Double Direct Templating of Periodically Nanostructured Inorganic Hollow Microspheres

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INTRODUCTION

Hollow capsules are both technologically and scientifically interesting. ‘Smart’ nano and micro containers could lead to structures for the controlled release of chemicals and materials that may even mimic properties of living cells. The synthesis of core-shell particles and capsules is a rapidly expanding research direction for these and other applications. 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. Significant efforts are similarly focused on the synthesis of inorganic mesoporous materials with 1 to 50 nm diameter pores, the ideal size for controlling macromolecule transport and adsorption. Among the numerous approaches for obtaining mesostructured materials, lyotropic liquid crystal templating emerges for its simplicity. 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 to 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. Here we present a ‘double direct templating’ approach to obtain hollow ZnS microspheres perforated with a periodic array of uniform pores. 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 demonstrate the entrapment of Au nanoparticles, and proteins within these microspheres as well as the effect of colloid surface chemistry on the fidelity of the templating process.

EXPERIMENTAL

We prepared a 50 % w/w mixture of a nonionic surfactant (Brij®97) and an aqueous solution containing a suspension of silica 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). 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 work-up. For some experiments, enzymes were entrapped within the silica colloids. The surface of the colloid was modified as necessary for experiments where the effect of colloid surface chemistry was evaluated.

RESULTS AND DISCUSSION

After etching the silica core, TEM observations of mesostructure of the ZnS shells were performed. Before etching, the shell mesostructure is difficult to observe because the colloidal core is too thick for optimal imaging. However, after etching of the core, TEM shows clear evidence of the hollow nature of the spheres; all particles show a defined and dark edge and much more transparent center (Figure 1). The fact that the core can be readily removed is a good indicator that the pores present in the ZnS wall allow the etching of the silica colloid. The surface chemistry of the colloidal template turns out to have a very significant impact on the quality of the shell wall. Although, bare silica colloids do yield a templated shell, the quality of the templating is not optimal. After investigating a wide range of possible surface chemistries, poly(acrylic acid) (PAA) functionalized colloids were found to yield the highest quality mesostructured ZnS shell wall (Figure 1). We suspect the PAA yields the highest quality templated ZnS because of the strong chelating of divalent ions, such as ZnS, with PAA.

Figure 1. ZnS hollow sphere obtained from a PAA modified silica colloid. The silica colloid has been etched with ethanolic HF.

Along with formation of the templated hollow sphere, we have also demonstrated a number of important properties for application. First, we have demonstrated that active enzymes can be entrapped within the hollow sphere. Second, we have demonstrated that the shell wall chemistry can be modified through cation exchange reactions. Although we have not finished our investigation, it is likely this will provide a pathway for modifying the diameter of the pores in the shell wall. Third, these hollow capsules are quite robust. They do not collapse, even under the strong forces imposed on drying from a high surface tension solvent such as water.
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REFERENCES