The current role of mesostructures in composite materials and device fabrication

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Abstract

This short review is intended to direct the reader to selected current literature where mesostructured (typically surfactant templated) materials have been characterized in terms of their potential applications. Only limited experimental data will be presented. However, one of the primary criteria in the literature selection for this review was that the research be closely related to an application, and ideally have some "figure of merit" results which could be directly correlated with current state of the art commercial performance. The use of mesostructured catalysts, while industrially very important, will not be covered since it is presented elsewhere in this volume. © 2001 Published by Elsevier Science B.V.

1. Introduction

The basic ideas underlying the advantages of structured composite materials in device and structural applications have been well known for some time [1]. In general, the ability to assembly composite materials that have well defined spatial domains monodispersed in size and interfacial structure can be used to synergistically enhance properties in a nonlinear fashion and to create function that is not accessible by simply mixing the components. This applies to applications ranging from separations and catalysis to those involving high tech ceramics.

A major impediment to creating appropriately functional composites has been the relatively slow development of the processing technologies needed to generate three-dimensional (3D) patterning and structure. Coupled with this have been economic pressures from seemingly disparate directions, but which nevertheless result in common demands. These include more efficient production and purification of bulk and fine chemicals and pharmaceuticals, faster and more efficient devices in telecommunication and information technologies, and environmental and energy concerns. Common requirements are to insist on higher performance at lower cost and to maximize the efficiency of use. A striking example of this has been Moore's law – the factor of two improvement in semiconductor technology every 18 months that has been realized over the past 3 decades. Such demands lead to the need for increasingly sophisticated materials and devices, with structures and functions controlled over a diversity of length scales. Recent progress

has been particularly dramatic in the mesoscopic size regime.

So where does the field of mesostructured materials stand with respect to the current societal and technological needs? We now have available a variety of types of mesoporous materials that maximize surface area/material volume on the length-scale of 2–50 nm. Mesostructured materials with multiple patterned domains can be coassembled to give composites with "guest" regions that have useful chemical, electrical, optical, or magnetic properties within a "host matrix" that possess equally desirable qualities such as large surface area, mechanical stability, electrical conductivity, low or high dielectric properties and optical transparency. In short, a great deal of exciting work has been carried out on the synthesis and understanding of the detailed mechanisms for the fabrication of mesostructured materials. However, questions have been, and continue to be raised concerning the potential usefulness of these materials, in particular their "figure of merit" properties relative to what is already commercially available. Here we seek to address these questions by providing examples where mesostructured materials have proven to be competitive with current technologies.

2. Macromolecules in confined spaces – polymers and biology

Porous mesostructured materials offer confined spaces on length scales relevant to polymers and biomolecules. Typically, pores are large enough to allow diffusion of monomer and polymer, but small enough that they effectively isolate individual (or small numbers of) polymer chains from one another. This allows for the production of polymers with characteristics that may be unattainable in homogeneous or typical heterogeneous polymerization reactions. Aida and coworkers have successfully taken advantage of meso-structured porous materials to perform unique free-radical [2] and catalytic [3] polymerization. By carrying out free-radical polymerization within the channels of MCM-41, they were able to obtain poly(methyl methacrylate) (PMMA) with a molecular weight

an order of magnitude larger and with a much smaller polydispersity index than obtained under identical conditions without the host material. The confinement of a cyclopentadienyl titanium catalyst within the channels of SBA-3 fibers has also made possible the high yield production of ultra-high molecular weight polyethylene that appears to consist almost entirely of extended-chain, high density, highly crystalline polyethylene.

In recent years there has been increasing interest in the immobilization of living cells, biomolecules and enzymes as biocatalysts in mesoporous structures. These studies have mainly focused on sol–gel glasses without ordered pore structures. For example, in a recent paper by Zink, Dunn and co-workers, the incorporation of heme proteins into a porous silica network is described [4]. Periodic mesoporous silicates have all the attractive properties of sol–gel materials (i.e., high surface area and chemical inertness) with the added benefit of controllable pore size, making them ideal for enzyme immobilization. Balkus' group has demonstrated the immobilization of a cytochrome enzyme in MCM-41 and MCM-48 and shown that it retains its activity [5]. They obtained nearly complete coverage of the internal surface area and prevented significant protein leaching by silylation of the pore openings.

In the production of proteins, purification is an important and challenging task. The recent availability of stable porous silica materials with pore sizes up to 50 nm provides a high surface area media for large molecule separation. Large pore mesostructured (SBA-15 type) materials have been tailored to selectively adsorb different proteins according to charge and size, thereby making it possible to purify a particular protein [6].

3. Other separations

A major environmental problem, especially in densely populated areas, is the pollution of fresh water sources. A continuing and expanding need is the design of selective filters for different types of pollutants, ranging from macromolecular pesticides to heavy metals. Among the traditional methods for the removal of organic pollutants are

destructive oxidation with hydrogen peroxide or ozone and adsorption onto porous solids such as activated carbon. However, both of these methods have drawbacks when large amounts of water are to be treated. Activated carbon is an effective adsorbent for organic species, but a disadvantage is that a substantial amount of carbon is lost when regenerated. None of the above methods are capable of removing heavy metals or other inorganic pollutants.

There have been numerous studies of modified mesoporous silicates that indicate that these materials surpass the present state of the art for the removal of different pollutants from water. The functionalization of MCM- and SBA-type materials has allowed for the efficient separation of heavy metals [7–11], other metal ions [11,12] and toxic anions such as arsenate [13]. In many cases the mesostructured materials show remarkably high selectivity for the target material in the presence of competing species, and due to their large surface area are capable of quite high levels of loading.

Commercial chromatographic applications of meso/macro porous materials are apparently close to being realized. Nakanishi and coworkers have published a series of papers describing the production of monolithic silica columns with a disordered templated mesoporous structure [14,15] and bimodal pore distributions. These materials have been shown to be ideal for use in HPLC, especially in the case where large analytes (such as proteins) are to be separated. The presence of a large pore volume with less supporting material allows column operation at 50–70% lower back pressure than traditional packed beds of particles. In some cases, this translates to nearly an order of magnitude increase in performance for the mesoporous materials, as measured by the separation impedance (E). Future work will emphasize further refinement of a 3D interpenetrating pore network, resulting in no dead space within the column material.

An industrially significant problem is the separation of carbon dioxide from methane in natural gas. A convenient method would be to have a membrane that is permeable to only one of the molecules. Membrane-based separations are energy efficient and cost effective, thus a great deal of effort has been put into the design of inorganic membranes for gas purification. In a traditional design, the membrane consists of a macroporous support that provides the mechanical strength for an overlying thin separation membrane that can be either dense or porous. A recent report by Brinker's group [16] describes the incorporation of a surfactant-templated cubic mesoporous silicate intercalated between the microporous top layer and the underlying macroporous support. This design improved the performance of the membrane significantly by (i) eliminating intrinsic defects on porous supports and (ii) preventing the microporous overlayer from penetrating into the support. The CO_2/CH_4 separation factor was increased to 200–600, which is superior to all other reported membranes.

4. Sensing

Mesoporous materials are ideal for use in sensing applications since they permit the confinement of optically or electrochemically active molecules within a matrix that can be constructed to have a variety of electrical or optical properties. One strategy that simply takes advantage of the enhanced surface area provided by mesoporosity, is the embedding of a functionalized mesostructured silica material within a conductive matrix. Walcarius et al. have demonstrated this technique for the sensing of copper(II) and mercury(II) using carbon paste electrodes that have been modified with amine-functionalized MCM-41 [17]. They found that the large number of available sites in the mesostructured material, relative to a standard silica gel or an organically modified silica gel (ORMOSIL), led to an increased sensitivity. Another approach, followed by Li and Kawi [18,19] is to make the mesostructure itself out of an electrochemically active material. They produced templated tin oxide electrodes, and found that the sensitivity of the material to hydrogen gas was directly proportional to its measured surface area. Attard's group has employed a similar technique to produce high surface-area platinum electrodes that may find applications in sensors [20,21].

Optical sensing techniques generally rely on either a change in fluorescence or coloration of a dye in the presence of the species to be detected, or on a change in the absorption spectrum of an evanescent wave of infrared light. Mesoporous silica lends itself to these applications since it allows for the physical confinement and isolation of dye molecules and is easily incorporated into optical systems. To date, work has focused on the use of sol–gel silica for the production of O_2 [22–24], CO_2 [25], pH [26], NO_2 [27–29] and glucose [30] sensors, among others. In the near future, it will likely be desirable to employ templated mesostructured materials in this area, since they combine all of the advantages of sol–gel silica with the additional power to exercise precise control over pore-size as well as 3D connectivity.

5. Optical devices

Fiber optic technology continues to grow in importance, while optical devices shrink in size. As a result, the development of advanced materials for optical devices such as waveguides, switches, and limiters is crucial. Mesoporous silica could potentially play a large role in this field since it allows for the incorporation of various photosensitive and non-linear optical devices within transparent materials that can be processed via the sol–gel route into films, fibers and coatings.

It has been demonstrated that mesostructured silica fibers can function effectively as waveguides [31] or as mirrorless lasers by inclusion of a suitable dye [32,33]. Incorporation of *para*-nitroaniline (*p*NA) into the one-dimensional mesoscopic pores of MCM-41 has been shown to induce ordering of the *p*NA, resulting in non-linear optical behavior [34]. The generation of second harmonics is comparable to the non-linear optical crystal potassium dihydrogen phosphate. In general, the characterization of these mesostructured optical materials has not been sufficient to demonstrate that they meet the requirements necessary to build real devices [35–37]. However, there is reason to believe that they may offer significant advantages over traditional sol–gel optical materials. As Lebeau and Sanchez discuss in their review, the incorporation of non-linear optical dyes into sol–gel matrices suffers from several major difficulties [38]. One is obtaining adequate dye loading in spite of poor dye solubility within the matrix. Another is obtaining orientation of the dye molecules within an isotropic sol–gel (this is usually accomplished by application of an electric field). Mesostructured materials have well-defined pores that provide a large surface area for grafting of dyes, as well as an inherent anisotropy in the case of the hexagonal phase. These properties make them ideal for the production of non-linear optical hybrid materials.

6. Electronics

As microelectronic devices become smaller, it will become increasingly important to find a replacement for traditional silica intermetal insulators. It is desirable to produce materials that possess good mechanical strength, large breakdown voltage, small leakage current, and a dielectric constant (k) as low as 2. Baskaran et al. have demonstrated the production of disordered templated mesoporous silica with k as low as 1.8 [39]. This is smaller than can be obtained with organic films [40], though not as small as has recently been demonstrated for a highly porous silica aerogel [41]. However, the ability to precisely control pore architecture and orientation in mesostructured films may provide significant advantages in terms of both mechanical and electrical stability.

Mesostructured materials may also prove to be useful in the production of the next generation of electronic devices. As the microelectronics industry reaches the limits of what is possible with photolithography, a new paradigm will be required for the production of conducting interconnects, semiconductor devices, and materials for data storage.

A substantial challenge in electro-optic chip applications has been the creation of sufficiently small interconnects between device nanocomponents. Wu and Bein were the first to create nanowires within the pores of a mesostructured host. They polymerized polyaniline within the channels of MCM-41, and via DC and microwave conductivity measurements were able to demonstrate

that the polymer chains were isolated from one another [42]. They subsequently produced graphitic carbon within the pores via pyrolysis of polyacrylnitrile [43]. In this case, the confinement provided by the channels not only isolated individual wires from one another, but also induced ordering in the graphitic carbon structure, resulting in an increase in the microwave conductivity by an order of magnitude as compared to the bulk material.

Tolbert's group has shown that by confining a semiconducting polymer (MEH-PPV) within the aligned hexagonal channels of mesostructured silica, control can be exercised over energy transfer [44,45]. When high-energy segments outside of the matrix are excited, they transfer energy to the lower energy, extended-conformation chains within the pores, thus resulting in energy migration along the pore direction. Individual chains are electrically isolated from one another within the silica matrix, and thus cannot exchange energy.

Recently, the production of nanowires of ruthenium oxide [46], platinum [47–50], silver [50,51], and gold [50] within mesoporous hosts has been demonstrated. However, very little has been reported about the electrical properties of these materials. Nonetheless, these experiments represent an important step in the production of nano-scale electronic materials, both in terms of fabrication and in the ability to study the behavior of confined conducting wires that are electrically insulated from their surroundings.

Sun, Murray, and coworkers have exploited a different approach to the preparation of mesostructured materials for magnetic data storage [52,53]. They have prepared stabilized colloidal nanocrystals of cobalt and iron–platinum that are subsequently allowed to self-assemble into a periodic mesostructure. Thermal annealing has been used to control the phase structure of metal atoms within the particles. In the case of FePt, they obtained an array of room-temperature ferromagnets that supported magnetization reversal transitions at densities up to 5000 flux changes per millimeter (fc/mm). They speculate that reduction in the thickness of the ferromagnetic assemblies should allow recording densities up to 10 times as large as media currently in industrial use.

7. Hydrogen storage and electrode materials

If hydrogen gas is to see widespread use as an energy source, the question of how to store it must first be addressed. Recently, it has been demonstrated that carbon nanotubes can effectively be used for hydrogen storage at room temperature [54]. The production of ordered mesoporous carbon [55] provides a convenient route to the synthesis of large amounts of materials with pore sizes that are comparable to single walled carbon nanotubes. Provided that pore size and large surface area are the important factors in hydrogen storage, then mesostructured carbon materials which have the same carbon covalency would be suitable for this purpose.

Mesostructured materials may also prove useful as high performance battery electrodes. Specifically, Attard and coworkers have made surfactant-templated films of tin that show surface areas as much as 35 times as large as a rolled tin foil [56]. The uptake of Li^+ for this material was measured to be 2500 C/g, nearly twice that of materials typically used for negative electrodes in lithium batteries.

8. Conclusion

There is little doubt that mesostructured materials can provide unique opportunities for new applications as well as improvements on existing technologies. In several of the different examples highlighted above, mesostructured materials have proven to be competitive with, or superior to, existing technologies. There are a number of cases, notably low-dielectric coatings, chromatographic separations, and a variety of catalytic applications that appear close to commercial viability. Undoubtedly, the near future will bring many more examples of realizable applications.

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