

Double Direct Templated Hollow ZnS Microspheres Formed on Chemically Modified Silica Colloids

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The effect of surface chemistry of SiO₂ colloids dispersed in a nonionic surfactant based lyotropic liquid crystal (LLC) on the double direct templating of hollow mesostructured ZnS capsules was investigated. In double direct templating, a LLC templates the mineralization of ZnS on the surface of a colloidal particle. Removal of the colloid results in a periodically mesostructured hollow capsule. After ZnS mineralization and a subsequent etching of the sacrificial SiO₂ core, the ZnS mesostructure was imaged using transmission electron microscopy (TEM). The highest quality mesostructure was observed for poly(acrylic acid) (PAA) functionalized colloids, while other surface chemistries, including bare silica, poly(ethylene glycol), amine, and thiol surface chemistries yielded much less favorable results. In the PAA system, the order of the hexagonally arranged 3 nm mesopores in the ZnS shell closely matched that of the lyotropic liquid crystal template. Detailed TEM revealed the presence of regions where the mesopores lay parallel to the colloidal surface and others where they were perpendicularly arranged. We suspect the PAA functionalization favored both the nucleation of ZnS and organization of the LLC template responsible for templating mesostructured ZnS shell around the colloidal particle.

Introduction

Along with solid colloidal particles, which have attracted immense attention, the synthesis and properties of hollow colloids are becoming of considerable interest due to their potential applications. When their permeability is properly designed, the capsule walls can act as physical or chemical filters, allowing selective transport of chemical species.^{1,2} The highly confined chemical environment within a hollow colloid may also result in enhanced sensors and nanoreactors through the potential of entrapment of individual or small numbers of molecules. We have focused in particular on the synthesis of hollow spheres containing a nearly monodisperse mesoporosity in the shell walls, formed through a process we termed “double direct templating”.³ The combination of a mesoporous shell wall containing ~3 nm pores surrounding a hollow interior with a diameter of hundreds of nanometers results in a system with unique and potentially biomimetic properties.⁴

Hollow capsules have been formed via a number approaches including surface initiated polymerization,⁵ galvanic displacement^{6–8} and ion exchange,⁹ vesicle polymerization,¹⁰ sol–gel chemistry,¹¹ layer-by-layer assembly,¹² synthesis in reverse emulsions,¹³ and spray drying. Often, the ultimate goal is to entrap an object or chemical species within the hollow capsule, which is generally done one of two ways: either the capsule is formed around a sacrificial core which also contains the desired species, after removal of the sacrificial core, the species remains entrapped,^{14,15} or a post synthetic reaction where the precursors can pass through the walls and assemble or react within the capsule.^{16,17} When using the sacrificial core approach, there are ample mild chemical procedures (e.g., sol–gel methods) that are able to encapsulate biomolecules and colloids in a rigid but benign

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matrix, such as silica,¹⁸ or a soft matrix, such as self-assembled polyelectrolytes.^{19,20}

In our approach of double direct templating, a colloidal particle is used as the sacrificial carrier, and the mesoporous shell wall is formed through liquid crystal templating.^{3,21–26} The advantage of liquid crystal templating (also referred to as *nanocasting*) is that there is direct control over the pore diameter and packing.²⁷ In lyotropic liquid crystal (LLC) templating, first, a mixture of a nonionic surfactant and water in various ratios self-assembles forming highly organized phases with hydrophobic and hydrophilic regions. Then, a mineralization chemistry, which only operates in the hydrophilic region of the LLC template, is initiated, resulting in an inorganic mesostructure that is a replica of the hydrophilic region of the liquid crystal. When properly applied, the result is a mesoporous structure with a defined geometry and pore size.^{23,27} In our most recent example, we applied double direct templating to synthesize mesoporous ZnS hollow spheres.³ In this work, the self-assembled hexagonal phase of a LLC formed by shear mixing a mixture of Brij 97 and water containing precursors for ZnS was used as a soft template to direct the mineralization of ZnS on the surface of silica and polystyrene colloidal templates. This LLC consists of a hexagonal array of hydrophobic rods immersed in a continuous hydrophilic matrix; ZnS heterogeneously nucleates on the surface of the colloids only where the hydrophilic regions of the LLC are in contact. Removal of the sacrificial colloidal particle thus results in a periodically mesostructured ZnS hollow capsule. The yield of this process, however, was low, and when a silica colloid was used as the sacrificial template, the fidelity of the templated mesostructure was quite poor. Since the silica template system has a much greater potential for entrapment of interesting species, the lack of fidelity of ZnS templating on silica was a significant shortcoming. Here we demonstrate that through careful control of the surface chemistry of the sacrificial silica colloidal particle that high fidelity templating of a mesostructured ZnS shell is possible. We also performed detailed transmission electron microscopy (TEM) analysis on the ZnS hollow spheres to develop a model for the organization of the templating LLC and thus the ZnS mesostructure around the silica colloid.

Experimental Section

Materials. The nonionic surfactant Brij 97 (polyoxyethylene 10 oleyl ether), poly(acrylic acid), and sodium salt (PAA, MW 2 kDa, ~100-mer) were obtained from Sigma, while thioacetamide (TAA), zinc acetate dihydrate, and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) were obtained from Acros Organics.

Silica particles were synthesized according to the Stöber method²⁸ from a mixture of ammonia, water, and tetraethoxysilane. All silanes were obtained from Gelest Inc. (Morrisville, PA (U.S.A.)) and used without further purification: (3-mercaptopropyl)trimethoxysilane (3-MPTS), (3-aminopropyl)triethoxysilane (APS), carboxyethylsilanetriol sodium salt, 25% in water, *N*-(trimethoxysilylpropyl)-ethylenediamine, triacetic acid, sodium salt, 45% in water (EDATAS), and 2-[methoxy(polyethyleneoxy)-propyl]trimethoxysilane (PEG).

Colloidal Surface Modification. Colloidal surface modification was performed following reported one-^{29–32} or two-step procedures:

(a) *One-Step Modification.* After colloid formation, a small aliquot (typically 20 μ L of a 1% or a 0.5% w/w ethanolic solution) of the desired silane was added to the Stöber reaction mixture and reacted for 24 h.

(b) *Two-Step Modification. PAA Modified Colloids.* One milliliter of a 1% w/v PAA solution was added to 10 mL of a suspension of ~0.1% v/v of APS modified colloids in H₂O. Then, 5 mM DMT-MM was added to attach the 100-mer polymer strands to the colloidal surface.³³ This solution was stirred overnight during which no signs of flocculation were observed. Following this procedure, particles were suspended and washed several times with H₂O.

Carboxysilanetriol Modified Colloids. Bare silica washed particles were suspended at 0.1% (v/v) in 0.1 M HCl. After stirring 10 min, a 1% (w/w) solution of the carboxysilanetriol was added and reacted overnight. Particles were cleaned by a minimum of six cycles of washing and centrifuging.

Dispersion of Particles in the LLC. Particles were dispersed in the LLC following our reported procedure.^{34,3} Briefly, the hexagonal mesophase was formed by mixing Brij 97 warmed to its melting point with an aqueous dispersion containing 0.025% (v/v) colloids in 20–100 mM zinc acetate and 0.1 M thioacetamide using two 3-mL syringes connected by a Luer-Lok stainless steel or plastic union. The contents were shear mixed at a rate of ~5 mL/s ensuring a complete dispersion of the colloidal particles. The mixture was reacted for 3–4 days, after which the contents were dispersed in ethanol and the particles recovered by multiple cycles of low speed centrifugation from ethanol.

Etching of SiO₂ Core. Etching of the hollow spheres was performed in an ethanolic solution of 1% (v/v) HF from 1 h to overnight, followed by centrifugation and washing with ethanol. Ethanolic etching conditions are required to remove the silica without disrupting or coarsening the ZnS mesostructure. When a pH 4 aqueous NH₄F/HF etchant was used, coarsening of the ZnS grains was observed, and the periodic mesostructure of the shell wall was lost, although the hollow shape was preserved.

Characterization. Colloidal particles were observed using a Phillips CM12 transmission electron microscope operating at an accelerating voltage of 120 kV and a Hitachi S-4700 scanning electron microscope (SEM). Shell thicknesses were estimated from the micrographs using ImageJ (NIH) for image analysis. Zeta potential electrophoretic measurements were acquired with a Malvern Mastersizer 2000 at a fixed ionic strength of 10 mM KCl and variable pH. Powder X-ray diffraction experiments were done with a Rigaku D/Max-b. Small-angle X-ray scattering (SAXS) was

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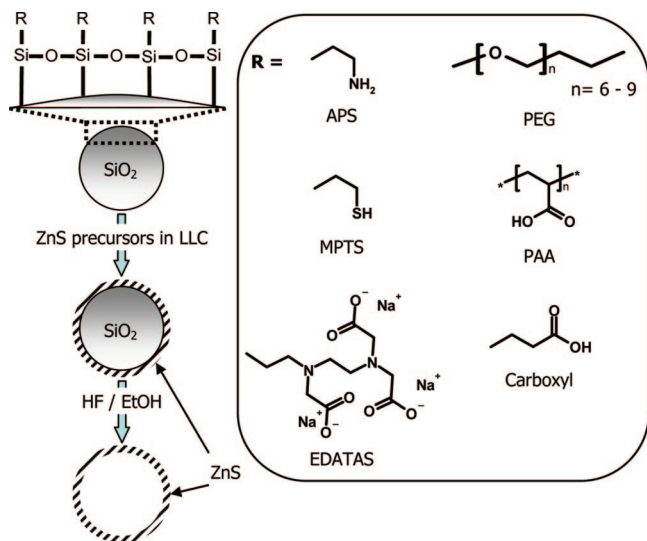


Figure 1. Generalized synthetic procedure for double direct templating (left) and library of surface chemistries attached to the surface of the silica colloids (right).

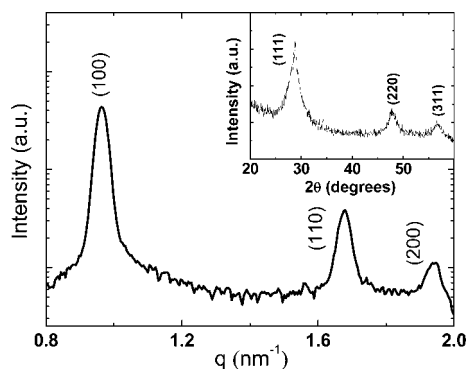


Figure 2. SAXS of 0.02% (v/v) of silica colloids in 20 mM zinc acetate and 100 mM TAA dispersed in the hexagonal LLC. Inset, X-ray powder diffractogram collected from the resultant hollow ZnS microspheres.

performed using an in-house X-ray spectrometer, and the data collected was analyzed with FIT2D.^{35,36}

Results and Discussion

Silica is an attractive colloidal material for studying the influence of surface chemistry on the formation of the ZnS shell, as silane based surface chemistry modifications are well understood. Thus, the impact of a library of surface chemical groups (Figure 1) on LLC templated ZnS mineralization can be readily explored. Surface chemistries studied here are relatively hydrophilic and other than polyethylene glycol (PEG) have potential affinity for Zn²⁺ ions (carboxylate, amino, and thiol). Hydrophobic colloids flocculate in solution during LLC formation and thus are not compatible with our experimental procedure.

Small- and wide-angle X-ray diffraction is performed to confirm the structure of the templating LLC and the resultant ZnS. Figure 2 presents SAXS collected from the dispersed colloidal silica particles in the hexagonal phase of the LLC

as well as wide angle XRD of the resultant ZnS hollow nanospheres. Three peaks, the (100), (110), and (200) reflections, confirm the hexagonal mesostructure of the LLC template under the mineralization conditions. A d spacing of 6.6 nm, which agrees with other published reports on this LLC,^{3,22} is calculated from the (100) peak. The mesophase, including the colloidal particles and ZnS precursors, is also studied using polarized optical microscopy; the observed texture is as expected for a hexagonal LLC, suggesting that the soft template mixture is not globally disrupted by the introduction of colloids and ZnS precursors. Broad peaks are observed in the powder XRD at 28.5°, 47.5°, and 56.3° corresponding to the (111), (220), and (311) reflections of cubic zinc blende structure (JCPDS No. 5-0566). A ZnS crystallite size on the order of 3 nm is obtained from the Scherrer formula of Δk versus k (the scattering vector) and the diffraction peaks from the (111), (220), and (311) planes after correcting for instrumental broadening. This crystallite size agrees with HRTEM observations.

After etching the silica core, TEM of the ZnS shells is performed (Figures 3–5). All particles show a defined and dark edge and much more transparent center as expected for a hollow spherical object. Note, in Figure 3, the contrast is reversed to improve the visibility of the hexagonal pore structure. The regular mesopore arrangement in the ZnS shell is generally apparent, however, because the electron beam passes through the shell wall twice, and the observed image is a convolution of the upper and lower wall of the capsule, somewhat obscuring the regular pattern. In localized regions, the hexagonal lattice can be clearly observed (Figure 3c). The pore diameters are all very close to 3 nm, which agrees very well with the diameter of the hydrophobic rods of the Brij 97 hexagonal mesophase, and the pore center-to-center spacing is about 7 nm (Figure 3b), matching the lattice of the mesophase (Figure 2). Images of multiple particles indicate the uniformity of the thickness of the ZnS wall (Figure 4).

The bare, carboxy, and PAA modified SiO₂ colloids consistently templated ZnS shells containing an ordered mesostructure (Figure 5), with qualitatively more uniform appearance, and greatest batch-to-batch reproducibility for the PAA modified colloids. Successful templating requires a surface that both encourages the heterogeneous nucleation of ZnS and has the proper interactions with the templating LLC. We suspect the PAA modified surface best meets these criteria, and experimentally, the most uniformly mesostructured ZnS shell was observed using the PAA modified colloids. The fact that nondissociated carboxylate groups in PAA can form hydrogen bonds with the oxygen atom of the hydrophilic ethoxy moieties of the surfactant is probably significant,^{37,38} as is the fact that carboxylate groups form metal coordination complexes with many divalent ions

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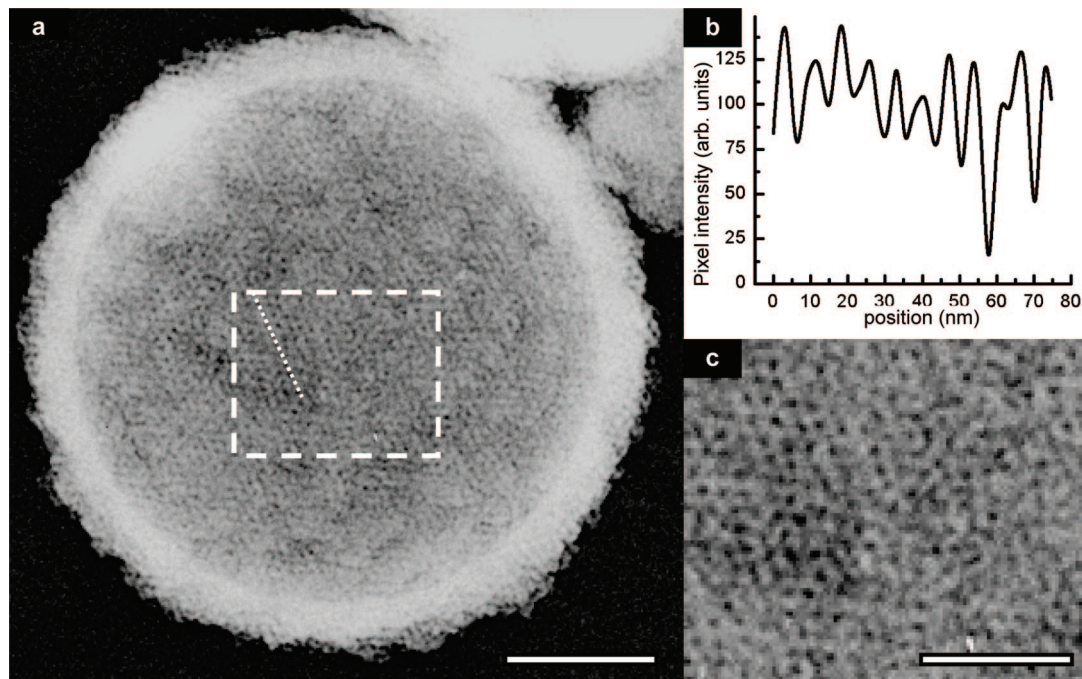


Figure 3. (a) TEM micrograph of ZnS shell formed using PAA modified colloidal SiO₂ template after SiO₂ removal (scale bar = 100 nm), (b) line plot profile of pixel intensity vs distance along dotted line in boxed region in (a), and (c) higher magnification image from boxed region in (a) (scale bar = 50 nm). Images (a) and (c) are negative images to show more clearly the mesopore structure.

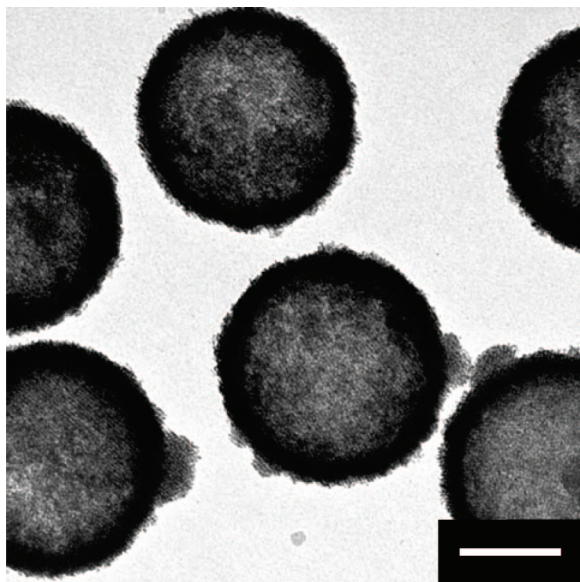


Figure 4. TEM micrograph of multiple ZnS shells after etching the PAA-modified SiO₂ colloidal templates. Scale bar = 200 nm.

including Zn²⁺.³⁹ We suspect the interaction of carboxylate groups and Zn²⁺ promotes nucleation and may also favor the initial anchoring of the ZnS shell. The polymeric nature of the PAA chains also provides the conformational freedom to enable rearrangements to maximize these interactions, for example, by partitioning into the hydrophilic regions of the LLC.⁴⁰ One might expect similar results for EDATAS and carboxy modified colloids, but this is not the case. EDATAS and the carboxy functionalization are small molecules, thus

cannot partition in response to the LLC, and may present a more “patchy” surface.

Thiolated (MPTS), aminated (APS), and PEG surfaces resulted in poorly templated ZnS shells or patchy ZnS clusters on the SiO₂ colloidal surface (Figure 6). The complete lack of ZnS shell formation on PEG modified silica particles was not surprising, as PEG was not expected to bind strongly to Zn²⁺ (or ZnS). The generally poor results for thiolated and aminated surfaces are probably due to a similar reason. Neither of these chemistries is expected to bind strongly Zn²⁺ under the acidic conditions used in the synthesis. Amine groups can complex Zn²⁺ ions, and thus one might expect high quality mesostructured ZnS when using aminated colloids. However, amine–Zn²⁺ complexes only form under basic conditions while the pH of the ZnS precursor solution is between 5 and 6. Under acidic conditions, NH₂ groups are protonated and do not complex with Zn²⁺. Consequently, heterogeneous nucleation of ZnS on the surface is suppressed, decreasing the quality of the mesostructured shell. Given that the pK_a of the thiolate group is ~10,⁴¹ only a small fraction of the thiolates are dissociated at pH 5–6, and thus similarly, the Zn²⁺ is not expected to complex with the surface of the thiolate modified colloids. However, increasing the pH for the ZnS synthesis is not an option as this leads to precipitation of Zn(OH)₂. Attempts were also made to form a mesostructured shell on negatively charged sulfate modified latex spheres. This resulted in aggregated colloids with attached clusters of poorly templated ZnS, suggesting that more than simple electrostatic interactions are required for formation of a templated shell (not shown). ζ-Potential measurements generally support these observations. PAA and EDATAS modified colloids have

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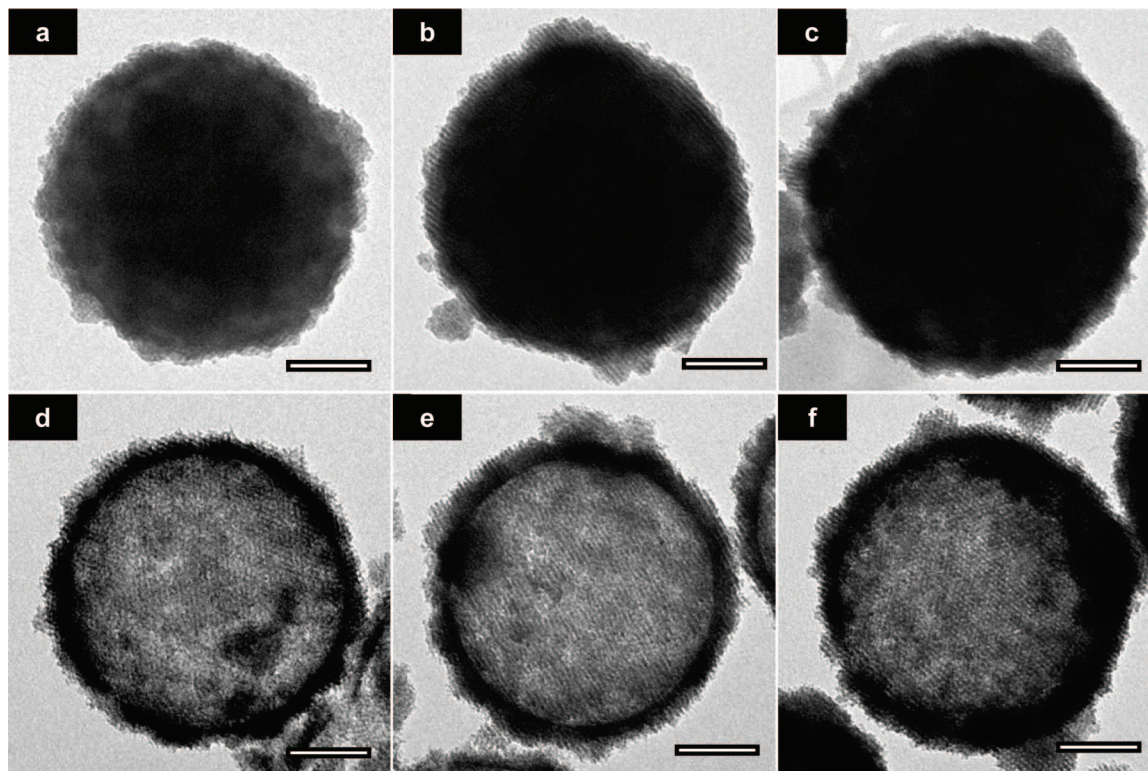


Figure 5. TEM micrographs of hollow mesoporous ZnS shells before (a–c) and after (d–f) etching the silica colloidal template, (a, d) bare silica, (b, e) EDATAS-modified silica, and (c, f) PAA-modified silica. All scale bars are 100 nm.

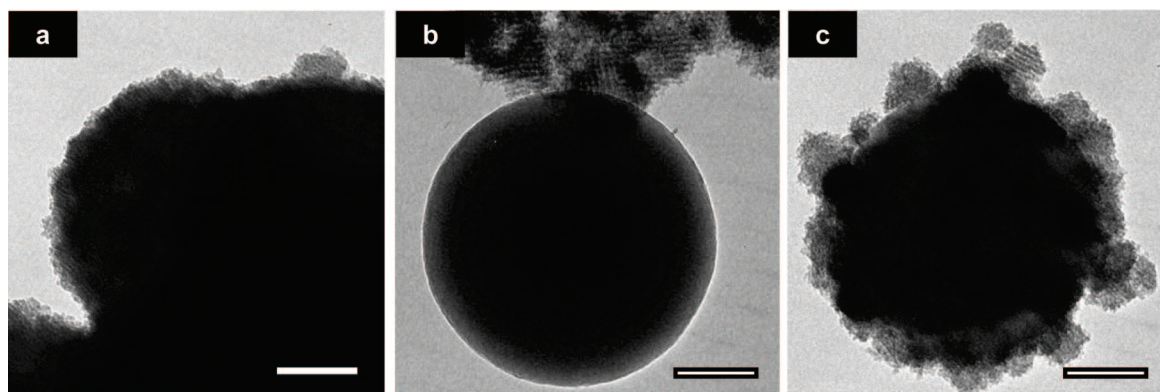


Figure 6. TEM micrographs of hollow mesoporous ZnS shells on modified silica colloidal template, (a) MPTS-modified silica, (b) PEG-modified silica, and (c) APS-modified silica. All scale bars are 100 nm.

strongly negative ζ -potentials, while the APS modified colloids have strongly positive ζ -potentials between pH 5 and 6 (Figure 7). The MPTS modified colloids have a slightly negative ζ -potential (-10 mV), probably due to unreacted silanol groups on the surface of the colloid, at low pH which gradually becomes more negative with increasing pH (-40 mV); over the measured pH range, it does not appear the thiolate groups dissociate.

Templated ZnS clusters were formed in the bulk of the LLC for all colloidal surface chemistries, proving that even for the systems where mineralization was not successful, the colloid surface chemistry does not globally affect mesostructured ZnS formation. Clearly, the chemistry presented at the surface of the SiO_2 colloidal particles strongly impacts ZnS mineralization.

The mesostructure in the ZnS shell is observed in Figure 3, as well as in higher magnification images of the particles

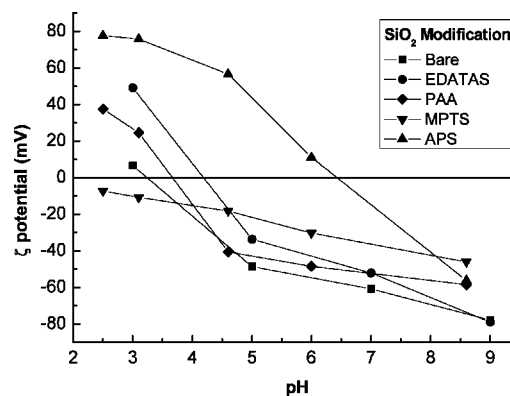


Figure 7. Zeta potential as a function of pH for bare, APS, MPTS, EDATAS, and PAA modified SiO_2 colloids. The ionic strength was kept constant at 10 mM KCl.

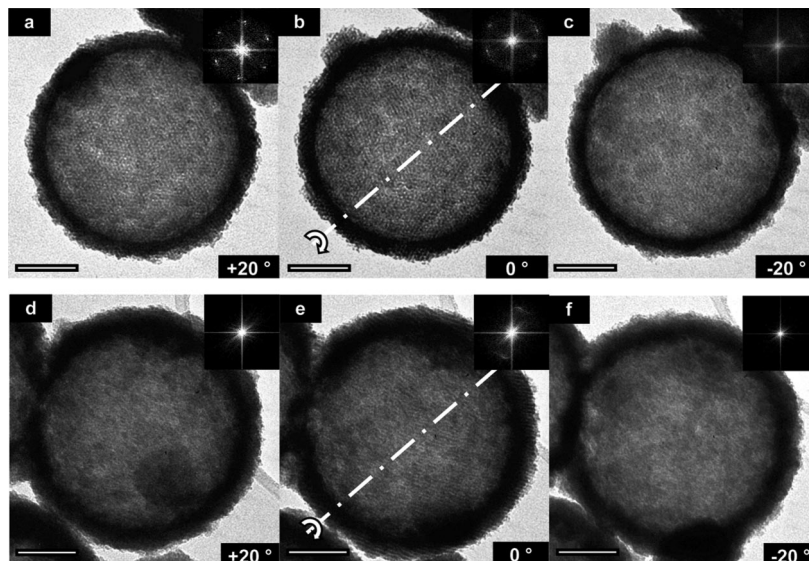


Figure 8. TEM micrographs of two different ZnS hollow spheres (a–c) and (d–f) formed on PAA modified silica colloids at various tilting angles. The axis of rotation is indicated on the center images and the viewing angle was varied from -20° to 20° as indicated on the images. Insets in the upper right corner of each image are FFTs calculated from the hollow spheres in the respective images. All scale bars are 100 nm.

presented in Figure 4 (not shown). Tilting the samples in the TEM microscope enables better understanding of the spatial orientation of the mesostructure in the double directed templated ZnS wall. Careful examination of Figure 8a shows a mixture of arrays of hexagonally ordered pores aligned perpendicular to the colloidal surface as well as regions where order is less evident. Pore to pore distance is coincident with the spacing of the hydrophobic rods in the LLC. Stepwise rotation of the hollow spheres (Figure 8b,c) causes the pores to disappear, as evidenced in the fast Fourier transform (FFT) image transformation of the hollow sphere (insets of Figure 8). In another hollow sphere (Figure 8c,d), the pores appear to run parallel to the colloidal surface, “wrapping” the sacrificial core. Visualization of these pores is most dramatic on the edges of the sphere where it is apparent that there is a common mesopore orientation around the particle. As previously discussed, polarizing optical microscopy and SAXS both demonstrate that the bulk of the LLC template is not globally disrupted by the colloids. However, locally, the order of the LLC must be perturbed by colloid inclusion as it must respond to local geometrical constraints imposed by the chemistry of the curved particle surface.^{42,43} The two extreme situations are homeotropic (perpendicular) or homogeneous (parallel) anchoring of the hydrophobic cores. For a spherical particle immersed in nematic liquid crystal media, homeotropic alignment results in a hyperbolic hedgehog defect or a disclination loop known as a “Saturn ring”;⁴⁴ homogeneous alignment results in two surface defects on the colloidal particle that are diametrically opposed and located at the poles (boojums defects). From TEM observations on the templated ZnS, it appears boojums-like defects are present; however, within the defect, homeotropic alignment is apparent. Stated another way, there

appears to be a parallel alignment of the rod-like pores in the ZnS that becomes perpendicular at the poles of the SiO₂ colloid. Atomic force microscopy, ellipsometry, and small angle neutron scattering observations of adsorption of C_nE_m nonionic surfactants to hydrophilic silica surfaces generally have shown micelles adsorbed with similar structures to those in bulk solution.^{45–47} This is because water molecules try to maximize the interaction between both the surface and the surfactant. On the contrary, hydrophobized silica surfaces showed surfactant bilayered structures.^{45,46} Given our colloids are hydrophilic, it is reasonable to expect a similar surfactant organization as on a hydrophilic surface but with the topological constraint given by the curved surface and the perpendicular anchoring of the hexagonal rods at the poles, resulting in the boojums-like defects mentioned previously. At the volume concentration used, SiO₂ colloids are well separated from each other and probably do not interact; under optical microscopy, the colloids do not appear clustered.

Additional information on the nature of the ZnS shell is obtained from SEM. Figure 9 presents the SEM micrographs of ZnS coated SiO₂ and the resultant ZnS shell after core removal. On bare silica colloids, the ZnS shell is rough and appears to be formed by irregular shaped crystals assembled into a “raspberry” like morphology; these shells are not uniform and often contain cracks as after etching of the SiO₂ core (Figure 9a,b). The ZnS shells formed on the carboxyl modified silica colloids have a finer grain structure than those formed on bare silica; however, some defects on the shell are apparent (Figure 9c). Those formed on PAA functionalized silica are substantially more uniform and robust and appear defect free at the resolution of the SEM (Figure 9d). For the PAA case, no exploded or incomplete hollow spheres

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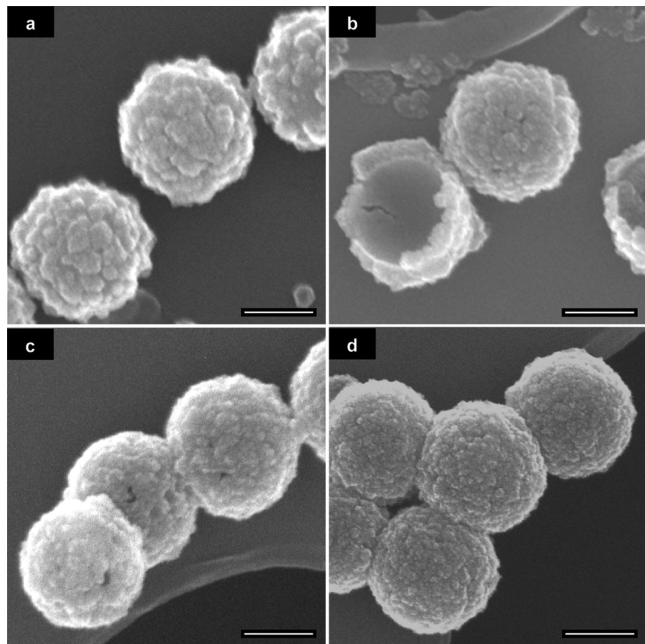


Figure 9. SEM micrographs of ZnS deposited on bare silica particles before (a) and after (b) silica etching and ZnS shells formed around (c) carboxylate modified SiO_2 colloids and (d) PAA modified SiO_2 colloids. All scale bars are 200 nm.

were observed, demonstrating the importance of the colloidal surface chemical modification for obtaining a uniform product.

Conclusions

It is clear that functionalization of the surface of the colloidal particles dramatically improves the fidelity of the

templating process.⁴⁸ Although we do not completely understand the details of the templating process, it is also clear from the data that both metal ion complexation and favorable LLC–surface interactions are important. It is also probable that the highly hydrophilic surface presented by PAA functionalized colloids improves the organization of the LLC around the colloid and thus the structure of the resultant ZnS. As previously mentioned, while ZnS templating was successful on both PAA and EDATAS modified colloids, the ZnS shells grown around these colloids sometimes showed “scars” or cracks while the PAA modified ones did not. The nature of the organization of the LLC template around the colloidal particle appears to be most consistent with the parallel anchoring of the hexagonal rods, with an expanded boojums-like defect at the poles.^{49,50}

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