin nanosheets, using multi-quaternary ammonium surfactants as a meso-/micropore dual structure-directing agent.[1] The zeolite synthesis condition was further controlled so that the nanosheets are self-arranged in a disordered manner to form a nanosponge morphology. The resultant nanosponge zeolite composed of a three-dimensional network of zeolite nanosheets exhibited high surface area and uniform mesopores of 4 nm in diameter. In particular, MFI zeolite nanosponge has attracted much attention as an acid catalyst and a support material due to its strong acid sites and mesoporous texture. Although the zeolite nanosponge shows many possibilities for advanced catalytic applications, the synthesis method of the zeolite nanosponge is not yet conveniently established. In previous reports, MFI zeolite nanosponge was prepared by the conventional hydrothermal method, which requires a large amount of solvent and a tumbling autoclave.[2] Herein, we investigated the synthesis of MFI zeolite nanosponges using dry-gel conversion (DGC) technique. The dry precursor gel with a similar composition was successfully transformed into the zeolite nanosponges in a static condition using a small amount of solvent. The overall quality of the dry-gel product was similar to that of conventional a hydrothermal product. We observed that the crystallization of MFI zeolite nanosponge proceeded through a pseudomorphic transformation, where the initial gel morphology was preserved. Furthermore, with the benefit of reduced reactor volume, 100 g of MFI zeolite nanosponge was easily synthesized using a single autoclave with a volume of 1.5 L. The DGC synthesis of nanosponge zeolite would be advantageous in large-scale industrial applications, as it allows a promising, safe, and continuous process for economic production of zeolite nanosponge.

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6. Enantioselective Separation on Supramolecular Templated Mesoporous Materials

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Supramolecular templates represent a unique class of pore forming agent that can result in chiral transcription within the internal pore space of the mesoporous silica produced. Thus, they are good candidates for chiral separation. [1,2] Here we demonstrate selective chiral separation of both D- and L- enantiomers without the need for surface functionalization, *i.e.* relying solely on the surface properties. We report that supramolecular template mesoporous silica materials, prepared with guanosine monophosphate (NGM-1) and folic acid (NFM-1) are suitable for enantiomeric separation. The chiral selectivity and kinetics of the mesoporous materials are measured by circular dichroism (CD) spectroscopy using the amino acids L-valine and D-valine and supported by structural data. [3] Furthermore, formation of gold nanoparticles in calcined and template extracted particles allows to probe the properties of the mesoporous chiral surface and its relation to the supramolecular template. [4] These results increase the possibilities of mesoporous materials in chiral separation and catalytic applications.

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7. Magnetoelectric Coupling in Mesoporous Composites of Bismuth Ferrite and Cobalt Ferrite

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This work examines the role of nanoscale structure in the control of magnetoelectric coupling in three-dimensional multiferroic composites. Mesoporous magnetostrictive cobalt ferrite (CFO) is conformally filled with piezoelectric bismuth ferrite (BFO) via atomic layer deposition. Tuning the thickness of the BFO layer allows for control of final composite porosity. We have found that the strength of magnetoelectric coupling depends heavily on this residual porosity, with higher porosity leading to greater magnetoelectric response. In a composite filled with only 25% BFO, we have found that an applied voltage on the composite causes a decrease in the saturation magnetization of the composite to about 50% its unpoled value, while the sample filled 100% with BFO shows little change in saturation magnetization. High-resolution X-ray diffraction confirms that the residual porosity is necessary for strain transfer to occur from the piezoelectric to the magnetostrictive component, as the porosity allows for mechanical flexing throughout the film.

8. Synthesis of MFI Zeolite Nanocrystals with Controlled Thickness by Cooperative Structure Direction of Diammonium Surfactants and Sodium Ions

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Zeolites are a family of crystalline microporous aluminosilicate materials. The microporous structure, generated by the structure-directing agent (SDA) such as alkali metal cations and ammoniums, enables zeolites to have a shape-selective catalytic function. Ever since the discovery of mesoporous materials (*e.g.*, MCM-41) using surfactant micelles as SDAs, there have been enormous efforts to develop synthesis strategies for mesoporous materials that are built with crystalline zeolitic micropore walls. In 2009, Ryoo and co-workers developed a synthesis route to hierarchically porous zeolites by using micropore-mesopore dual generating surfactants as SDAs.[1] For example, the $C_{22}H_{45}\text{-}N^{+}(CH_{3})_{2}\text{-}C_{6}H_{12}\text{-}N^{+}(CH_{3})_{2}\text{-}C_{6}H_{13}(Br^{-})_{2}$ (in short, $C_{22\text{-}6\text{-}6}$) surfactant was able to generate MFI zeolite nanosheets of 2.5 nm thickness under hydrothermal synthesis conditions. The synthesis principle for MFI zeolite nanosheets was well-established, but the expensive cost of $C_{22\text{-}6\text{-}6}$ surfactant has been mainly responsible for its economic infeasiblity in a scale-up process.

Herein, synthesis of hierarchically porous MFI zeolite nanosheets was attempted with minimized amount of $C_{18}H_{37}$-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2$-$C_6H_{13}(Br^-)_2$ (denoted as $C_{18\text{-}6\text{-}6}$) surfactant.[2] In particular, inexpensive sources of Na^+ or TPA^+ were partially introduced in place of $C_{18\text{-}6\text{-}6}$. This investigation revealed that the structure-directing functions of $C_{18\text{-}6\text{-}6}$ and Na^+ could be used in a concerted manner to control the zeolite thickness. When a small amount of the $C_{18\text{-}6\text{-}6}$ was present in a Na^+-rich synthesis condition, the $C_{18\text{-}6\text{-}6}$ initially generated 2.5 nm MFI zeolite nanosheets. Subsequently, Na^+ ions have directly participated in the growth of the nanosheets. As a result of the work, we were able to demonstrate that the thickness of MFI zeolite nanosheets could be systematically controlled at over 2.5−20 nm. The strategy for the zeolite thickness control might be useful as a principle for the design of porous materials for various applications such as adsorption, separation, and catalysis.

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9. ZSM-5 zeolite templated synthesis of porous carbon using metal cation effect

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Ordered porous carbons with controlled pore diameters have been of great interest in a wide range of applications, due to their pore-size effects.1-5 Zeolite templating is one of the most effective ways to obtain ordered microporous carbons. However, the synthesis was limited to the use of large-pore zeolites with 12-membered ring (12MR), such as FAU, beta and EMT, or larger ones. Small-pore zeolites with 10 membered ring (MR) pore apertures were considered as unsuitable templates for carbon synthesis, owing to the diffusion limitation of carbon precursors in the extremely narrow pores.

In the present work, we report an effective way to use ZSM-5 zeolite, which is one of 10MR zeolites, as a template for carbon synthesis.6,7 ZSM-5 zeolite is an attractive template for carbon synthesis, due to its characteristic porous structure. For the synthesis of carbon, Ca2+ ions were incorporated into ZSM-5 to promote acetylene carbonization selectively inside the zeolite micropores. In this work, we also tested various cations as a catalyst for the synthesis of carbon using ZSM-5 zeolite. Among the tested cations, the resultant carbon obtained from the Ca2+ ion- exchanged zeolite had the similar morphology of ZSM-5 zeolite. It exhibited an ordered array of ultra-micropores of 0.5 nm in diameter, which was very close to the thickness of a pentasil layer in the ZSM-5 zeolite framework. In addition, the electrochemical performance of the resultant carbon was explored in aqueous solution.

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10. Synthesis and Applications of Mesoporous Metal-Silicate

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Since the discovery of mesoporous silicas, the surfactant-templating method has been widely applied to synthesize the mesostructural materials of high-surface area, tunable pore size and large pore volume for the applications in adsorption, catalysis, enzyme-stabilization, and optical devices. A synthetic route with the advantages of flexibility, simplicity and large-scale production is still desired. Here, we provided a new non-templating method to prepare the metal/silica meso-structural platelets of high surface area, large pore size and pore volume by hydrothermally treating the metal hydroxides precipitate in the presence of the silicate species. According to our results, a transformation model of “silicate-exfoliation ➔ asymmetric metal-silicate bilayer ➔ bilayer curving” should open a new synthetic strategy to prepare different mesoporous metal-silicates in nanotubule, nanofoam or cured nanoplatelet morphology on a kilogram-scale.

To understand the transformation mechanism of metal hydroxides to metal-silicate mesostructure, a time-dependent XRD patterns, N_2 adsorption-desorption isotherms, and TEM images of the intermediates from the metal-silicate reaction solutions were taken after different reaction time. As the hydrothermal time increases, the low-angle XRD patterns of the mesostructure become clear, but the intensity of the high-angle XRD peaks from the metal hydroxides crystalline structure gradually decreased. After an appropriate hydrothermal treatment, metal silicate with ordered or disordered mesostructure was generated instead. Based on these results, we proposed that the lattice mismatching between the metal hydroxide and silicate species is the driving force for the formation of the metal-silicate mesostructure. In addition to using mesoporous silica as silicate source, fumed silica (surface area $\approx 200\ m^2g^{-1}$) and industry-grade sodium silicate solution can also be used as silica source. Accordingly, the metal silicates with large surface areas ($> 200\ m^2g^{-1}$) and porosity, and compositions have been synthesized using a mixtures of metal salts under the hydrothermal treatment condition.

In brief, we have developed an environmental-friendly method for preparing the mesostructural metal-silicates with large surface areas and large pore volumes without using disposable organic template and producing toxic wastewater. For application, the copper-silicate with large surface area (≈ 250–350 m^2g^{-1}), high accessibility to the environment, and well dispersed CuO active sites would exhibit high efficiency in toxic-gas absorption and decomposition. The resulted copper-silicate exhibits a high catalytic efficiency toward the oxidation of the toxic phosphine (PH_3) gas releasing from integrate circular industry even at [PH_3] ≈ 500 ppb. The catalytic efficiencies of Mn–silicate catalysts toward the low–temperature selective catalytic reduction (SCR) of NO with NH_3 were also examined. A high NO conversion (>99%) was achieved over Mn–10%Ce–silicate at 200ºC. The MnO-silicate demonstrates a high catalytic activity toward ozone decomposition. The nickel-silicate can be used as high-performance catalyst for NH_3 oxidation.

11. Sequential Progression from Nanoporous Folic Acid Material to its Absolute Hemin Counterpart

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We report the synthesis of classic nanoporous folic materials (NFM-1) and their derivatives (NFM-1_Hemin) by incorporating hemin in an orderly sequential manner as mixed templates system and its absolute hemin counterpart named nanoporous hemin material (NHM-1), with the aim of enhancing or imparting photoactive and fluorescence functionality to the framework. In this regard, in situ conductance measurements were conducted on the first few minutes of synthesis to understand the nucleation and growth stage. The nature of the mesophases and the ordering of the pores were determined by X-ray diffraction analysis, whilst electron microscopy was employed for morphology information as well other analytical techniques were employed to confirm the formation of folic/hemin-based silica. It was observed that peaks at the mesoscale and one corresponding to stacking array of the petrin of the folate decline in intensity as the ratio of hemin to folate increases, hence, analogous stacking of hemin starts to appear at a lower angle. And besides, the morphology of the samples synthesized at room temperature gradually evolves from mix mesostructures of rods and spheres to predominately homogenous spherical particles as the hemin progressively replaces folic acid template, while the sample with total hemin constitutes flower-like nanostructures.

12. Synthesis of Ultralarge-Pore Mesoporous Carbon Nanospheres from a Fast Emulsion Self-Assembly Route

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Mesoporous materials show a more excellent performance as compared to nonporous and microporous materials, because of the less limited diffusion. Invoking mesoporoes, especially ultralarge-sized mesopores, smooth mass transport for large reagent molecules can be realized.1-3 In this study, a novel nitrogen-doped mesoporous carbon nanosphere with high-level nitrogen-containing and tunable ultralarge pore diameters from a fast emulsion self-assembly approach was synthesized. Dopamine and commercial surfactant Pluronic F127 were employed as the nitrogen and carbon source and template, respectively. Trimethylbenzene (TMB) was used as an organic co-solvent and pore-swelling agent. The synthesis was carried out in an oil-water biphase reaction system, which allowed the fast self-assembly of reactants taking place in the oil-water interface. The obtained mesoporous carbon nanospheres were found to exhibit uniform particle size (~130 nm), high surface area (~800 m2 g-1) and large pore volume (~1.4 cm3 g-1). Moreover, the pore diameters of the mesoporous carbon nanospheres can be tuned from 7 to 39 nm through various adding amount of pore-swelling agent TMB. Due to the high-level nitrogen-containing (~4.9 wt%) as well as ultralarge pores, these uniform nanosphere are capable of providing more accessible active sites for oxygen reduction and efficient mass transfer environment for reactants and electrolytes, contributed to excellent electrocatalytic activity for oxygen reduction reaction in alkaline electrolyte.

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13. Strategies Toward Controllable Fine Tuning of Pore Size Distribution in Soft Templated Mesoporous Carbons for Gas Separations

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We have soft templated mesoporous carbons by combining phenolic resins with sacrificial amphiphilic surfactants, such as F127, a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer. The resulting mesostructure is dependent on self-assembly due to extensive hydrogen bonding interactions in acidic solution. Herein we show tailorable mesoporosity through systematic variations in the synthesis and casting of the polymeric nanocomposite. The effect of alternate solvent systems for casting the resin or the addition of low molecular weight polymers during the self-assembly process can produce variations in the median pore size and distribution as well. Following pyrolysis, characterization of the mesoporous carbons includes analysis of morphology, surface area, pore volume, and pore size distributions. The potential application in gas separations is discussed with reference to CO_2 capacity and selectivity at room temperature, along with implications from variations in the mesoporous structure.

14. Epitaxial Growth of CD-MOFs Based on Host-Guest Strategy

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Epitaxial growth of surface-attached metal−organic frameworks (MOFs) is an important way to integration of MOF into devices or nano/microsystems. It can be achieved through anchoring either the metal or metal-oxo nodes with the functionalized organic groups on the surface using a conventional approach.[1] Herein, a class of green MOFs—namely, CD-MOFs[2]—has been grown epitaxially as the films on the surface of a substrate modified with self-assembled monolayers (SAMs) of γ-cyclodextrin (γ-CD), a construct which can be achieved by the host-guest complexation between γ-CD tori and the covalently modified pyrene groups on the surface. The CD-MOF film has a continuous polycrystalline morphology with an area of several square millimeters and a thickness of ~2μm as well as a structural orientation of an out-of-plane (c-axis). This host-guest strategy has been applied successfully in growing CD-MOFs as the shell on the curved surface of microparticles as well as in the integration of CD-MOF film into an electrochemical device for sensing carbon dioxide (CO_2). Epitaxial growth of CD-MOFs, based on this host-guest strategy not only provides the opportunity to develop this green porous framework material for a range of different applications, but also expands the liquid-phase epitaxy with the limitation of paddle-wheel structure metal linkers.

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15. Photocatalytic Degradation of Famotidine over Ordered Mesoporous Titania

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Titania is one of the well-studied metal oxides for energy and environmental applications. Several attempts have been made to enhance its optical, electronic and textural properties by tuning the morphology and/or employing different synthetic approaches [1,2]. In this context, ordered mesoporous titania (OMT) prepared using surfactants show promise [3-8]. We report here the synthesis, characterization and photocatalytic characteristics of various OMTs, e.g., TMF-127, TMP-123 and TMF-108, prepared using F-127, P-123 and F-108, respectively as templates [5-8]. Our research depicts XRD patterns and famotidine degradation results. Noticeably, all the materials show enhanced photocatalytic activity compared to commercial titania (P25) suggesting the importance of textural properties, and the associated defects. Among the OMTs, TMP-123 showed enhanced activity in light, which could be attributed to an improved adsorption in the dark. Further work is in progress to understand the high activity.

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16. Mass Production of Large-Pore Phosphorus-Doped Mesoporous Carbons for Fast-Rechargeable Lithium-Ion Batteries

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To date, diverse carbonaceous materials, such as disordered carbon, graphitic carbon and carbon nanotubes, have been widely explored as anode materials for lithium ion batteries (LIBs) and shown to display high electrochemical performances.[1,2] However, it is still a crucial issue to develop advanced carbon materials with desirable architectures for increased number of lithiation sites, especially higher lithium diffusivities and electronic conductivities for fast charging and high energy density LIBs.

A facial and scalable method has been developed for the successful mass production of large-pore P-doped mesoporous carbons with a high P content through an evaporation induced coating and self-assembly on a sacrificial scaffold of polyurethane (PU) foam process, wherein tricresyl phosphate was used as a precursor, phenolic resol as a carbon precursor and triblock copolymer F127 as a template. In this synthesis, tricresyl phosphate not only act as a source, but also a good pore swelling agent which can accommodate into the hydrophobic microdomains of the Pluronic F127 micelles due to the hydrophobic character and co-assemble with F127 and resol to form mesostructures, thus ensuring the successful synthesis of large-pore P-doped mesoporous carbons. The obtained P-doped mesoporous carbons possess well-opened large mesopores (6.6-14.2 nm), high surface area (338-630 m^2/g), and high P content (up to 1.90 at%). Benefiting from the appealing structural features, the resultant P-doped mesoporous carbons exhibit excellent electrochemical performances as anode materials for LIBs, including high reversible capacity (up to 500 mAh/g after 200 cycles at 0.5 C), excellent rate capabilities (e.g., 236 mAh/g at a high current of 8 C) and long-term cycle life (high capacitance retention over 90 % at 10 A/g after 10000 cycles).

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17. Exploring the Effect of Nanoscale Architecture on Thermal Conductivity of Nanoporous SiO2 Films

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Mesoporous silica has been studied as a promising material for applications that requires low thermal conductivity or low dielectric constant. In the former case, applications in thermal insulating window coating are of particular interest. Previous studies have shown that porous structures effectively decrease the thermal conductivity in thin films through increased phonon scattering. We have designed and fabricated SiO_2 sol-gel and nanoparticle based porous films via evaporation induced self assembly method, and characterized the thermal conductivity using time domain thermo-reflectance method. By varying film thickness from 100 nm to 1 μm, porosity from 10% to 72%, and pore size from 3 to 68 nm, we have examined the effect of the porous structure on the thermal properties. We have also compared sol-gel and nanoparticle based porous networks. The films have thermal conductivity as low as 0.1 W/mK (compared to 1.4 W/mK for bulk SiO_2) with transmittance > 90% and haze <1%, making them suitable for optically clear window application. The facile synthesis method allows tuning of the structure in both pore size and pore fraction, and can be scaled up to a few micrometers. This work indicates exciting potential of translating the materials design rules and physical understanding to industrial scale production of window coatings capable of reducing energy consumption.

18. Hollow Sandwich Structured SiO_2@SnO_2@TiO_2 Nanosphere for Stable Lithium-ion Storage

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SnO_2-based lithium-ion batteries have received a great deal of attention due to their low cost and high energy density, but their rapid capacity fades are still an intractability problem during lithiation/delithiation owing to phase aggregation and cracking. A hollow structure and coating protection layer are the solutions to the problem. Herein, we report the fabrication of a hollow sandwich structured SiO_2@SnO_2@TiO_2 nanospheres (H-SiO_2@SnO_2@TiO_2) by successive hydrothermal and sol-gel coatings. The H-SiO_2@SnO_2@TiO_2 nanospheres have ~160 nm diameter cavity and sandwich structured shells ~10 nm SiO_2, ~20 nm SnO_2 and ~7 nm TiO_2 shells (from internal to external shell, respectively). Compared with the hollow double shells structure H-SiO_2@SnO_2 nanospheres (without the exterior TiO_2 shells), the hollow sandwich structured H-SiO_2@SnO_2@TiO_2 nanospheres achieved excellent cycle performance (650 mA·h·g^{-1} at 0.2 A·g^{-1} after 250 cycles) when being evaluated as an anode material for lithium-ion batteries. This superior performance is attributed to the uniform hollow sandwich structure with flexibility internal (SiO_2 shells) and external (TiO_2 shells) double protection shells, which restrain phase aggregation and cracking during lithiation/delithiation process.

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19. Yolk-shell structured Fe_3O_4@mesoporous carbon anodes through an interface-directed carbonization approach for lithium storage

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Yolk-shell structured anodes for lithium-ion battery have attracted more attention due to the well-designed void space to accommodate the large volume expansion.[1,2] While the synthesis of yolk-shell structures with uniform mesoporous shells still remains great challenges. Here, yolk-shell structured Fe_3O_4@void@ mesoporous carbon nanospheres were fabricated *via* a facile interface-directed carbination-asmmetrical shrinkage approach and demonstrated as an advanced and cheap anode material for LIBs. The resultant nanospheres show a foam-like shell with uniform mesopores (18 nm) and high surface area (412 m^2 g^{-1}). When used as anodes for lithium-ion battery, the Fe_3O_4@void@mesoporous carbon nanospheres exhibit excellent rate capability (292 mA h g^{-1} at 1 A g^{-1}) and perfect cycle performance (768 mA h^{-1} at 0.5 A g^{-1} after 200 cycles). The excellent electrochemical performance was attributed to the mesoporous carbon shell which facilitate the transform of electrolyte and ions. In addition, the well-designed void can buffer the volume change of Fe_3O_4 during charge-discharge process. It is believed that the well-designed yolk-shell structure at the atomic and nanometer scales paves a promising way to develop high performance anode materials for LIBs.

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20. Synthesize of Carbon Nanotubes@Meso/microporous Nitrogen-Doped Carbon Composite Nanowires for Enhanced Oxygen Reduction

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The combination of the graphitized carbon nanotubes (CNTs) core and the meso/microporous nitrogen-doped carbon shell can be an ideal strategy for high-efficiency NC catalysts for ORR, which provides superior electronic conductivity, abundant active sites and sufficient mass transfer. Herein, various fascinating carbon nanotubes@meso/microporous nitrogen-doped carbon composite nanowires (denoted as CNTs@amNC) are fabricated by a surfactant-templating assembly coating method, followed by an oxygen activation. The obtained CNTs@amNC nanowires exhibit adjustable N-doping level (9.1-4.3 at.%), high surface areas (634-887 m^2 g^{-1}), large pore volume (0.53-0.64 m^3 g^{-1}) and uniform shells (~25 nm in thickness) with bimodal pores size distribution (~1.0 and 4.9 nm). When the CNTs@amNC nanowires are used as an ORR catalyst, the pyrolysis temperature has a significant impact on the activity. The optimized catalyst pyrolyzed at 800 °C shows superior ORR catalytic activity in (half-wave potential of -0.19 V vs. Ag/AgCl electrode and diffusion-limited current of 5.2 mA cm^{-2}) alkaline media. Moreover, it also shows outstanding long-term durability and methanol-tolerance.

21. Fabrication of monodispersed ultra-small mesoporous TiO2 nanoparticles based on linear block co-polymers

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Ultra-small monodispersed functional nanostructures have recently received tremendous attention due to the high performance and good thermal stability in optics, electronics, mechanics, drug delivery, and catalysis domains. However, the synthesis of small TiO_2 nanoparticles with uniform sizes and large mesoporosity still remains great challenges. Here, we for the first time demonstrate a general and robust strategy for the synthesis of ultra-small monodispersed mesoporous TiO_2 nanoparticles *via* triblock copolymer poly(styrene-b-4-vinyl pyridine-b-ethylene oxide) (PEO-PVP-PS) as a soft template in polar solvent. This kind of co-polymer can form stable uniform micelles because of the repulsive force by the protonated PVP blocks between each micelle in acid condition. After the titania oligomer precursors interact with the co-polymers, the sizes of TiO_2/copolymer composite micelles decreased from 57 to 35 nm. The mesoporous hollow structures were generated after the template was removed. This strategy enables a high degree of control over the size, architecture, surface chemistry, and properties of 3D monodispersed metallic oxide, nonmetallic oxide, and metallic nanostructures, which shows great performance in catalysis applications.

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POSTER SESSION II

22. Ammonium-functionalized mesoporous MFI zeolite for highly dispersed supported metal catalysts

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Dispersion of supported metal catalysts on porous material is an important issue in heterogeneous catalysis.[1] The metal dispersion can be generally controlled by proper choices of supporting material, metal precursor, and supporting method.[2] However, there are still many problems associated with the low dispersion of metal catalysts.[3] In particular, light transition metal elements (*e.g.*, Fe, Co, Ni and Cu) have low atomic polarizabilities, and accordingly, they have weak van der Waals interactions with the surface of the supporting materials. Hence, the light transition metals are more susceptible to the agglomeration than platinum group metals such as Pt, Ir and Rh, which have stronger metal-support interactions. In this work, we introduce a method to achieve high dispersion of light transition metals, using a mesoporous MFI zeolite nanosponge as a support, which possesses 4-nm wide mesopores surrounded by 2.5-nm thick microporous frameworks.[4] Our strategy is to functionalize the mesopore walls with basic $–C_3H_6\text{-}N^+(Me)_3(OH)^-$ groups prior to supporting metal precursors as hydroxide forms through deposition precipitation. In the hydroxide precipitation process, the ammonium groups could increase the internal basicity within the porous environment, which caused regioselective nucleation of inorganic metal precursors inside the zeolite mesopore. This can lead to high dispersion of Ni, Cu, and SnO_2 nanoparticles even at a loading amount up to 25 wt%. The obtained Ni catalyst exhibit a superior catalytic activity for CO_2 methanation reaction as compared to the cases using unfunctionalized catalyst supports. In addition, supported Cu based catalyst showed higher catalytic activity than Pt based catalyst in preferential oxidation of CO. Such a high catalytic activity should be attributed to the large number of active sites resulting from the high dispersion of supported metal species.

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23. Sol-gel Encapsulated Ionic Liquid as a Pseudosolid-state Sodium-ion Electrolyte

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Flammability issues remain a major concern for traditional liquid electrolytes. Though generally nonflammable, solid electrolytes are limited in their efficacy by poor ion transport and interfacial kinetics. To address both of these issues, “ionogels” are synthesized in which an ionic liquid is encapsulated in a mesoporous silica network through sol-gel chemistry. This technique provides the conductivity of a liquid, but confined in a macroscopic solid. Thermal stability and a wide electrochemical window further increase the possibilties for high-performance battery operation. Utilization of this one-pot synthesis also allows for liquid-based fabrication processes whereby the ionogel can be made into various shapes and thicknesses.

In this work, [PYR14][TFSI] ionic liquid was incorporated into a PDMS-modified silica scaffold to produce flexible ionogel monoliths. Ionogel electrolytes (up to 80% v/v ionic liquid) were tested for ionic conductivity (1mS cm^{-1}) and electrochemical window (6 V). Interfacial reactions with sodium metal reference/counter electrodes were characterized and shown to be responsible for inefficient ion transport. Overcapactive carbon electrodes are shown to act as a sufficient pseudo-reference electrode and more accurately represent performance. Electrochemical cycling performance was assessed with half-cell, galvanostatic cycling of $Na_3V_2(PO_4)_3$ and $NaTi_2(PO_4)_.$ Ultimately, full-cell devices were constructed and demonstrate stable cycling for over 100 cycles.

24. How to Make Silica Aerogel Transparent and Not Translucent?

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This study aims to develop design rules to achieve transparent mesoporous silica slabs. Mesoporous silica including aerogels have been considered for both their optical transparency and thermal insulating properties to increase the energy efficiency of windows solutions and solar receivers, for example. However, silica aerogels tend to be translucent and hazy due to scattering by the largest pores. Experimental optimization of mesoporous silica by trial and error can be time-consuming. Alternatively, numerical simulations can quickly generate silica aerogel structures with various nanoscale architectures and predict their optical properties. In this study, the Diffusion-Limited-Cluster-Cluster-Aggregation method was used to numerically generate three-dimensional mesoporous silica aggregates consisting of monodisperse or polydisperse spherical silica particles connected by either point-contact or surface-contact. The porosity ranged from 50% to 95% and the silica particle radius from 1 nm to 10 nm. The T-matrix and Discrete-Dipole-Approximation algorithms were used to calculate the scattering cross-section and asymmetry factor of point-contact and surface-contact structures, respectively. Finally, the normal-hemispherical and normal-normal transmittances and the haze of mesoporous silica slabs were predicted by the Monte Carlo method. Haziness of silica aerogels was found to increase with increasing silica particle radius, decreasing porosity and with overlapping among adjacent particles. The results can be used to design mesoporous silica material with desired optical performance.

Furthermore, we explored the possibility of cross-linking boron-rich clusters with organic monomers to form densely cross-linked polymeric materials. The reaction between B_{12}-based clusters and diisocyanates produced a highly cross-linked polyurethane gel with a mesoporous architecture. It shows an interesting swelling/deswelling property as a function of its environment. Given the mesoporous and stimuli-responsive nature of the polymer gel, it can be potentially used for bio-medical applications. Moreover, co-condensation between B_{12}-based clusters and diboronic acids created a new type of 3-dimensional polymeric networks with spherical morphologies. These materials are expected to have significantly improved thermal/mechanical properties due to the covalently cross-linked nature. The successful modification of the materials ranging from inorganic metal oxides to organic polymeric materials demonstrates the value of molecular cross-linking as a new and previously unattainable strategy to induce change in the properties of materials for diverse applications.

25. Ytterbium-containing ordered mesoporous titania: A promising material for solar hydrogen production

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In recent years, extensive research efforts have been devoted to synthesize high quality ordered mesoporous titania.[1-4] In this regard, trivalent metals ions stabilized phases are seem to be promising as they inhibits the phase transformation by forming mesoporous structure.[3,4] In this work, we present ytterbium-containing highly ordered mesoporous titania (OMT), designed as Yb-TMF-127, with bimodal pore size distribution. The OMT was prepared *via* controlled hydrolysis of titania precursor under non-aqueous medium using Pluronic F-127 as structure directing agent, and systematically characterized by various analytical, imaging and spectroscopic techniques.

Photocatalytic hydrogen production indicate higher hydrogen evolution rate for the ytterbium-stabilized OMT as compared to the commercial titania catalyst (P-25) thereby showing promise for photocatalytic applications.

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26. Nitrogen-Rich Hierarchically Porous Carbon as a High-Rate Anode Material with Ultra-Stable Cyclability and High Capacity for Capacitive Sodium-Ion Batteries

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Carbon-based anode materials hold a promising future for sodium-ion batteries (SIBs) due to their natural abundance and low cost of development. In spite of carbon’s important role in the commercialization of lithium-ion batteries (LIBs), further exploration is necessary in order to find high-performance, high-rate carbon anode materials for SIBs. A honeycomb-like, nitrogen-rich (17.72 at%), hierarchically porous(macropore-mesopore-micropore), and highly disordered carbon (N-HC) with an expanded interlayer distance (0.44 nm in average) is synthesized by spray drying followed by pyrolysis under flowing NH_3. The hierarchically porous structure and rich nitrogen doping result in a large specific surface area (722 m^2 g^{-1}), more defects and active sites, and greater functional interface accessibility for the active porous carbon material and electrolyte. When N-HC is used as the anode material for SIBs, the batteries display favorable discharge capacities (255.9 mA h g^{-1} in the 3000th cycle at 500 mA g^{-1}) and good capacitive-energy-storage behavior (67% at a scan rate of 0.5 mV s^{-1}) with excellent high-rate performance and ultra-stable cyclability over 10000 cycles at 5000 mA g^{-1}. Our results show that the combination of the hierarchically porous structure and nitrogen doping lead to improved energy storage by increasing the capacitive energy storage, which enhances the high-rate performance of N-HC. Additionally, a full cell comprising the N-HC anode and a $Na_3V_2(PO_4)_3$/C cathode shows a high capacity (even in the restricted voltage range from 2.0 to 3.5 V) and favorable cyclability (180.4 mA h g^{-1} after 200 cycles at 100 mA g^{-1} with capacity retention of 85.5% compared with the second cycle).

27. Ionic liquid immobilized on MIL-101-NH2 for the synthesis of propylene carbonate from CO2 and propylene oxide

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It has been well recognized that the efficient transformation of CO_2 into useful chemicals is an important contribution in terms of green chemistry[1]. In this regard, cycloaddition of CO_2 with epoxide to produce carbonates, raw materials for polycarbonate and fine chemical

intermediates, has received increasing attention. Forever, the low CO_2 capture quantity of corresponding catalysts limited the catalytic efficiency of cycloaddition of CO_2 for cyclic carbonate. Herein, a novel type of acid-base bifunctional catalysts of ionic liquid immobilized in MIL-101-NH_2, denoted as IL/ MIL-101-NH_2, was prepared by an ingenious strategy and tested for propylene carbonate (PC) rapid and facile synthesis from CO_2 and propylene oxide (PO).
The CO_2 pressure on PC yield and CO_2 absorbed mass about IL/MIL-101-NH_2 have revealed that the introduction of amino groups may indeed be conducive to adsorption of CO_2.The catalytic results indicated that IL/MIL-101-NH_2 was an efficient and recyclable heterogeneous catalyst towards the solvent-free synthesis of PC from PO and CO_2. The excellent performance of IL/MIL-101-NH_2 is attributed to the synergetic effect of acid sites for ring opening of epoxide as well as to basic sites for adsorption and activation of CO_2. And the catalysts can be easily recovered and five times reused without significant loss of activity and selectivity.

The synergetic interaction between a Brønsted base (-NH_2) of strong CO_2 chemical capture capacity and a Brønsted acid (-COOH) of strong hydrogen bond donor leads to the high catalytic efficiency of IL/MIL-101-NH_2 for carbonate synthesis from CO_2 and PO without any additive. This design idea of specific catalyst and the acid-base synergetic strategy provides new insights into the design of powerful catalyst systems for the CO_2 conversion.

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28. Mesoporous Zeolite Nanosponges Supporting Nickel Nanoparticles for Catalytic Hydroisomerization of n-Dodecane

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Hydroisomerization of linear paraffins to branched isomers is an important petrochemical process, which commonly uses bifunctional catalysts of Pt supported on zeolites.[1] The Pt is the best metal element for high catalytic performance in the hydroisomerization process, due to its high intrinsic activity for hydrogenation/dehydrogenation (HDH) of paraffins and high dispersion on zeolite supports. Nevertheless, an inexpensive Ni has been considered as an alternative for the high cost Pt in the hydroisomerization.[1] The replacement of Pt by Ni on zeolites often resulted in significant loss on the catalytic performance. This was because of the poor intrinsic activity on the Ni for HDH. This cannot be resolved by simply increasing the Ni-loading on the zeolites. Since the Ni is a light element having low polarizability and week interaction with the support, it easily migrates from the micropore to the exterior of zeolite crystal. Then, the Ni forms large particles by sintering process on the external surface of bulk zeolite crystal. For these reasons, the use of Ni has remained challenging in the hydroisomerization.
In this presentation, we show the high possibility of using Ni as a metal component in *n*-dodecane hydroisomerization, when mesoporous zeolite nanosponges (MZN) were used as an acidic support. When we compared 0.5 ~ 1.0 wt% Pt-loaded conventional MFI and *MRE zeolites to 1.0 ~ 2.0 wt% Ni-loaded MFI and *MRE MZN, the Ni-supporting MZN showed even better catalytic performance than those of the Pt-supporting conventional zeolites in the hydroisomerization. The 2.0 wt% Ni / MFI MZN exhibited very similar catalytic performance to that of 1.0 wt% Pt / MFI MZN. The high catalytic performance of Ni/MZN was attributed to the tiny Ni nanoparticles (*ca.* 2 ~ 3 nm in diameters) stabilized on the large external surface area by the confinement effect of the mesoporous walls.

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29. Mesoporous SiO2/TiO2 coatings as transparent, thermally insulating coatings

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About a quarter of the energy used as heat is lost through single pane windows during the winter months in colder climates. While double pane windows are currently used to help reduce heat loss, replacing single pane windows with double pane ones can be costly. Retrofitting single pane windows with ones that have lower thermal conductivities has the potential to save $12 billion per year to consumers. In this work, we are developing ways to producing nanoporous silica coatings that can dramatically reduce the thermal conductivity of single-pane windows. It has been shown that having a porous structure can effectively lower thermal conductivity in SiO_2[1]. To create films capable of being used as thermally insulating transparent barrier coating, we have used evaporation induced self-assembly to synthesize polymer templated SiO_2/TiO_2 films; thermal degradation of the template leads to the production of a porous films after calcination. Both pores and the TiO_2 domains (which can be controlled synthetically), create phonon mismatch which results in phonon scattering and reduced thermal conductivity. Compared to pure SiO_2 mesoporous films with similar porosities, the addition TiO_2 is seen to decrease the thermal conductivity. The facile synthesis method allows tuning of the structure in both pore size and porosity, and can be applied in other composite systems to leverage phonon mismatching to reduce thermal conductivity.

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30. Confine Interfacial Monomicelle Assembly for Precisely Controlled Coating Single-Layered Titania Mesopores

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Mesoporous core-shell nanostructures have recently been receiving extensive scientific interests, however, reliable approaches for coating mesoporous materials still remains exiting challenges except amorphous silica. We report, for the first time, a confined interfacial monomicelle assembly method for controlled coating anatase TiO_2 with single-layered ordered mesopores on diverse surfaces, opening up the area of coating ordered mesoporous crystalline materials which possess mesopores originated from self-assembled surfactant instead of accumulated nanocrystals. This facile and repeatable methodology relies on solvent confinement effect of glycerol during assembly process and monomicelle hydrogels preformation by selective evaporation of double-solvent precursors. This assembly process shows precise controllability and great versatility, endowing the coated TiO_2 layers with highly tunable thickness, mesopore size and switchable coated surfaces. The ultrathin monolayered mesopores of such mesoporous TiO_2 shells, in combination with their high surface area and crystalline nature, afford them excellent rate capability and superior cyclability for sodium-ion storage.

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31. Using Pair distribution function to investigate changes in structural distances of drug molecules loaded in mesoporous silica

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It is estimated that 40% of approved drugs, and 90% of new drug molecules are poorly soluble with limited *in vivo* bioavailability, and therapeutic effectiveness (1). The restriction in the molecular mobility of drugs loaded in mesoporous silica has been demonstrated to stabilize the formation of amorphous solid dispersions with enhanced solubility properties (2). However, the characterization of the amorphous state within the mesopores is limited by the lack of long range order. We have used atomic pair distribution function analysis (PDF) to characterize the molecular ordering of a range of poorly soluble drugs loaded in mesostructures MCM-48, and SBA-15 at different concentrations (9-50 wt%). The PDF is a sine Fourier transform of the total scattering function resulting in the number of atoms in a spherical shell at a distance from the reference atom. It is thus a useful way of measuring the degree of disorder of the drug within the pores.

The atomic PDF of Albendazole (ABZ) loaded into SBA-15 silica showed an increase in peak intensity with increased drug loading, representing higher drug ordering. ABZ loaded into MCM-48 silica showed a lack of crystalline features from X-ray diffraction and PDFs of drug loaded samples were similar to that of the amorphous silica material. Furthermore, PDF scattering profiles were able to identify small changes in the local structural distances of Hydrocortisone (HYD) and Indomethacin (INDO) loaded in SBA-15. These changes are likely due to ordering of the drug within the pores at higher loadings. Further molecular modelling simulations from PDF data and sampling with more diverse range of drugs will be required to determine an accurate and predictive kinetic release model under nanopores confinement, which is the aim of our work.

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32. Synthesis and characterization of V-MCM-41 catalysts for liquid-phase acetylation of acetone with glycerol

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In recent years catalysts containing vanadium have been used in oxidation and dehydration reactions, due to the multifunctional characteristic of vanadium of being acidic and the capability to adopt multiple redox states ($V^{+3}/V^{+4}/V^{+5}$). For dehydration reactions, Avila *et al.*[1] demonstrated that well-dispersed V_2O_5 has an enhanced acidity, a great feature for acidy catalyzed reactions. For dispersing vanadium oxides, it is interesting the use of mesoporous materials such as SBA-15 and MCM-41[2] due to their high surface area and an organized system of channels. Is this work VMCM-41, synthesized hydrothermally from a reaction mixture containing vanadium, and SiMCM-41 impregnated with vanadium species were studied as acidic catalysts for liquid-phase acetylation of acetone with glycerol.[3] Chemical analysis measurements showed that the insertion of vanadium in the silica matrix is limited to 6.8 % (V/(V+Si) mole ratio). The other synthetized compositions were 0.4, 3.1, 6.1 and the impregnated 3.1(i). SAXS curves showed that VMCM-41 maintained the structure of SiMCM-41, except for impregnated sample, which presented curves with less intense peaks. Nitrogen adsorption isotherms presented the same behavior for impregnated and as-synthesized samples. Pyridine chemisorption indicated the presence of weak Lewis acid sites that were proportional to the number vanadium atoms inserted in the silica framework. These materials were used as catalysts for acetylation of glycerol, a reaction that occurs on acid sites producing 2,2 dimethyl-[1,3] dioxane-4-yl-methanol), known as solketal, a fuel additive, and in lower quantity 2,2 dimethyl-dioxane-5-ol. Glycerol conversion was proportional to the amount of acid sites, as previously reported by Casilda *et al.*[4]. Recycling tests were performed and it was found that impregnated catalysts suffered a strong deactivation caused by solubilization and consequent leaching of vanadium species. On the other hand, VMCM-41 catalysts exhibited a negligible decay in activity as vanadium species are part of the silica framework.

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33. MCM-41 Silicas Modified with Basic or Acidic Functionalities as Heterogeneous Catalysts

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Mesoporous silicas of MCM-41 type have attracted increasing attention as catalysts’ supports in the heterogeneous catalysis due to their large surface area, ordered mesoporous structure and uniform channels with diameters ranging from 2-50 nm.[1] These materials are also characterized by easily modifiable external and internal surfaces, where different functional groups can be introduced. Incorporation of acid or base functionality into/onto the surface of mesoporous silicas is of particular interest in the field of organic synthesis and green chemistry because they may lead to the high selectivity and yields.[2] Thus, the aim of the presented study was to investigate catalytic properties of the MCM-41 type materials modified with acidic or basic functional groups. Catalytic activity of the obtained materials was tested in the two heterogeneous catalysis reactions: Friedel-Crafts alkylation and Knoevenagel condensation.

MCM-41 materials bearing acidic or basic functionalities were obtained using co-condensation and grafting procedures. In order to obtain materials containing acidic functional groups (3-mercaptopropyl)trimetoxysilane was introduced as a source of thiol groups. Materials modified with basic functionalities were synthesized by using vinylbenzylaminoethyl-aminopropyltrimethoxysilane (Z-6032) and aminoethylaminopropyltrimethoxysilane (Z-6020) as sources of amino groups. Additionally, thiol-modified materials were oxidized by H_2O_2 in order to obtain catalytically active forms of sulfonic-functionalized mesoporous materials. Before using materials in the catalytic reactions, physicochemical properties were characterized.

Mesoporous silicas functionalized with amino groups were tested as basic catalysts in the Knoevenagel condensation between benzaldehyde and ethyl acetoacetate, while materials containing sulfonic groups were examined in the Friedel-Crafts alkylation of anisole with benzyl alcohol. The obtained results confirmed the possibility of using this type of materials as basic or acidic catalysts, since substantial conversions of substrates and high selectivity to the desired products have been observed.

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34. Bifunctionalized Mesoporous Silica Materials – Preparation and Characterization of their Physicochemical Properties

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Ordered mesoporous silica materials possess uniform pore channels, which make them easier for target molecules to reach the active sites. However, silica has only silanol groups on the surface of the pore walls, which considerably limits its application, e.g. in catalysis.[1] Nevertheless, surface of silica can be modified with different moieties to create new properties. For example, introduction of the sulfonic or amino functionalized organic groups predestinates silica-based materials for applications in acidic or basic catalysis or adsorption processes, whereas addition of metallic species enables their use as redox catalysts.[2]

Our studies were focused on obtaining bifunctionalized mesoporous silica materials modified with platinum species as well as organic functional groups containing nitrogen or sulfur atoms. Pristine mesoporous materials of MCM-41 type were synthesized using TEOS and cetyltrimethylammonium bromide (CTABr) as a silicon source and structure directing agent, respectively. Bifunctionalized mesoporous materials were obtained by grafting of organic groups onto the surface of channels and subsequent impregnation with platinum species. Three different organosilanes were used as sources of amino groups, namely: vinylbenzylaminoethyl-aminopropyltrimethoxysilane (Z-6032), aminoethylaminopropyltrimethoxysilane (Z-6020) and bis(3-trimethoxysilylpropyl)amine (BTMSPA). Additionaly, (3-mercaptopropyl)trimetoxysilane (MPTMS) served as a source of thiol groups, though in order to obtain sulfonic-functionalized mesoporous materials thiol groups were oxidized with H_2O_2. An aqueous solution of hexachloroplatinic(IV) acid was applied as a metal precursor.

The obtained bifunctionalized mesoporous materials of MCM-41 type were characterized with several techniques, like: low and wide angle X-ray diffraction (XRD), transmission electron microscopy (TEM), low temperature N_2 adsorption-desorption measurements, infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and elemental analysis. The obtained results showed that organic functional groups and metal species were successfully anchored onto the silicas’ surface. Moreover, in most samples the ordered mesoporous structure was still present.

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35. Hierarchical zeolites as catalysts for various catalytic reactions

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In recent years, hierarchical zeolites have attracted significant attention because this type of materials allows molecules of substrates to access the active sites that are located within micropores and reduce the removal time of product's molecules from catalysts, leading to increase reaction rates and catalyst life-time (i.e. slower deactivation).[1]

This work focuses on the synthesis and characteristics of hierarchical zeolites containing niobium and catalytic activity in various reactions, such as: oxidation of anisole, oxidation of cyclohexene or Bayer-Villiger oxidation of citral.

Zeolite HY was dispersed in a mixture containing cetyltrimethylammonium bromide, water, ethanol and ammonia solution under ultrasonic treatment. Then, sources of silicon (TEOS) and niobium (ammonium trisoxalate of niobium(V)) were added and stirred for 4 h at 338K. Next, the solid product was recovered by filtration and washed with water and ethanol. The template was removed by calcination at 873K for 5 h in air.

All the synthesized materials were characterized by using: X-ray diffraction (XRD), transition electron microscopy (TEM), scanning electron microscopy (SEM), SEM/EDX, elementary analysis, N_2 physisorption, FTIR and UV-Vis spectroscopies, X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) of ammonia.

The crystal structure is one of the first characteristics assessed in the preparation of hierarchical mesoporous zeolites. It was confirmed by low-angle XRD patterns that all materials show characteristic diffraction peaks at a 2Θ value of approximately 2.5°. Additionally, wide-angle XRD patterns proved the Y zeolite structure retention. TEM microscopy proved the mesoporous character of all materials. XPS spectroscopy verified the oxidation state and coordination of niobium species. TPD of ammonia was used to assess the acidity strength.

The hierarchical zeolites were found to be more active than mesoporous niobosilicate materials. Niobium species was properly isolated (oxidation strength) and localized (acidity) thus providing the proper active site coordination for the oxidation of different molecules. Understanding the active site locations, while being the key to the understanding of the catalytic properties of this material, remains a great challenge in catalysis. Redox coordination-compounds oxidation-state determines the activity.

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36. Synthesis and Characterization of Spider Silk – Mesoporous Silica Nanocomposites

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We aim to investigate the adsorption and assembly of spider silk mini spidroin peptide mimics on Mesoporous Silica Nanoparticles (MSNs). Dragline spider silk (major ampullate) fibers are comprised of two proteins, major ampullate spidroin 1 and 2 (MaSp1 and 2), that have highly repetitive core sequences consisting of certain consensus motifs, mainly poly(Ala), Poly(Gly-Ala), Poly(Gly-Gly-X) and Gly-Pro-Gly-X-X.[1] This study is focused on synthesizing and characterizing the spider silk peptide mimic $(Ala)_5$ that comprises the region that forms the spider silk's β-sheet core and hypothesized to impart spider silk its remarkable strength. The peptide is being synthesized using a CEM High Efficiency Solid Phase Peptide Synthesizer (HE-SPPS)[2], purified using reverse phase High Performance Liquid Chromatography (HPLC), and structurally characterized with Matrix Assisted Laser Desorption Ionization Mass Spectrometry (MALDI-MS) and multinuclear, multidimensional solution Nuclear Magnetic Resonance (NMR) spectroscopy. In parallel, MSNs are being synthesized via sol-gel methods[3] and characterized using Transmission Electron Microscopy (TEM), Thermogravimetric Analysis (TGA), Raman spectroscopy, Solid State Nuclear Magnetic Resonance (SSNMR) spectroscopy, and Brunauer–Emmett–Teller (BET). The long-term goal of the project is to interface the spider silk peptide mimics with silica MSNs to produce spider silk-silica nanocomposite materials. Recently, our research group illustrated that certain nanostructured silicas can catalyze the thermal condensation of amino acids such as Ala simply, and with high yield.[4] We are in the process of testing this chemistry to crosslink spider silk peptide mimics on the surface and in the pores of MSNs to fabricate the material. Such a bio-nano composite is envisioned to have significant potential in hard tissue repair (bone and teeth) and drug delivery systems.

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37. Synthesis and study of lamellar MOR and MFI zeolites and their modification by pillaring treatment.

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Zeolites has been one of the most exploited materials for many years. Their structural and chemical properties, such as microporosity with a well-defined structure and acid sites, have strengthened their use as sorbents and catalysts. Nowadays, the use of bulk zeolites in certain applications is more difficult due to diffusion limitations imposed by the size of micropores. One of the latest strategies for solving the problem was to create shorter diffusion paths by creating mesopores in microporous materials[1]. The development of *bi-dimensional* zeolite materials assisted by the use of an organic agent has allowed the improvement of its textural properties and reduce its diffusion limitations. The foregoing was achieved by modifying the material in the previous stage to the final calcination by implementation of a method of pillaring between the layers[2]. In this study, we report the synthesis of two different zeolitic materials (MOR and MFI) with a 2D morphology using the previously described method, which uses CTAB as a mesoporogen agent[3] and their posterior modification by a pillaring process to provide them with mesoporous structure. Samples were analyzed by different techniques, such as X-ray diffraction at low angle, N_2 adsorption-desorption, and transmission microscopy (TEM) to analyze their structure, textural properties and morphology, respectively. The results displayed materials with mesoporous structure features (inter-lamellar spacing d about 4.3-4.5 nm), better textural properties of pillared zeolites than conventional bulk zeolites, and a much more definite structure of laminar materials after the pillaring process.

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38. Self-Locomotive Diatom Microbubbler for Active Biofilm Removal

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Bacterial cells form a biofilm on and within any materials and living tissues, negatively impacting human health and sustainability. Tremendous efforts have been conducted to remove biofilms from the substrates using various antibiotics and disinfectants. However, bacterial cells residing in biofilms are deemed 100 to 1,000 times more resistant to antibiotics and disinfecting agents than planktonic cells because the extracellular polymeric substances (EPS) matrix limits the transport of the anti-microbial agents and neutralizes them chemically. Therefore, removing biofilm remains a grand challenge despite tremendous efforts made so far, particularly when they are formed in confined spaces.

To overcome this challenge, we present a bubbling porous microparticle that can actively penetrate and rupture biofilm matrix in confined spaces by generating, fusing, and bursting microbubbles. The bubbling microparticle was fabricated by doping manganese oxide (MnO_2) nanosheets onto porous diatom silica particles. In antiseptic hydrogen peroxide (H_2O_2) solution, the MnO_2 nanosheet-doped diatom became self-motile by generating oxygen gas bubbles. Subsequently, the diatom microbubblers infiltrated the biofilm formed in micro-grooves of substrates. Within the EPS matrix, the diatom bubblers keep producing micro-sized bubbles that merged and, in turn, converted surface energy to mechanical energy high enough to fracture the biofilm. As a result, H_2O_2 molecules efficiently diffused into the biofilm and killed bacterial cells.

Overall, this study provides a unique and powerful tool that can significantly impact current efforts to clean a wide array of bio-fouled products and devices.

39. Intensely and Broadly Absorbing Noble Metal Clusters Sensitized Mesocrystal Titanic Oxide Heterostructures

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Metal clusters can be considered as a new type of photosensitizers to extend the photoactivity of titanic oxide (TiO_2).The gold (Au) or silver (Ag) clusters composed by only few metal atoms, have molecule-like electronic levels, non-plasmonic multiple discrete absorption bands covered UV, Vis and near-infrared range with high extinction cross-sections, as well as long-lived charge-separated states. Despite the gains, most significant shortcoming for metal nanoclusters is the agglomeration and losing the unique properties during long-term stability test, which can potentially be overcome by combining them with mesoporous structures. On the other hand, highly ordered mesocrystal mesoporous TiO_2, with good crystallinity and low number of defects, high surface area and controllable exposed facets, as well as high pore accessibility, represents one of the most promising materials for the photocatalysis, hydrogen generation, and solar cells systems. Here, three types of clusters (Ag_{44}, $Au_{12}Ag_{32}$ and $Au_{24}Ag_{20}$) have been tested to optimize the discrete energy levels engineering with TiO_2. For practical device applications, different morphology mesocrystal porous TiO_2, such as sphere, spindle, 2D sheet and nanowire arrays, have been synthesized by the novel evaporation-driven oriented assembly method. We also evaluate the influence of the pore size, exposed facet and surface functional group of TiO_2 on the interfaces coupling with metal clusters and resulting solar energy conversion efficiency.

40. SiO_2/ZrO_2 thin films for thermally insulating coatings on single pane windows

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Single paned windows leak heat in cold weather, wasting about one fourth of heating energy. One solution to this problem is double paned windows, but double paned windows are expensive and difficult to install. Thermally insulating coatings for single pane windows would be an effective, easy to apply, and inexpensive alternative. Such coatings have the potential to save consumers $12 billion each year. We are developing low thermal conductivity coatings made from mesoporous SiO_2. Mesoporous SiO_2 possesses properties that make it optimal for window coatings, including good optical qualities and a porous structure that lowers thermal conductivity by providing boundaries for phonon scattering. Introducing additional phonon scattering sites in the form of mismatched atomic impurities can further lower thermal conductivity. Specifically, we are exploring ZrO_2 nanoparticles as such an impurity. The negative surface charge on ZrO_2 nanoparticles allows them to be stable in the same environment as SiO_2 nanoparticles, making ZrO_2 an optimal choice for addition to the SiO_2 structure. We synthesize SiO_2/ZrO_2 nanoparticle thin films through an evaporation induced self-assembly process. The film structure is formed around polymer, and upon calcination the polymer degrades, leaving a mesoporous structure. SiO_2/ZrO_2 films show porosity, well-distributed ZrO_2, and good optical properties. We have found that the thermal conductivities of SiO_2/ZrO_2 films are similar to those of SiO_2 films.

41. Nitrogen-Doped Mesoporous Carbons with Large Surface Areas for High Pressure CO_2 Capture

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Excessive emission of carbon dioxide (CO_2) have caused serious environmental problem of global climate change over the past years.[1-3] Advanced technologies and new materials are urgently developed for capture and storage of atmospheric CO_2. Here we employed a multivariate co-assembly approach by solvent evaporation to prepare novel nitrogen-doped mesoporous carbons (N-C) with large surface areas. In the synthesis process, triblock copolymer F127 was used as structure-directing agent, dicyandiamide (DCDA) was used as nitrogen resource, with low-polymerized phenolic resins and tetraethylorthosilicate (TEOS) were used as “reinforced concrete” structured frameworks. Upon carbonization at 600 ^oC under inert atmosphere and removal of silica by HF, the N-C nanocomposites have large surface areas (1300-1800 cm^2/g). Ordered 2D hexagonal mesostructure was proved by TEM, SEM, and SAXS results. The nitrogen content can vary from 3 wt% (NC-3) to 9 wt% (NC-9) with different addition of DCDA. The sample of NC-3 shows high selectivity for CO_2 compared to N_2, and high CO_2 adsorption capacity of 25.9 mmol/g at about 0 ^oC and 30 bar. It exhibits highly stable performance after five times reused as well. Futhermore, the CO_2 adsorption capacity can be improved to 32.8 mmol/g at about 0 ^oC and 30 bar by optimizing the surface areas and nitrogen content (NC-5).

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42. Polarized Optical Spectroscopy of Semiconducting Polymers in an Aligned Silica System for the Study of Exciton Dynamics

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Semiconducting polymers have a wide variety of applications in organic electronics including solar cells, thermoelectric devices and LED displays, however the exciton and polaron dynamics that determine the efficiency of these devices are not well understood, particularly in terms of intra-versus inter-chain dynamics. So, we have developed a system of polymers in aligned mesoporous silica films, which allows for both isolation of small numbers of polymer chains and elongation of the polymer backbone. Because optical transitions in polymers occur along the backbone our system allows interchain and intrachain interactions to be probed separately using polarized optical spectroscopy. By using a wide variety of polymers, including push-pull polymers in this mesoporous silica system, we can use the optical studies to understand the effects of both chain conformation and aggregation across all types of semiconducting polymers. From our absorbance and fluorescence studies we have shown that polarization ratios of more than 20 can be achieved when the polymers are in the pores. We can also study the peak shift of the emission peaks, and thus the exciton delocalization, in the aligned samples. We have seen that crystalline polymers are more likely to delocalize excitons between chains, even when confined to the pores while more amorphous polymers see a significant increase in intra-chain delocalization when aligned in pores. Overall we have shown that this system can be used across all types of semiconducting polymers to understand the exciton and polaron dynamics in both inter and intrachain interactions.

43. Synthesis of Uniform Mesoporous P25 TiO_2 Microspheres for Efficient Solar Water Splitting

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As a benchmark photocatalyst, commercial P25 TiO_2 show an excellent photocatalytic efficiency but possess a poorly porous structure with a low surface area. Herein, high performance mesoporous P25 TiO_2 photocatalysts with well-defined sphere morphology, radially oriented mesochannels and controllable anatase/rutile phase junctions were synthesized by a coordination-mediated self-assembly approach. The uniform mesoporous P25 TiO_2 microspheres have a high surface area (~78.6 $m^2\ g^{-1}$), large pore volume (~0.24 $cm^3\ g^{-1}$), large pore size (~7 nm), abundant surface defects, and intimate contact anatase/rutile interfaces which make a clear junction for high photoconversion performances. We show that the ratios of anatase/rutile in the resultant microspheres can be facilely adjusted as desired by controlling the coordination group in the acidic system. More importantly, we showcase the benefits of the resultant mesoporous P25 microspheres (anatase:rutile = 77:23) as a photocatalyst for H_2 generation, which deliver an ultrahigh solar-driven H_2 evolution rate (12.6, *vs* 4.74 mmol $h^{-1}\ g^{-1}$ of the commercial P25) under AM 1.5G. More significantly, the mesoporous P25 spheres show remarkable photocayaltic H_2 generation rate as high as 293 μmol $g^{-1}\ h^{-1}$ under visible-light ($\lambda > 400$ nm). Time-resolved fluorescence spectroscopy and surface work functions indicate that the unique structure of the mesoporous P25 can greatly enhance visible-light adsorption and the photogenerated electrons-holes separation efficiency. This coordination-mediated self-assembly approach paves a new way toward the design and synthesis of high performance mesoporous photocatalysts.

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44. Synthesis of Defects Riched Ru/MoS_{2-x} and Enhanced Ammonia Borane Dehydrogenation Activity under Visible Light

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Hydrogen (H_2) has been regarded as a promising energy carrier in next generation, but controllable storage and delivery are still big challenges. Ammonia borane (NH_3BH_3), due to its low molecular weight, high hydrogen content (19.6 wt%), high solubility, stability in water solutions at room temperature and non-toxicity, has been thought as a potential hydrogen storage candidate. To release the stored hydrogen in ammonia borane, efficient catalytic reaction is considered as a satisfactory solution. MoS_2, a layered structured transition metal dichalcogenide (TMD) with large surface area and high catalytic activity makes it an attractive material in catalysis field. Defects engineering such as S-vacancies or hybrid phase engineering has been reported as a promising way to further activate MoS_2. Firstly, introduction of S-vacancies will expose surrounding atoms, makes the uncoordinated Mo atoms allowing their d-states to bind with adsorbed species as active sites. Furthermore, while MoS_2 mainly exists in semiconductive 2H phase which only the edges are catalytically activity, metallic 1T phase of MoS_2 is unstable but catalytically active in both basal plane and the edge. However, the instability of 1T phase MoS_2 brings a big challenge to synthesize 1T phase MoS_2 in a mild condition. Here, we synthesized an incorporated 1T/2H phase MoS_2 by a simple hydrothermal method. Ru was supported and treated with a hydrogen reduction process. During the hydrogen reduction process, Ru^{3+} species were reduced to active Ru^0 and sulfur vacancies were introduced. The as-prepared Ru/(1T/2H) MoS_{2-x} catalyst shows enhanced ammonia borane dehydrogenation activity compared with Ru/SiO_2.