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Hierarchical Assembly of Zeolite Nanoparticles into Ordered Macroporous Monoliths Using Core−Shell Building Blocks

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There are a number of strategies available for introducing structural organization into inorganic materials. Currently, the most popular and widely applicable method is template-directed assembly, which affords ordered materials at a range of length scales. In general, this approach uses alkoxide precursors in conjunction with molecular,[1] supramolecular,[2] or colloidal crystal[3] templates to prepare microporous, mesoporous, or macroporous materials, respectively. The method has been further developed to produce hierarchical silica-based materials containing bimodal-sized pore networks by dual templating procedures.[4] Alternatively, materials with higher order architecture can be prepared using self-,[5] directed-,[6] templated-,[7] and layer-by-layer[8] assembly of *preformed nanoparticles*. Herein, we report on the preparation of a hierarchical zeolite material with ordered nano-, meso-, and macroporosity using a novel combination of these strategies in a simple stepwise manner. In essence, alternating layers of preformed zeolite (silicalite) nanoparticles and oppositely charged polyionic macromolecules are sequentially adsorbed onto micrometer-sized spherical latex beads to produce nanostructured composite shells of controlled thickness. These prefabricated micrometer-sized core/shell building blocks are then assembled into close-packed structures over macroscopic dimensions. Subsequent calcination removes the organic components of the zeolite framework, composite shell, and latex template to produce the hierarchically ordered monolith with controlled wall thickness and pore diameters.

We used silicalite nanoparticles as the primary building unit because of the general importance of zeolite thin films and membranes in catalysis and molecular separations.[1a] Silicalite is an archetypal pure silica zeolite that can be routinely synthesized in the form of discrete nanoparticles in the presence of the molecular structure-directing agent, tetrapropylammonium hydroxide (TPAOH).[9] The as-synthesized particles prepared in our experiments[10] were relatively uniform in size with a mean diameter of 57 (light scattering) or 47 ± 10 nm (TEM).[11] The ζ-potential of the colloid was −80 mV with an isoelectric point at pH 4.9 (electrophoresis measurements). Electron diffraction, XRD, and FTIR data were consistent with the orthorhombic structure silicalite.[9,12]

The as-synthesized TPA−silicalite-1 nanoparticles were assembled into core−shell structures by layer-by-layer deposition on monodisperse 640-nm-diameter polystyrene (latex) beads. Previous studies using flat substrates[13] or spherical polymer beads[8,14] have shown the sequential adsorption of oppositely charged molecules or particles can be used to prepare fictionalized hybrid thin films and shells of controlled wall thickness, respectively. As the zeolite nanoparticles were nega-

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(10) Sixteen grams of TEOS (Aldrich, >98%) was added to 27.32 g of 1 M TPAOH (Aldrich) aqueous solution in a polypropylene bottle with stirring (final molar ratios; 9:25:354:100 TPAOH:SiO_2:H_2O:EtOH). The mixture was stirred for 24 h at room temperature to allow hydrolysis of TEOS. The transparent precursor solution was then refluxed in a preheated paraffin oil bath kept at 80 °C for 4 days without stirring. The colloidal particles produced were separated by repeated centrifugation at 12 000 rpm and washing with deionized water. A colloidal solution (pH 10−11) was obtained by redispersion of the TPA−silicalite-1 sediment in deionized water after washing 2−5 times.

(11) TEM and selected area electron diffraction (SAED) studies were conducted with a JEOL JSM1200 EX instrument operated at 120 keV. Specimens for EM were prepared by air-drying a drop of the aqueous colloidal dispersion onto Formvar-covered, carbon-coated copper grids. Particle sizes and electrophoretic mobilities were measured in the absence of added electrolyte using a Malvern Zetasizer 4. TGA was performed on a Netzsch TG209 instrument at a heating rate of 5 °C/min from room temperature to 800 °C in a nitrogen/air atmosphere with a flow rate of 90 mL/min. Calcined samples were also prepared by drying the suspension onto a quartz slide and then heating in air to 800 °C at a rate of 1 °C/min in a Carbolite furnace. The residue after calcination was embedded in resin and thin sectioned for TEM analysis. SEM and EDXA were carried out using a JEOL JSM5600L instrument operated at 5 keV for uncoated samples or at 20 keV for gold-coated samples. The samples were mounted onto Al stubs, using carbon sticky pads.

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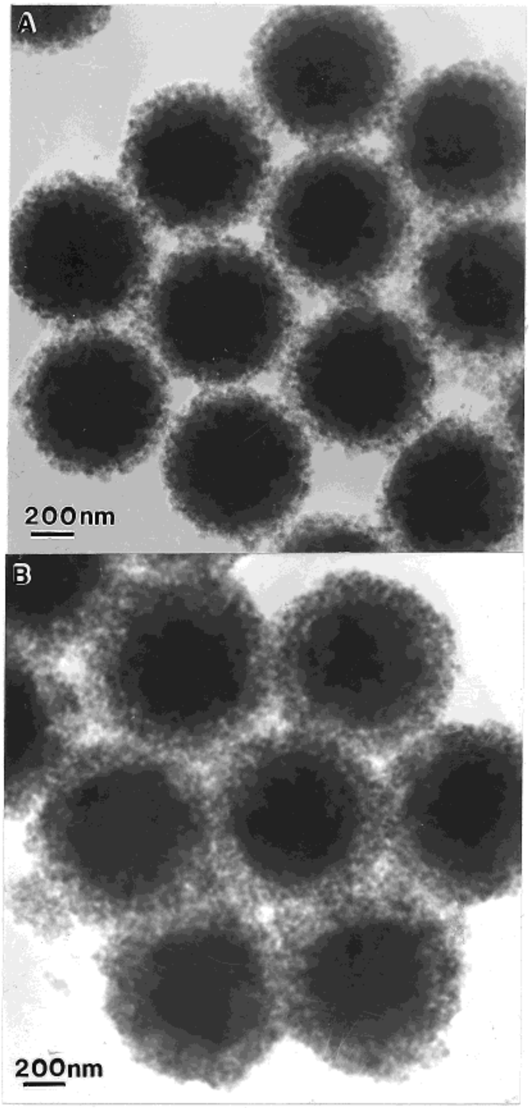

Figure 1. Transmission electron microscopy (TEM) images of latex beads coated with alternating layers of silicalite particles and oppositely charged polyelectrolytes: (a) two- and (b) five-layer pairs.

tively charged, multilayered shells were constructed on the latex beads by alternating the deposition of silicalite with a polycationic layer of poly(diallyldimethylammonium chloride) (PDADMAC).[15] This procedure was initiated by priming the beads with a PDADMAC−PSS−PDADMAC trilayer coating (PSS: poly(sodium styrenesulfonate) and then repeated to give core−shell structures consisting of up to five silicalite−PDADMAC-layer pairs. Corresponding electrophoresis measurements showed that there was an associated switch in the sign of the surface potential at each stage of the deposition cycle,[11] indicating layer formation throughout the assembly process.

Samples were retained at each stage of layer pair buildup for subsequent examination by TEM and single-particle light-scattering (SPLS) measurements.[16] The final coating on all these samples was a positive PDADMAC layer as the above data indicated that these would be more stable to aggregation over time. TEM images (Figure 1) showed an increase in diameter and surface roughness of the latex beads associated with the adsorption of silicalite nanoparticles onto the template. Both TEM and SPLS measurements indicate that there is only submonolayer coverage of the first silicalite layer adsorbed. However, there is a linear increase in particle diameter as each subsequent layer (layers 2−5) is deposited. In general, these shells were regular in thickness and contained a uniform distribution of closely packed nanoparticles. On the basis of these data, the average silicalite−PDADMAC-layer thickness determined from the TEM measurements was 39 nm. The corresponding value determined from the SPLS data was slightly higher (40 nm) as expected. The latter was calculated using the Rayleigh−Debye−Gans theory[17] and an estimated refractive index of 1.39. These values for layer thickness are lower than would be expected for discrete layers, on the basis of the diameter of the primary silicalite particles because of interlayer mixing, as particles pack predominantly in the interstitial space created by the previously absorbed layer.

Thermogravimetric analyses of the zeolite-coated latex spheres show the most substantial weight loss occurs between 350 and 450 °C, corresponding to the removal of the organic components (latex, polyelectrolyte, and TPAOH) of the hybrid material.[11] The TGA residue obtained after heating above 800 °C was a white inorganic powder consisting of hollow silicalite shells (Figure 2). The intact spherical morphology implies that although the nanostructured shell is comparatively thin (94 ± 10 nm, for three-layer pairs), fusion of the constituent nanoparticles within and between layers by silanol condensation during calcination is sufficient to stabilize the hollow shell architecture.

The tendency of the coated latex particles to close pack upon air-drying onto the TEM substrate (Figure 1) suggested that it should be possible to use core−shell colloids as a combined building block and template for three-dimensional hierarchical structures. We tested this idea by preparing macroscopic close-packed assemblies of the silicalite-latex particles on centrifuge filters. The core−shell colloid was centrifuged at speeds of 2000 min^{-1} in an Eppendorf rotor to produce close-packed superlattices. Calcination to remove the organic components produced a monolithic macroporous sili-

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(15) Dilute solutions (1 mg/mL) of polyelectrolytes, poly(sodium styrenesulfonate) (PSS), and poly (diallyldimethylammonium chloride) (PDADMAC) were prepared in 0.5 M NaCl. PSS ($M_w = 70\,000$) and PDADMAC ($M_w < 200\,000$) were obtained from Aldrich. PDADMAC was used as received, whereas PSS was dialyzed against Milli-Q water (cutoff 14 000) and lyophilized before use. Negatively charged sulfate-stabilized polystyrene (PS) latex particles of diameter 640 nm were coated with a primer layer of polyelectrolytes (PDADMAC/PSS/PDADMAC). Zeolite nanoparticles were then adsorbed onto the templates for 15 min followed by four centrifugation and washing cycles per layer. Centrifugation speeds of 7000 rpm (Eppendorf rotor) were sufficient to settle the coated latex particles. A layer of PDADMAC “cement” was then adsorbed in a similar manner, with between one and five of these layer pairs being built up onto the template.

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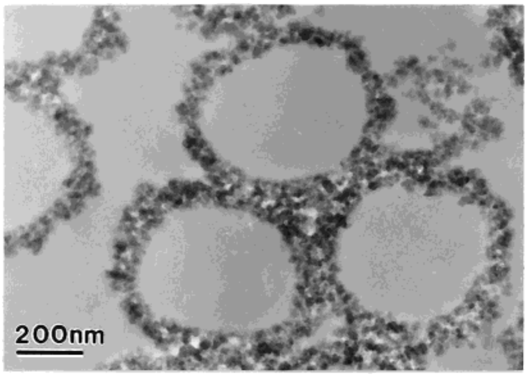

Figure 2. TEM image of a thin section of a sample of spherical silicalite shells prepared by calcination of composite particles consisting of a latex core coated with three-layer pairs of polyelectrolyte and silicalite nanoparticles.

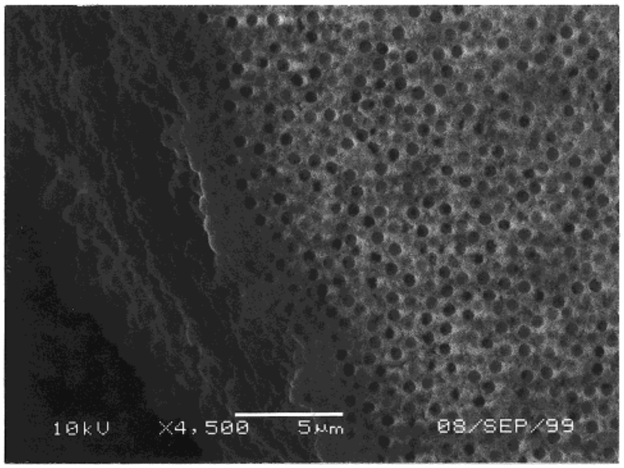

Figure 3. SEM image of an ordered macroporous monolith formed by calcination of a close-packed assemblage of latex-silicalite particles with a five-layer pair shell.

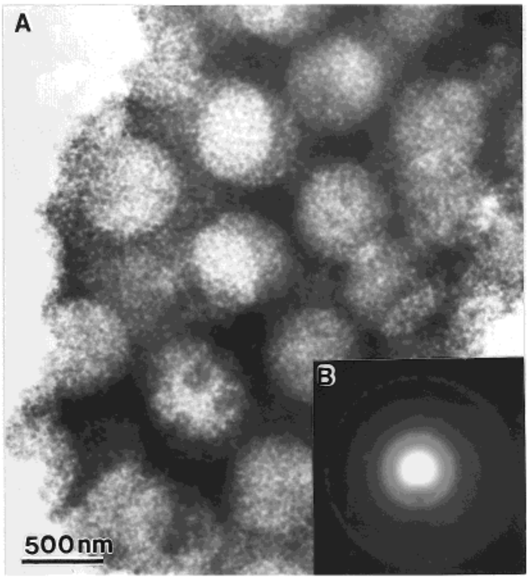

Figure 4. (a) TEM image and corresponding diffraction pattern (b) obtained from a fragment of the macroporous silicalite framework shown in Figure 3.

calite with a pore size of ≈500 nm (Figure 3). This was approximately 20% less than the diameter of the latex template and indicated some shrinkage/densification of the structure upon calcining. TEM images (Figure 4) showed well-defined curved walls that were ≈200-nm thick for a monolith prepared from core−shell particles comprising five silicalite−PDADMAC bilayers. The continuous wall structure consisted of a dense array of silicalite nanoparticles that contained disordered mesopores associated with the interparticle voids. The crystalline nature of the nanoparticulate walls was confirmed by electron diffraction, which showed d spacings (d_{hkl} = 1.12 nm {011}, 1.00 nm {200}, 0.56 nm {202}, 0.50 nm {400}, 0.38 nm {051}, 0.33 nm {600}, and 0.30 nm {053}) consistent with the silicalite orthorhombic lattice.[12]

In conclusion, we have presented a simple stepwise approach to the formation of materials with higher order structure. We have illustrated this strategy by producing a silica-based material containing a hierarchy of pore structures at the nano-, meso-, and macroscopic length scale. The approach utilizes the layer-by-layer assembly of a nanostructured inorganic phase (zeolite nanoparticles) into the shell structure of spherical core−shell particles that in turn can be used as prefabricated units in colloidal crystallization. The key aspect of the strategy is that the core−shell structures are exploited as a combined building block and porogen (sacrificial template) for the construction of the hierarchical structure. This is in marked contrast with previous approaches[3,4,7] that have used the infiltration of colloidal crystals, polymer gels, or ordered superstructural templates, to prepare hierarchical materials. These methods have the disadvantage that the wall thickness is often limited by the void spaces of the preformed template architecture, which in general cannot readily be adjusted. In comparison, by using the assembly of precoated templates into extended structures, it should be possible to fine-tune both the thickness and composition of the wall structures comprising the macroporous monoliths. For example, we are currently investigating how varying the core−shell diameters affects both pore and wall dimensions as well as the mechanical stability of the macrostructure. These data and associated porosity and surface area measurements will be reported in more detail elsewhere. Moreover, the inherent flexibility of the core−shell building block approach allows the chemistry of the wall to be systematically modified and tailored through the deposition of two or more different types of nanoparticle layers onto the substrate.

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Supporting Information Available: Electrophoresis measurements showing the switch in the sign of the surface potential at each stage of the deposition cycle. This material is available free of charge via the Internet at http://pubs.acs.org.

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