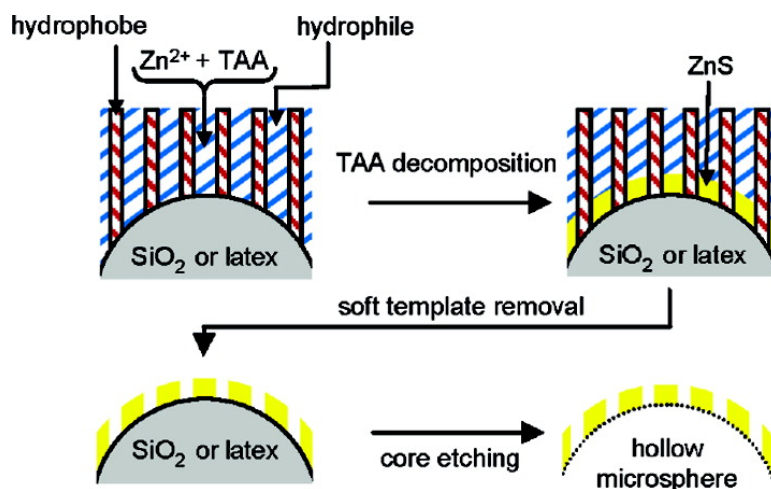


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Double Direct Templating of Periodically Nanostructured ZnS Hollow Microspheres

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Hollow capsules are both technologically and scientifically interesting. “Smart” nano- and microcontainers could lead new catalysts, structures for the controlled release of chemicals, and materials that may even mimic some properties of living cells.^{1,2} The synthesis of core–shell particles and capsules is a rapidly evolving area for these and other applications.³ In this context, several groups have synthesized and analyzed the permeation of polymeric hollow capsules using a combination of electrostatic or hydrogen bonded layer-by-layer self-assembly, colloid templating, and sacrificial core etching.^{3a,4} Significant efforts are similarly focused on the synthesis of inorganic mesoporous materials with 1–50 nm diameter pores, the ideal size for controlling macromolecule transport and adsorption.⁵ Among the numerous approaches for obtaining these mesostructured materials, lyotropic liquid crystal templating emerges for its simplicity.⁶ This approach uses the self-assembled structure formed by the mixture of an amphiphilic molecule (e.g., a nonionic surfactant) with water to template the formation of a mineral phase. Within the self-assembled structure, there exist chemically and spatially distinct environments with characteristic dimensions of 2–10 nm that serve to define the morphology of the mineral phase. Mesostructured semiconductors, including ZnS, oxides, and metals, have been successfully templated in hexagonal and lamellar lyotropic liquid crystals.^{6,7} Here we present a “double direct templating” approach to obtain hollow ZnS microspheres perforated with a periodic array of uniform pores and demonstrate the entrapment of Au nanoparticles within these microspheres. In double direct templating, a lyotropic liquid crystal templates the mineralization of ZnS on the surface of a silica or polystyrene colloidal template. Removal of the templates results in a periodically mesostructured ZnS hollow capsule.

We prepared a 50% w/w mixture of a nonionic surfactant (Brij97) and an aqueous solution containing a suspension of colloids and the precursors for ZnS, zinc acetate, and thioacetamide (TAA). Upon mixing, a hexagonal lyotropic liquid crystal is formed. This hexagonal phase serves to both spatially define the formation of ZnS and prevent aggregation of the colloids. The slow release of sulfide ions from the hydrolysis of the thioacetamide induces over a few days the heterogeneous nucleation of ZnS on the surface of the colloids (Scheme 1).⁸ Although ZnS deposition is not surface activated, heterogeneous nucleation is sufficiently favored to result in the formation of a ZnS shell. Some small (~50 nm) ZnS particles are also formed, but these are easily removed during workup.

Figure 1a presents a polarized optical microscope image of the hexagonal liquid crystal phase containing the colloids and the ZnS precursors. The image displays the expected fan texture for the hexagonal phase. The optical microscope images also did not show any signs of colloid aggregation. Figure 1b presents small-angle X-ray scattering spectra (SAXS) collected from a similar liquid crystal mixture. Three peaks are clearly visible at q values of 0.96, 1.68, and 1.94 nm⁻¹, a ratio of 1:1.75:2.02, in excellent agreement

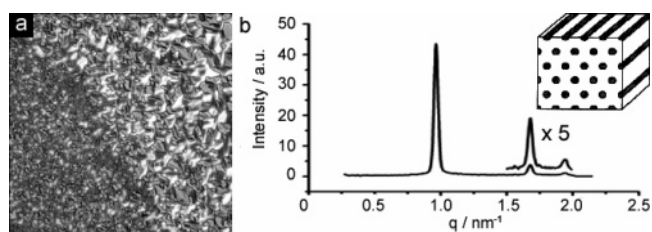
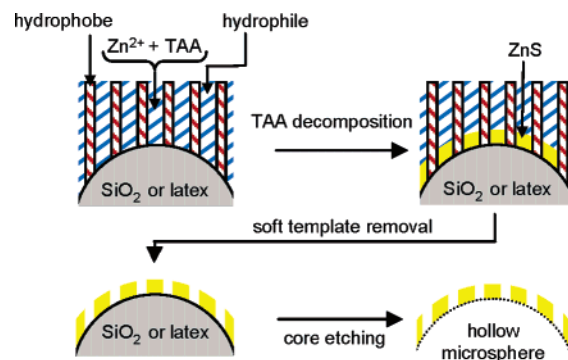


Figure 1. (a) Polarized optical microscope image of 0.02% v/v of carboxylated latex colloids in 20 mM Zn(OAc)₂ and 0.1 M TAA dispersed in the hexagonal liquid crystal. (b) SAXS spectra of the same mixture.

Scheme 1. Mesostructured Hollow Microspheres Formation Process



to the theoretical ratio of 1:√3:2 for the 100, 110, and 200 planes. A 100 plane spacing of 7.5 nm is obtained, similar to that observed by other groups,^{6b} suggesting that the liquid crystal order of this phase is not disrupted with the introduction of ZnS precursors and colloidal microspheres.

Figure 2a presents a transmission electron microscopy (TEM) image of a hexagonally templated ZnS hollow microsphere after etching the latex colloid with an organic solvent. The ZnS shell is ~15 nm thick, and the hexagonally templated mesopore structure is apparent. Although the ZnS appeared to have cracked during etching of the colloid, perhaps due to swelling of the colloid prior to dissolution, the templated mesostructure and overall shape were preserved. These capsules were conclusively identified as spherical by tilting in the electron microscope. The hexagonal pore structure can generally be observed (Figure 2b), although some regions do not appear as ordered as others, in part, because the electron beam is passing through both sides of the shell, and thus the observed structure is the convolution of both walls of the capsule. A Fourier transform image analysis of a small region of the shell (inset Figure 2b) gives six bright equally spaced spots corresponding to a 2D hexagonal array with a 6.4 nm center to center distance, matching the dimensions and symmetry of the lyotropic liquid crystal template. The dark spots on the surface of the hollow microsphere (Figure 2a) are small clusters of physically adsorbed ZnS.

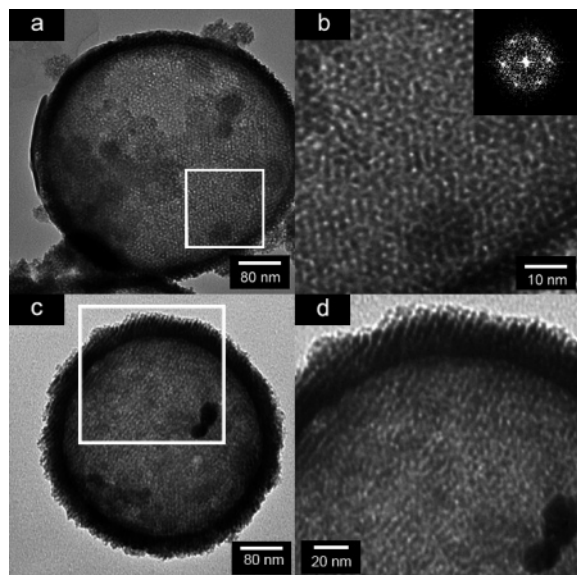


Figure 2. TEM micrographs of hollow mesoporous ZnS shells (a) after etching of the polystyrene colloidal template, (b) higher magnification image and FFT of the region marked in the white square of (a), (c) after etching of the Au nanoparticle (visible in lower right of white square) containing silica colloidal template, and (d) higher magnification of the white square in (c).

Cracking of the shell wall by swelling of the latex colloid during dissolution can be addressed by employing a different core material. Silica colloids represent an attractive alternative because they can be chemically etched without swelling. In addition, a wide variety of materials can be encapsulated in silica, including metal nanoparticles, quantum dots, enzymes, and cells.⁹ Thus, it should be possible to trap a species inside the silica, grow a mesostructured shell around the colloid, and finally dissolve the silica, resulting in a caged species.^{3a} As an example, we formed a mesostructured ZnS shell around silica colloids containing small numbers of gold nanoparticles. After etching the silica with ethanolic HF, a caged Au nanoparticle was obtained (dark feature in Figure 2c,d). The mesopores enabled the removal of silica, but were too small for the Au nanoparticle to escape, leaving the gold nanoparticle within the ZnS shell. As an indication of the robust nature of the capsule, it was not cracked by capillary forces upon drying when the sample was prepared for electron microscopy.

Careful examination of Figure 2d shows a series of stripes with periodicities similar to the hexagonal phase of the surfactant employed, indicating templating of the growth of the ZnS by the liquid crystal. In this case, it appears the cylindrical micelles making up the liquid crystal tend to lie on the surface of the silica colloid. This is suggested by TEM images of the early stages in the formation of ZnS clusters (see Supporting Information) and other works.^{2c,10} Multiple reports on surfactant self-assembly and mineralization on surfaces have shown that numerous factors affect the final mineralized structure, including substrate surface chemistry and topology, growth kinetics, and condensation of the inorganic network and interactions with the surfactant template.¹¹

Our results demonstrate the formation of a mesostructured hollow ZnS microsphere through double direct templating. This process takes place at room temperature, employing a hexagonal lyotropic liquid crystal as a soft template for the mesostructure and a colloidal

template for the hollow morphology. The regular controlled pore structure of the shell wall opens the possibility for the encapsulation of nanoparticles, polymers, and biological macromolecules. Small chemical species can diffuse rapidly through the shell wall, while the larger species originally sequestered in the colloidal template remain entrapped. We have demonstrated this concept using Au nanoparticles and are currently working on the entrapment of more sophisticated compounds. Also, we speculate that this approach for patterning the surface of a colloid in the nanometer scale may be a starting point for obtaining novel “patchy” microspheres with interesting self-assembly properties.¹²

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Supporting Information Available: Experimental procedures and TEM images of ZnS on silica colloids. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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