

PREPARATION AND PROCESSING OF MONODISPERSE COLLOIDAL SILICA-CADMIUM SULFIDE NANOCOMPOSITES

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ABSTRACT

A novel synthetic methodology has been developed for preparing monodisperse colloidal silica-cadmium sulfide nanocomposite spheres in the 50 - 300 nm size regime. This methodology uses water-in-oil microemulsions as the reaction medium. Monosize silica colloids are first produced by the controlled hydrolysis of tetraethyl orthosilicate in the micro water droplets of the microemulsion. Cadmium sulfide quantum dots are incorporated into the silica colloids during synthesis by the introductions of Cd²⁺ and S²⁻ microemulsions. Various morphologies of the nanocomposite are fabricated by controlling the heterogeneous coagulation of CdS and SiO₂. Unique high surface area silica particles can be prepared when nitric acid etches out the CdS and leaves behind topologically defined voids. The CdS nanocomposites are new materials useful for non-linear optics, while the high surface area silica particles should have novel applications in areas such as catalysis.

INTRODUCTION

Development of methods to synthesize monodisperse particles is important for the advancement of numerous areas of science and technology¹. The development of new methods which give well defined but complex morphologies will present new opportunities in materials science. In this paper we describe a novel methodology to prepare monodisperse composite particles in the 50 nm to ~300 nm size range. Our major interest is to use these spherical particles in colloidal self-assembly processes for preparing crystalline colloidal arrays²⁻⁸ useful for novel optical devices. These nanoscale periodic materials are useful for fabricating optical devices because the spherical particles array themselves at the lattice sites of body centered cubic or face centered cubic arrays; these arrays efficiently diffract light in the visible and near IR spectral regions.

We are developing optically nonlinear

crystalline colloidal arrays (CCA) where the colloidal spheres are prepared from nonlinear materials.⁸ High incident light intensities alter the sphere refractive indices such that the array diffraction properties change. The nonlinear CCA would act as an optical limiter or switch. This application requires a material with a high nonlinear coefficient. CdS quantum dots may have among the largest optical nonlinearities known. Thus, we have developed synthetic methods to prepare CdS quantum dot inclusions in much larger monodisperse colloidal spheres.

This article describes the fabrication of a new nanocomposite composed of CdS quantum dots (ca 25 Å) uniformly dispersed in monodisperse silica spheres (40-150 nm). Furthermore, this method can be applied to fabricate nanocomposites where the CdS forms a core within each sphere, or where the CdS forms patches on the surface, or where it forms multidecker shells of silica, CdS, silica, etc.

MATERIALS AND PROCEDURES

The detailed procedures for preparing the CdS-silica nanocomposites are reported elsewhere.⁹ Cadmium nitrate (certified grade, Fisher), ammonium sulfide (certified grade, Fisher), and nitric acid (70.4%, Mallinckrodt) were used as received. The non-ionic surfactants Igepal CO-520 (GAF chemicals) and Triton N-101 (Rohm & Haas) were used to formulate water-in-oil microemulsions containing water, cyclohexane (Mallinckrodt) and hexanol (Aldrich). Typically, a reaction utilized a 250 ml microemulsion containing 0.127-0.184 M of NH₃, 0.086-0.537 M of Igepal CO-520 or Triton N-101, and 0.053-0.179 M of 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 Cd²⁺ and S²⁻ ions. The CdS inclusions were implanted through the precipitation of CdS during the simultaneous condensation of silica. This CdS implant results in yellow nanocomposites. However, the yellow CdS inclusions can be dissolved to recover white silica alone when washed with concentrated nitric acid.

Transmission electron microscopes (JOEL 2000FX and Zeiss 902) and a x-ray diffractometer (X'pert, Philip) were used to determine the morphology/size and structure of the particles. Surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beta Scientific Corp.).

RESULTS AND DISCUSSION

Silica Particles Synthesis

Previous work¹⁰ has shown that monodisperse SiO₂ spheres can be grown in the size range of 40 to 70 nm by controlled

hydrolysis and condensation of TEOS within Igepal reverse micelles. The particle size and size distribution are sensitive to the microemulsion formulation, i.e. the ratio of water to surfactant concentration, w , and the ratio of water to alkoxide concentration, h . The polydispersity depends strongly on the alcohol concentration because of the sensitivity of the microemulsion phase diagram to the alcohol content. Increasing the alcohol concentration generally increases the polydispersity. This therefore limits the maximum concentration of TEOS which can be used for good monodispersity since the TEOS hydrolysis and condensation releases ethanol. Nevertheless, we find that higher concentrations of TEOS can be utilized in microemulsions containing Triton N-101 because this microemulsion is less sensitive to alcohol content. In this case the presence of the co-surfactant hexanol improves the particle size distribution.

The reaction kinetics were examined by monitoring the particle size evolution using TEM. Figure 1 shows the effects of w and h on particle growth in Igepal CO-520 microemulsions. For a constant ratio of water to TEOS of $h=4.8$, a decrease in the total water content (smaller w) results in a faster growth rate and larger spheres. This is exactly the opposite of what would occur in the Stober process. A decrease in water concentration is also reported to yield more polydisperse silica spheres.¹⁰ In contrast, we observe little dependence. Our synthesis with $h=4.8$ and $w=5$ gave 46 nm spheres with a size relative standard deviation of 5.2%, while for $h=4.8$ and $w=1$ the 55.8 nm spheres had a size relative standard deviation of 4.0%.

For a constant w , an increase in h decreases the growth rate and the particle size. The synthesis in a microemulsion with $w=1$, $h=4.8$ yields 55.8 nm spheres, while a synthesis with $w=1$, $h=10$ yields 50.4 nm spheres. This is contrast to that in Stober process, where an increased h increases the

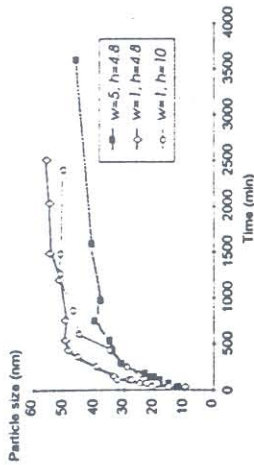


Figure 1. Growth kinetics of silica colloid in Igepal CO-520 microemulsion.

hydrolysis rate and increases the particle size.¹² We examined the dependence of the microemulsion reaction on ammonia concentration, and found little dependence. This also is much different than in the Stober process, where the NH_3 concentration determines the hydrolysis rate and the particle size.

Silica-CdS Sphere Composites

CdS quantum dot inclusions in the monodisperse silica spheres were obtained by injecting microemulsions containing Cd^{2+} and S^{2-} ions into the growing silica sphere microemulsions. This process involves the controlled co-precipitation of SiO_2 and CdS. By altering the order and timing of the injections, various tailored morphologies for the composite particles can be obtained. Figure 2 schematically demonstrates the types of morphologies we have prepared. These types including homogeneously distributed CdS spheres (raisin bread), large patches of CdS, cores of CdS, shells of CdS, CdS sandwiches and exterior bound CdS quantum dots (freckles). A typical micrograph for the raisin bread type is given in Fig. 3 where it is easy to visualize the ultrafine CdS dots dispersed in silica particles.

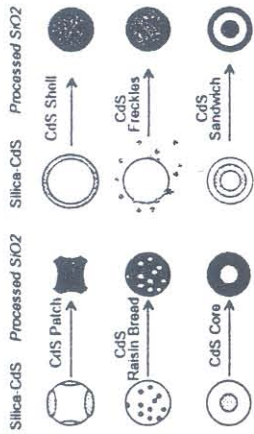


Figure 2. Schematic diagrams of various SiO_2 -CdS nanocomposites before and after acid etching.

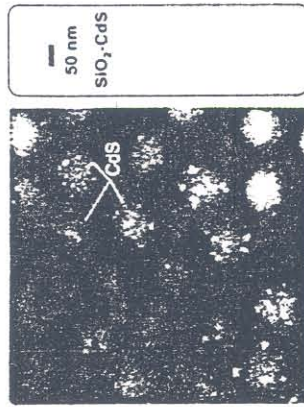


Figure 3. Typical SiO_2 colloids with CdS homogeneously dispersed within.

Chemical Composition and Structure

Elemental composition of the CdS- SiO_2 sphere composites were determined by using SEM/EDS. A typical spectrum of EDS is given in the upper right of Fig. 4 where the separate peaks from the Si, Cd and S were used to determine the relative atomic concentrations. X-ray powder diffraction measurements, also shown in Fig. 4, of the silica spheres give a broad peak that indicates that the SiO_2 is not crystalline, but is instead amorphous. The silica-CdS sphere composites show sharper peaks for the CdS

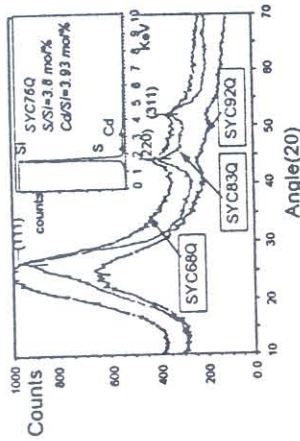


Figure 4. SEM/EDS and x-ray powder diffraction spectra for SiO_2 -CdS nanocomposite colloids.

inclusions. The positions of these diffraction peaks indicate that the CdS inclusions are in a cubic phase of a Hawleyite structure.¹³

The CdS diffraction peaks are relatively broad due to the small size of the inclusions. Using the Scherrer diffraction formula we obtain 25 Å for the diameter of the CdS inclusions.

Quantum Confinement

CdS quantum dots show blue shifts of their band edge due to quantum confinement effects associated with the small size of the particles. Figure 5 shows the UV-visible absorption spectra of the pure silica spheres and the silica-CdS nanocomposite spheres. No absorption of the silica spheres is evident until ca 330 nm, although some increase in the background is evident from the increased light scattering which occurs at shorter wavelengths. For the silica-CdS composites a band edge occurs at ca 430 nm from the CdS inclusions. From the experimental correlation of band edge and quantum dot size¹², we estimate that the inclusion size is ca 24 Å, which is close to that estimated from both the TEM photographs and the x-ray diffraction peak width measurements.

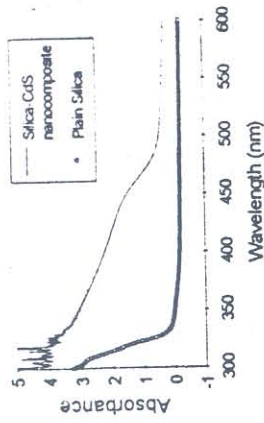


Figure 5. UV-visible absorption spectra for SiO_2 -CdS and plain SiO_2 colloidal suspensions.

Processing of SiO_2 -CdS Nanocomposite Particles

As indicated schematically in Fig. 2, CdS inclusions can be incorporated in monodisperse silica spheres in a variety of morphologies. The CdS inclusions can be prepared as large patches on the surface, or as uniform quantum dot inclusions within the spheres (raisin bread), or as the cores of the silica particles, or as annular shells within a silica-CdS sandwich arrangement, or as small quantum dots on the surface (freckles).

Pure silica does not react with strong acids except for HF. In contrast, CdS is very soluble in strong acids. Acids readily dissolve the CdS inclusions to leave a white silica residue. For example, Fig. 6 shows a CdS-silica nanocomposite with CdS patches on the surface after acid etching. Crater appear on the surface.

The TEM micrograph (Fig. 7) taken after acid etching of 50 nm raisin bread CdS silica nanocomposite spheres show numerous dimples on the surface and suggestions of internal voids. Figure 8 shows a TEM micrograph of acid etched 30 nm silica colloids which originally contained 4 - 8 nm CdS cores. The dark



Figure 6. SiO₂-CdS nanocomposite colloids with CdS patches after acid etching.

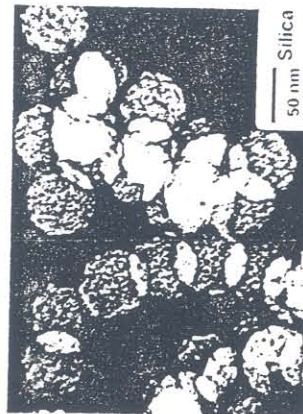


Figure 7. SiO₂-CdS raisin bread nanocomposite colloids with CdS after acid etching.

central spots result from small hollow spherical voids. We also can create larger hollow cavities as shown in Fig. 9. These hollow particles are ca 90 nm in outer diameter with ca 30 nm in inner diameter holes. Silica colloids can be constructed with diameters as large as 300 nm with hollow cores of any size desired.

The creation of these voids causes an increase of sphere surface area. BET nitrogen absorption measurements were employed to characterize this increase. Table I shows the surface areas of three samples before and after acid etching. The surface



Figure 8. SiO₂-CdS nanocomposite with CdS cores after acid etching.

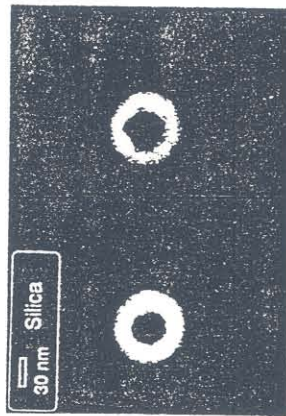


Figure 9. SiO₂-CdS composite colloids with large CdS core after acid etching.

Table I. Measured BET surface areas for silica-CdS composite spheres before and after acid etching.

sample	surface area (m ² /g)	
	measured before etching	measured after etching
68Q	62	104
121Q	80	61
122Q	84	76
		152
		232
		208

area increases are between 1.5- to 4-fold. Thus, this methodology can be used to create high surface area porous materials.

CONCLUSIONS

Silica colloid synthesis in water-in-oil microemulsions can be combined with co-precipitation of other materials to form complex nanocomposites with complex morphologies. We demonstrate the production of homogeneously dispersed CdS quantum dot-silica sphere composites, as well as other composites where the CdS inclusions are larger and are situated either at the particle centers or on the surfaces. These quantum dot composites are designed to be useful as new highly nonlinear optical materials. Our intention is to incorporate them into crystalline colloidal arrays for optical switching.

These nanocomposites can be further modified by the application of additional processing. We demonstrate the fabrication of new class of high surface area topologies in silica particles made by the etching removal of the CdS inclusions. These porous materials will be useful as matrices for catalysis support applications.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the Air Force Office of Scientific Research through grant number F49620-93-1-0008 to SAA and from the University of Pittsburgh Materials Research Center through the Air Force Office of Scientific Research Grant AFOSR-91-0441.

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