Creation of Templated Complex Topological Morphologies in Colloidal Silica

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Abstract: We have developed a new method to create complex monodisperse silicon dioxide particles which contain voids with unique morphologies. These particles are prepared from monodisperse silica spheres (*ca.* 100 nm) which contain CdS inclusions organized as large patches on the silica sphere surfaces, as small quantum dots within the spheres, as interior spherical shells, or as the central cores of the silica spheres. We create voids with the identical morphology as the CdS inclusions by etching out the CdS inclusions with strong acid. The silica sphere–CdS composite particles are prepared within a microemulsion reaction medium as described in the accompanying paper (Chang, S.-Y.; et al. *J. Am. Chem. Soc.*, preceding paper in this issue). The etched silica particles have craters on their surface, 2.4-nm diameter spherical voids dispersed within the silica spheres, hollow cores, or hollow shells separating silica shells from silica cores. In addition, we have formed unique ellipsoidal cavities within doublets of silica spheres. These doublets were formed through the attachment of silica spheres by CdS patches on the silica surfaces. A silica shell was subsequently grown around the sphere doublets. Etching away the CdS results in ellipsoidal caverns connecting the two spheres of each doublet. These high surface area materials have geometrically tailorable voids and may prove useful as novel catalyst support media.

Introduction

One major frontier of chemical synthesis is the development of novel methodologies to create tailor-made complex morphologies within macromolecular complexes. The argument is that these complex morphologies can be used for creating sophisticated chemical processes where an assembly line of chemical reactions can be linked within connected regions of macromolecular entities. In the accompanying paper[1] in this issue, we describe the microemulsion synthesis of *ca.* 40–300-nm monodisperse silica–CdS colloids, where the CdS inclusions were incorporated within porous silica spheres. These inclusions were synthesized as quantum dots uniformly dispersed in the silica spheres, as large surface caps, as surface quantum dots, as cores of CdS surrounded by silica shells, or as a set of concentric spherical shells of silica, CdS, silica, etc., i.e., multidecker sandwiches.

We describe here a method to further process these nanocomposite spheres in order to form complex voids within the silica colloids. This processing forms voids identical in shape and volume to the original CdS inclusions by quantitatively etching out the CdS inclusions. For the homogeneously dispersed quantum dots, this results in numerous small (*ca.* 2.5 nm) spherical voids, while the CdS core–silica sphere composites yield silica spheres with spherical voids at their centers. More complex annular voids are formed from the silica–CdS shells, while craters are formed from the silica spheres with surface CdS patches.

Numerous other research groups are also developing approaches to create complex nanostructure morphologies in various materials. For example, a number of groups have prepared hollow inorganic powders by dehydration and decomposition of aerosol particles or through the removal of solvent from the interior of particles. However, these approaches do not permit careful control of the void sizes and shapes.[2–4] Matijevic's group has prepared hollow particles by the thermal decomposition of the polymer cores of particles prepared such that a polymer core was overcoated by a shell of thermally stable inorganic material.[5]

Our approach described here[1] allows us to create these voids at room temperature; in addition, our silica particles contain voids within pure silica cavities. These cavities can be further modified using the standard chemical approaches for silica surfaces. We expect that the approach outlined here is of general utility and can easily be extended to other materials such as titania and alumina. We expect that these porous materials with well-defined voids will find utility in areas of technology such as catalysis.

Materials and Procedures

The detailed procedures for preparing the CdS–silica nanocomposites are given in the accompanying paper.[1] Typically, a reaction utilized a 250-mL microemulsion containing 0.127–0.184 M NH_3, 0.086–0.537 M Igepal CO-520 or Triton N-101, and 0.053–0.179 M tetraethyl orthosilicate (TEOS, Fluka), with the remainder of the reaction mixture consisting of cyclohexane and hexanol.

Nanocomposite colloids of silica–CdS were synthesized using either Igepal or Triton microemulsions containing Cd^{2+} and S^{2-} ions. The CdS inclusions were implanted through the precipitation of CdS during the simultaneous condensation of silica due to the simultaneous injection of TEOS. The resulting yellow nanocomposites were solvent exchanged into water and washed several times with concentrated nitric acid until the yellow CdS inclusions were completely dissolved and the turbid solution became white. The final product was a pure colloidal silica suspension. Surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beta Scientific Corp.).

Results and Discussion

As indicated in the preceding paper,[1] CdS inclusions can be incorporated in monodisperse silica spheres in a variety of morphologies. These morphologies are determined by the timing and the precipitation rate of the CdS during the growth of the silica spheres in the microemulsion reaction medium. As indicated schematically in Figure 1, the CdS inclusions can be prepared as large patches on the surface, as uniform quantum dot inclusions within the spheres, as the cores of the silica particles, as annular

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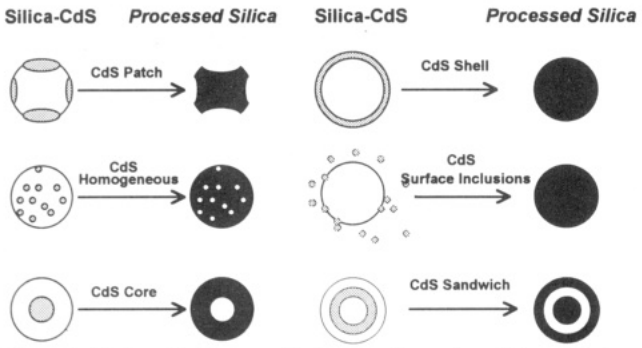
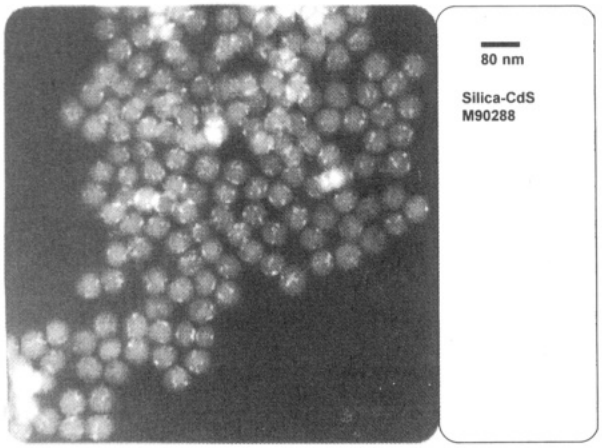


Figure 1. Schematic diagram illustrating the various silica–cadmium sulfide nanocomposites that can be synthesized and the resulting particle formed after the acid etching removal of the CdS inclusions.



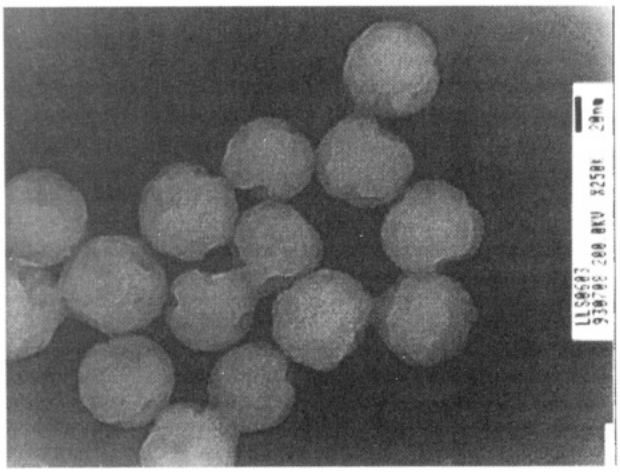


Figure 2. (a) TEM micrographs of nanocomposite particles with cadmium sulfide surface patches before nitric acid etching. (b) TEM micrographs after etching. The bare silica particles show craters on the surface where the cadmium sulfide patches were removed.

shells within a silica–CdS sandwich arrangement, or as small quantum dots on the surface.

Pure silica does not react with strong acids except for HF. In contrast, CdS is very soluble in strong acids, which readily dissolve the CdS inclusions. Figures 2a and b show a CdS–silica nanocomposite with CdS patches on the surface before and after acid etching; acid etching forms craters on the surface.

Figure 3 shows a TEM micrograph of *ca.* 50-nm CdS–silica nanocomposite spheres with homogeneously dispersed CdS quantum dots after acid etching. The figure demonstrates numerous dimples on the surface. It is difficult to clearly visualize the interior small 2.5-nm voids by TEM. However, the fact that the sample is no longer yellow indicates that the interior CdS inclusions have been removed. Further, the BET surface area

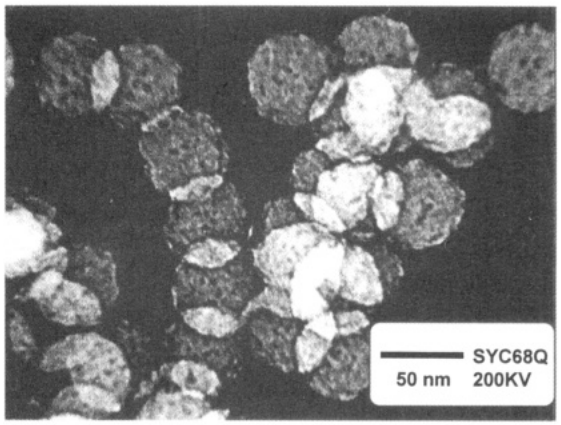


Figure 3. TEM micrographs of nanocomposite particles with cadmium sulfide quantum dots homogeneously distributed after etching. The bare silica particles show dimples where the cadmium sulfide quantum dots were removed on the surface. The interior voids cannot be clearly visualized.

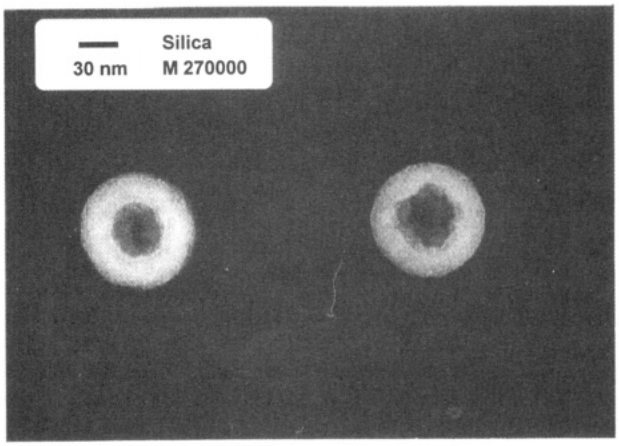


Figure 4. TEM micrograph of spheres where large *ca.* 30-nm CdS cores were removed by acid etching to leave large spherical voids.

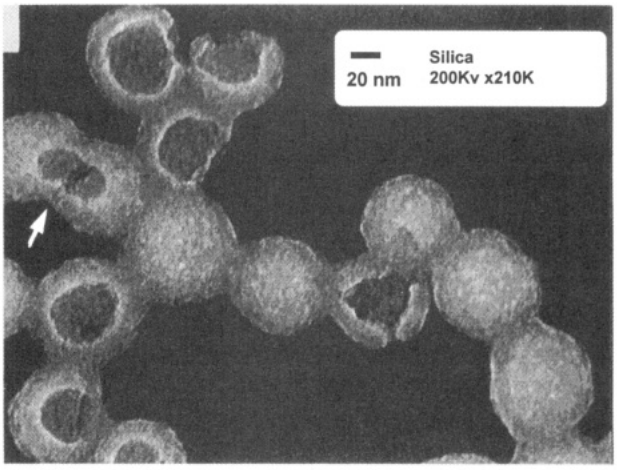


Figure 5. TEM micrograph of silica sphere doublets after acid etching. These doublets were formed during the synthesis of silica spheres with CdS patches.[1] The doublets are attached at CdS welds, and the doublets are overcoated with silica shells. Acid etching of the doublets resulted in ellipsoidal caverns joining the sphere doublets.

measurements discussed below demonstrate that the particles contain numerous *ca.* 2.5-nm diameter spherical cavities.

Acid etching of *ca.* 30-nm silica colloids which originally contained 4–8-nm CdS cores results in central voids. Our accompanying paper shows a TEM photograph of this preparation after acid etching. The dark central spots result from the small hollow spherical voids. We also can create larger spherical

Table 1. Calculated and Measured BET Surface Areas for Silica–CdS Composite Spheres before and after Acid Etching

			surface area (m^2/g)			
			measured		calculated	
sample	particle morphology	particle size (nm)	before etching	after etching	before etching[a]	after etching[a]
SYC121Q	shell, plus doublets and triplets	80	61	232	39	169
SYC122Q	shell, plus doublet and triplets	84	76	208	37	179
SYC68Q	homogeneous holes	62	104	152	51	102

[a] Ignoring aggregates and assuming density of 1.9 g/cm^3.

cavities. Figure 4 shows hollow *ca.* 90-nm particles with *ca.* 30-nm diameter holes. We can easily construct silica colloids with diameters as large as 300 nm with hollow cores of any size desired.

Figure 5 shows acid-etched doublets of silica spheres. These doublets were formed through the attachment of silica particles by welds of CdS surface patches. Subsequently a silica shell was formed around the sphere doublets. Acid etching results in ellipsoidal cavities where the CdS welds between the spheres were removed to form ellipsoidal caverns joining the spheres.

We directly measured the increase in the sample surface area by BET nitrogen absorption measurements after acid etching. Table 1 shows the measured surface areas and that calculated using simple models for samples SYC121Q and SYC122Q, where the CdS was formed as annular rings within the silica spheres, and sample SYC68Q, where CdS quantum dots were homogeneously distributed in the silica spheres. The samples with the CdS annular shells had large concentrations of doublet and triplet spheres.

If the spheres are nonporous, we can calculate that the surface area, A (m^2/gm), of the silica sphere–CdS composites is simply the surface area of the spherical particles:

$$A = 6000W/d\rho$$

where W is the weight of the sample (1.0 g), d is the sphere diameter (nm), and ρ is the density (g/cm^3) of the silica–CdS sphere composites.

We see that prior to etching the area measured is approximately 2-fold greater than that calculated. The larger surface area of the sample probably results from pores within the silica spheres; silica colloids made by the Stöber process are often highly porous,[1,6] with porosities as large as 11–15%. However, varying the preparation conditions can dramatically decrease the porosity.[7,8] The silica–CdS composite spheres prepared here appear to be much less porous than the highly porous Stöber silica spheres. The surface areas associated with the pores can be very large, depending on the pore diameters. For example, 10% porous 80-nm silica spheres with 0.4-nm diameter pores are calculated to show surface areas greater than 600 m^2/g. Our silica–CdS composite samples show silica sphere internal surface areas 10-fold smaller. However, our silica–CdS composite spheres are at least somewhat porous, since the entire particle volume is readily accessible to chemical reagents such as nitric acid, which dissolves the CdS.

After etching, the surface area increases 3–4-fold for samples SYC121Q and SYC122Q and by 50% for sample SYC68Q. For samples SYC121Q and SYC122Q, we modeled the increase in surface area to be that associated with the surface area of the void shell that originally contained CdS. For sample SYC68Q, the surface area increase calculated was that which resulted from the 2.4-nm spherical voids formed by removal of the CdS quantum dots in the spheres:

$$A_c = 6000WR/\rho_c d_c$$

where A_c is the surface area which results from the voids created by removal of the CdS quantum dots, R is the weight ratio of CdS to silica ($R = 0.105$ for sample SYC68Q), ρ_c is the density of CdS, and d_c is the diameter of the voids (2.4 nm).

The measured increases in surface area are very close to those calculated from the simple models. This result supports the idea that we have tailored voids in the silica spheres which are geometrically well defined in size and shape and in their location within the silica spheres.

Conclusions

We have demonstrated a new method to form silica particles with voids of a variety of morphologies. The relative amounts, sizes, and positions can be easily and accurately controlled. These monodisperse silica spheres are porous, and additional chemistry can be used to further modify the cavity surfaces. These materials will be useful for catalyst support applications and for novel other applications where it is important to carry out chemical reactions in separate small chambers.

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