CHEMISTRY OF MATERIALS

VOLUME 20, NUMBER 3 FEBRUARY 12, 2008

Editorial

Preface to the Special Issue: Templated Materials

Templating is one of the most frequently used methods of synthesizing materials with structural units ranging from nanometers to micrometers, as in the cases of zeolites and photonic crystals, respectively. The templates can come in a variety of forms including molecules, supramolecular aggregates, nanoparticles, colloids, and even biological materials such as viruses. Usually, organic molecules or supramolecular aggregates are used as soft templates to impart structural features to the porous solid formed. Conversely, the resulting porous solids can be used as hosts (hard templates) to structure the guests, often being inverse replicas of the hosts. The key for a successful templating synthesis is to select a template which ensures the formation of a desired nanostructure and can be easily removed without damaging it.

Templated materials have many different applications, both on the technical scale and in emerging fields such as photonics and molecular electronics. While zeolites synthesized by molecular templating are used on the multi-thousand ton per year scale in various applications in catalysis and other fields, ordered mesoporous solids templated by supramolecular aggregates have only entered the commercialization stage recently and are being applied in initial technical processes. Photonic materials based on colloidal crystals, on the other hand, are just emerging, and templating methods compete with other structuring technologies, such as laser processing or micromachining, for the best pathways to synthesize these types of materials.

Zeolites, with a research history exceeding 150 years, constitute the longest known class of materials with crystalline frameworks and ordered porosity; however, their pore sizes are in the range of micropores only (i.e., below 2 nm). A true renaissance in zeolite chemistry was initiated in the early 1960s by the introduction of quaternary ammonium cations as structure directing agents (molecular templates) for the synthesis of these materials. Initially, the significance of molecular templating was not fully recognized—it took over thirty years to extend this revolutionary idea to supramolecular templating, which initiated a new era in the design and synthesis of materials with tailored mesoporous structures. Namely, 1992 brought the first reports on ordered mesoporous silicas (OMS)—MCM-41, MCM-48, and MCM-50—synthesized in the presence of cationic surfactants via a supramolecular templating mechanism. Since 1992 the self-assembly of various inorganic and organic species in the presence of surfactant and block copolymer templates became a powerful method for the synthesis of nanoporous molecular sieves of tailored framework compositions, porous structures, pore sizes, and desired surface functionality. Remarkably, what began as the discovery of ordered silica mesostructures developed into a separate research field spawning thousands of publications.

The past fifteen years of intensive research in the area of ordered mesoporous materials (OMM) brought several important discoveries, providing fresh incentives for further innovations. As far as the synthesis of OMM is concerned, the most important milestones which appeared after the discovery of the ionic surfactant-templated OMS are: (i) synthesis of large pore OMS using block copolymers as soft templates, (ii) self-assembly of silsesquioxanes leading to ordered mesoporous organosilicas with bridging groups, (iii) nanocasting synthesis of ordered mesoporous carbons (OMC) using OMS and colloidal crystals as hard templates, (iv) synthesis of OMC using block copolymers as soft templates, and (v) fabrication of mesoporous materials with crystalline walls. These examples show that the self-assembly of organic and inorganic precursors creates almost unlimited opportunities for designing the framework, porous structure, and surface chemistry of OMM. Also noteworthy is the fact that the past fifteen years of remarkable progress in the synthesis of OMM have been accompanied by the development of a wide variety of potential applications of these materials,

10.1021/cm7034294 CCC: $40.75
Published on Web 02/12/2008

ranging from adsorption, catalysis, separations, gas storage, and environmental cleanup to drug delivery, sensing devices, optoelectronics, nanotechnology, energy storage, and conversion.

This Special Issue on "Templated Materials" provides a survey of the current topics and major lines of development in this rapidly growing research area. It contains around fifty invited reviews and original contributions which cover a broad spectrum of templated materials, ranging from zeolites, silicas, organosilicas, carbons, polymers, and metal oxides to metal alloys and nanocomposites. Although in most cases the resulting materials were prepared in the form of particles, other morphologies such as films, fibers, and monoliths were studied as well.

In the templating synthesis of materials, the template plays the most important role in controlling the types of porous networks as well as the sizes and shapes of pores. Thus, as expected for the issue on "Templated Materials", a variety of templates (such as single organic molecules, dendrimers, ionic surfactants, block copolymers, ordered mesoporous silicas and carbons, colloids, colloidal crystals, anodic alumina, ice, lipid nanotubes, and others) have been used to create the aforementioned nanomaterials.

In the preface to the 1996 Special Issue on "Nanostructured Materials", Thomas Bein and Galen Stucky wrote the following: "The exploration of nanostructured materials is just at the beginning of an exciting journey. Numerous physical properties and potential applications are being studied with nanostructured materials, including structural, nonlinear optical, magnetic, and electronic effects, as well as catalytic reactions." The current Special Issue sheds light on the significant progress made during the past decade in the design and synthesis of templated materials; prior to this, the synthesis of ordered carbon nanostructures, as well as OMM frameworks with crystalline pore walls, was unknown. For instance, we are still at the beginning of this exciting journey to a combined molecular and supramolecular templating synthesis of ordered mesoporous zeolites. Another challenge in this area is to find viable applications for templated nanostructures. We hope that this Special Issue will stimulate further developments in this fascinating area.

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CM7034294