Preparation and Properties of Tailored Morphology, Monodisperse Colloidal Silica–Cadmium Sulfide Nanocomposites

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Received February 4, 1994®

Abstract: We have developed a new synthetic methodology for preparing *ca.* 40–300-nm monodisperse silica–cadmium sulfide nanocomposite spheres. This methodology uses water-in-oil microemulsions in which monodisperse silica colloids are produced by the controlled hydrolysis of tetraethyl orthosilicate (TEOS) in water nanodroplets. The resulting pure silica spheres can be grown to between 40 and 80 nm in diameter and can be used as seed particles for production of larger silica colloids upon further reactions with TEOS in the microemulsion. Cadmium sulfide quantum dots are incorporated into the silica colloids during the silica sphere synthesis by the simultaneous coprecipitation of cadmium nitrate and ammonium sulfide in the water nanodroplets. The CdS can be introduced as a homogeneous dispersion of CdS quantum dots (*ca.* 25 Å diameter), as large inclusions, as surface caps, as the central core of a silica particle, or as shells of CdS interleaved between silica shells. These different nanoscale complex morphologies in silica are created by controlling the coprecipitation of CdS. Techniques including TEM, SEM/EDS, X-ray diffraction, and light scattering were used to characterize the elemental analysis as well as particle morphology. In addition, we have prepared doublet and triplet spheres which are connected by welds of CdS. This silica–CdS nanocomposite is a new material with potential utility for nonlinear optics. Further processing makes this material useful for a new class of high surface area catalytic supporting materials.

Introduction

Synthetic chemistry is a mature science which has developed a host of successful strategies for fabricating complex molecular structures. For example, methodologies have been developed to make clusters of atoms and molecules such as, buckminsterfullerene[1] and CdS quantum dots.[2-6] The present frontier of chemical synthesis involves development both of strategies to create even larger assemblies, with molecular weights greater than 10^9 g/mol, and of assemblies composed of complex composites of macromolecular size.

In this regard, numerous groups have developed synthetic methods to form monodisperse particles of organic polymers[7,8] or of inorganic materials.[9] Generally these particles are spherical and have molecular weights greater than 10^9 g/mol. In special cases these particles can be nonspherical and may have unique materials science applications.

One objective of this work discussed here is to use these monodisperse particles for new ceramic materials or for use as catalyst supports. One major interest, however, is to use these spherical particles in colloidal self-assembly processes for preparing crystalline colloidal arrays.[10-16] 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, which efficiently diffract light in the visible or near-IR spectral regions.

It would be desirable to prepare nonlinear crystalline colloidal arrays where the colloidal spheres were prepared from nonlinear materials which changed their refractive indexes such that the diffraction properties of the array changed at high incident light intensities. The material could act as an optical limiter or switch. In this regard, the refractive indices of the spherical colloidal particles would change as the incident light intensity increased. Our choice for the nonlinear material has centered on CdS quantum dots.

CdS quantum dots have among the largest optical nonlinearities known. In this report we describe the fabrication of new nanocomposites composed of CdS quantum dots (*ca.* 25 Å) uniformly dispersed in monodisperse silica spheres in the size range of 40–150 nm. In addition, our preparation can be used to fabricate nanocomposites where the CdS forms patches within the spheres and on the surfaces of the spheres, as well as forming a CdS core in the silica spheres. In addition, we can form multidecker shells of silica, CdS, silica, etc.

In an accompanying paper[17] we demonstrate that we can selectively etch out the CdS inclusions to form silica spheres with complex cavities and porosities. These porous systems will be useful for novel supporting materials for catalytic applications.

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® Abstract published in *Advance ACS Abstracts*, June 15, 1994.

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Our approach for this new synthesis utilizes water-in-oil microemulsions where the silica spheres are synthesized by the hydrolysis of tetraethoxysilane (TEOS), followed by its condensation in the water nanodroplets. This microemulsion method of formation of silica spheres was recently reported by Ossea-Asare and Arriagada.[18] We have combined this method of synthesis of silica spheres with the controlled precipitation of CdS particulates in water nanodroplets in these water-in-oil microemulsions. This work follows previous demonstrations by others that monodisperse CdS quantum dots can also be synthesized in water-in-oil microemulsions.[2-6] We have combined these approaches to, for the first time, prepare monodisperse CdS quantum dot inclusions in monodisperse silica sphere colloids.

Our microemulsion approach, which yields more uniform spheres than the classic Stöber process[19] for the smaller size range (30–150 nm), gives comparable uniformities for larger spheres (150–300 nm). We believe we have developed a simple general approach for creating nanocomposites with complex morphologies which can be used for a variety of materials, such as CdSe, etc., in silica spheres or for synthesizing spherical colloids made of other materials, such as alumina, etc. We also have developed an approach to synthesize doublets and triplets of spheres where the CdS acts as a weld between spheres.

Experimental Section

Water-in-oil microemulsions were prepared from nonionic surfactants using procedures similar to those of Osseo-Asare and Arriagada.[18] We used two nonionic surfactants, poly(oxyethylene) nonylphenyl ether with an average of five oxyethylene groups per molecule (Igepal CO520) from GAF Chemical and obtained from Aldrich Chemical and Triton N-101 from Rohm and Haas (obtained from Fluka). Both surfactants were used without further purification. The tetraethyl orthosilicate (TEOS, 99%, Fluka) was distilled before use. The other chemicals, such as cyclohexane (Fisher Scientific), hexyl alcohol (Aldrich), ammonium hydroxide (29%, Mallinckrodt), cadmium nitrate (certified, Fisher Scientific), ammonium sulfide (22%, Fisher Scientific), and deionized water (obtained using a Nanopure water purifier, Barnstead Co.), were used as received.

The microemulsion reaction matrix was prepared using either Igepal CO-520 or Triton N-101. Although different detailed recipes were used for each preparation, a typical recipe would involve 270 mL of a microemulsion prepared at ambient temperature in a 500-mL four-neck reaction flask stirred by a Teflon paddle connected to a high torque stirring motor. The microemulsion reactant concentrations were 5.20 M cyclohexane, 0.72 M H_2O, 0.18 M hexanol, 0.12 M Triton N-101, and 0.094 M NH_4OH. The Igepal CO-520 microemulsions contained a similar surfactant concentration but contained no hexanol. Ten milliliters of pure TEOS liquid was injected within 10 min into the stirred microemulsion matrix by using a syringe pump. As the reaction proceeded over a period of 24 h, the TEOS slowly hydrolyzed, and $Si(OH)_4$ precipitated and condensed within the water nanodroplets to eventually form monodisperse SiO_2 spheres.

The SiO_2–CdS quantum dot sphere composites were made by injecting separate microemulsions containing Cd^{2+} and S^{2-}. To produce 10% (by mole) CdS quantum dot inclusions, we injected approximately 54 mL of two microemulsions containing either $Cd(NO_3)_2$ or $(NH_4)_2S$. These microemulsions contained the following final reactant concentrations: 26.85 M cyclohexane, 1.65 M H_2O, 0.41 M hexanol, 0.275 M Triton N-101, and 4.48×10^{-3} M $Cd(NO_3)_2$ or $(NH_4)_2S$. These microemulsions were prepared by addition of the aqueous salt solutions to the microemulsion.

The order and timing of injection of the TEOS and the $Cd(NO_3)_2$ and $(NH_4)_2S$ microemulsions determine the CdS morphology within the SiO_2 spheres. For example, to make uniformly dispersed CdS quantum dots in the SiO_2 spheres, we first injected the TEOS solution within 10 min and 1 h later began injecting the $Cd(NO_3)_2$ and $(NH_4)_2S$ microemulsions. We simultaneously injected these two solutions over a period of 24 h. It is important to note that the TEOS reaction rate is much slower in the microemulsions than that in the Stöber process.

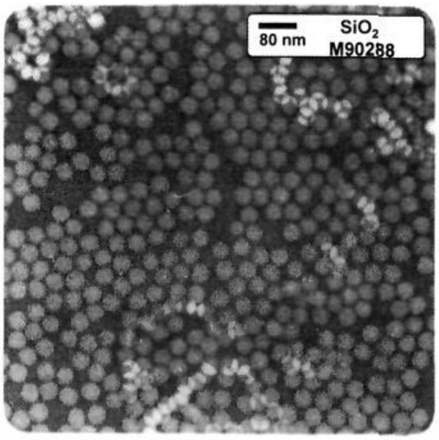

Figure 1. TEM micrograph of monodisperse silica spheres synthesized in an Igepal CO-520 microemulsion with $w = 5$, $h = 4.8$, 0.0537 M TEOS, and 0.1269 M NH_3 (size relative standard deviation is 4.2%).

The particle morphology was examined by transmission electron microscopy (TEM) (JEOL 2000FX/LINK AN10000 and Zeiss 902). The micrographs were analyzed by using a digital imaging system (BioScan, Inc., WA). Energy dispersive scanning electron microscopy X-ray analysis (JEOL 35CF) was employed for semiquantitative element determinations. The samples were prepared for SEM/EDS by drying a dispersion of the reaction products on a carbon stage and transferring this stage to the microscope. The colloids were washed, solvent exchanged, and dialyzed before Zeta potential determinations made by using a Malvern Zetasizer 4 electrophoretic light scattering instrument. Particle surface areas were measured by using the BET nitrogen absorption method (Automatic Surface Area Analyzer 4200, Beta Scientific Corp.). The crystal structures were determined by X-ray powder diffraction measurements of freeze-dried nanocomposite particles (Philips X'PERT). Absorption measurements to investigate CdS quantum confinement effects were performed by directly examining the liquid reaction products by using a UV–visible/near-IR spectrometer (Perkin-Elmer, Lambda 9).

Results

Silica Sphere Growth. Previous studies by Arrigada and Osseao-Asare[18] demonstrated that monodisperse, small SiO_2 spheres can be grown in the size range of 40–70 nm by controlled hydrolysis and condensation of TEOS within reverse micelles. We have scaled up this synthesis by 50-fold for preparative purposes and developed new synthetic methods for creating complex nanocomposites. Figure 1 shows a TEM micrograph of 41.3-nm SiO_2 spheres prepared by using a microemulsion with Igepal CO-520 surfactant. The reaction utilized a concentration 0.0537 M TEOS and 0.1269 M NH_3 with a water-to-surfactant concentration ratio, w, of 5 (w = [water]/[surfactant]) and a water-to-TEOS concentration ratio, h, of 4.8 (h = [water]/[TEOS]). The silica sphere diameter and the diameter distribution are sensitive to reactant concentrations; the w value is most important for determining size. Increasing the alcohol concentration gradually increases the polydispersity because of the sensitivity of the microemulsion phase diagram to the alcohol content. This limits the maximum concentration of TEOS which can be used since TEOS hydrolysis releases ethanol. For example, we find that the relative standard deviation in particle size increases from 5% to 14% as we increase the TEOS concentration from 0.09 to 0.179 M.

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 hexanol as a cosurfactant improves the uniformity. For example, we synthesized silica particles with an average diameter of 76 nm with a relative standard deviation of 4.8% by using a triton N-101 microemulsion containing 0.179 M TEOS and 0.15 M NH_3 with $w = 6$, $h = 6$, and $cs = 4$ (cs = [water]/[hexanol]).

Arragada and Osseo-Asare have shown for Igepal microemulsions that increasing w decreases the particle size and results in

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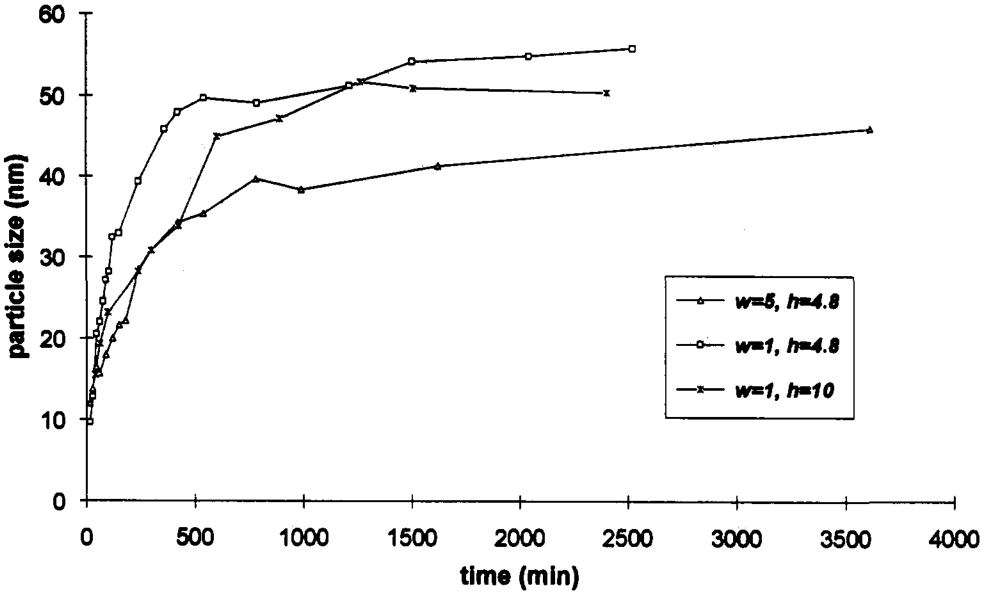

Figure 2. Particle size evolution for silica spheres synthesized in Igepal CO-520 microemulsions with different values of *w* and *h*.

better uniformity. However, we observe that Triton N-101 microemulsions permit higher *w* values, which allow us to double the particle diameter while maintaining an excellent uniformity. Although Triton N-101 and Igepal CO-520 have similar chemical structures, they have different molecular weights. Our results indicate that Triton N-101 microemulsions can be used to synthesize larger monodisperse silica spheres.

We examined the reaction kinetics by monitoring the time dependence of the particle size by using TEM. Figure 2 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 Stöber process. A decrease in water concentration is also reported to yield more polydisperse silica spheres.[18] 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 56-nm spheres had a size relative standard deviation of 4.0%.

For a constant *w*, increasing *h* decreases the growth rate and the particle size. The synthesis with $w = 1$, $h = 4.8$ yields 56-nm spheres, while a synthesis with $w = 1$, $h = 10$ yields 50-nm spheres. This contrasts to the Stöber process, where an increased *h* increases the hydrolysis rate and increases the particle size.[20] We find little dependence of the reaction on ammonia concentration. This differs from the Stöber process, where the NH_3 concentration determines the hydrolysis rate and the particle size.

Nucleation and Growth of Large Particles. To obtain larger silica spheres, we continued the growth of small monodisperse spheres by adding additional TEOS after the original growth phase. This technique is similar to that demonstrated by Unger's group for the Stöber process.[28] We probably can grow monodisperse silica spheres as large as 300 nm by this process. This process also allows us to accurately synthesize any desired particle diameter in the range of 40–300 nm since the final diameter is determined solely by the initial size of the seed silica sphere and by the additional TEOS added, which totally condenses upon the seeds without formation of any new silica spheres. This is evident from Table 1, which compares the size expected to that determined for the larger silica spheres grown from the smaller silica nuclei.

Table 1. Results of Second Growth of Silica Colloids in Triton N-101 Microemulsions

sample	initial size (nm)	no. of particles	additional TEOS (mol)	expected size (nm)	determined size (nm)
SYC101RG	77 ± 5	1.2×10^{15}	2.2×10^{-2}	134	129 ± 6
SYC107RG1	77 ± 4	1.2×10^{15}	1.8×10^{-2}	110	103 ± 5
SYC107RG2	76 ± 4	1.2×10^{15}	1.8×10^{-2}	110	112 ± 7
SYC107RG4	76 ± 4	1.2×10^{15}	6.7×10^{-2}	150	147 ± 6

Silica–CdS Sphere Composites. CdS quantum dots incorporated in the monodisperse silica spheres were obtained by injecting microemulsions containing Cd^{2+} and S^{2-} ions into the growing silica spheres. This process involves the controlled coprecipitation of SiO_2 and CdS. As shown in Figure 3, different morphologies could be prepared by altering the order and timing of the injection. These morphologies include homogeneously distributed CdS quantum dots, large patches of CdS, cores of CdS, shells of CdS, CdS sandwiches, and exterior bound CdS quantum dots.

Homogeneously distributed CdS dots were prepared by pulsed injection of the Cd^{2+} and S^{2-} microemulsions, with a pulsation rate proportional to the increasing volume of silica spheres. Figure 4 shows a TEM micrograph of silica spheres containing uniformly dispersed *ca.* 25-Å CdS quantum dots (vide infra) at a final CdS concentration of 3 mol %. These *ca.* 100-nm composite silica–CdS spheres were synthesized by using 50 mL of a Triton N101 microemulsion with $w = 6$, $h = 6$, and $sc = 4$ to grow silica sphere nuclei of 76 nm. After formation of these nuclei, 4 mL of pure TEOS was quickly injected, and two streams containing Cd^{2+} and S^{2-} microemulsions were injected in a pulsed mode over a period of 24 h. Initially the Cd^{2+} and S^{2-} microemulsions were injected in 10-s pulses to each deliver 5×10^{-4} mol of Cd^{2+} and S^{2-} ions. A 40-s interval followed each 10-s injection. Over a period of 24 h, we gradually increased the injection time to deliver an increasing amount of Cd^{2+} and S^{2-} ions during each cycle to ultimately result in a final concentration of 3 mol % CdS inclusions in the silica spheres.

Figure 5 shows a TEM micrograph of silica spheres with

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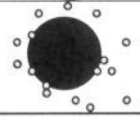
CdS distribution in SiO_2	Morphology of composite particles
CdS Homogeneous	
CdS Surface Patch	
CdS Core	
CdS Shell	
CdS Sandwich	
CdS Surface Inclusions	

Figure 3. Schematic illustrating the fabricated morphologies of silica–CdS composites.

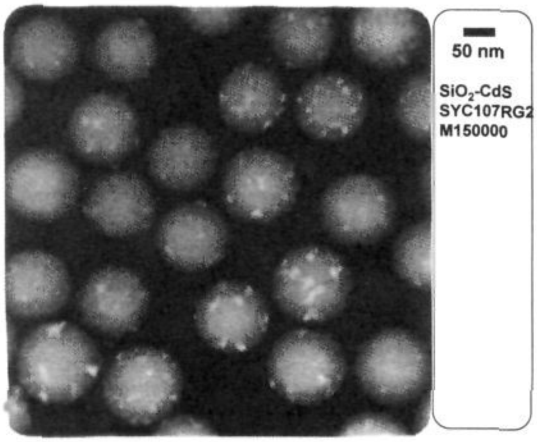


Figure 4. TEM micrograph of homogeneously distribution of CdS dots in silica–CdS nanocomposite spheres.

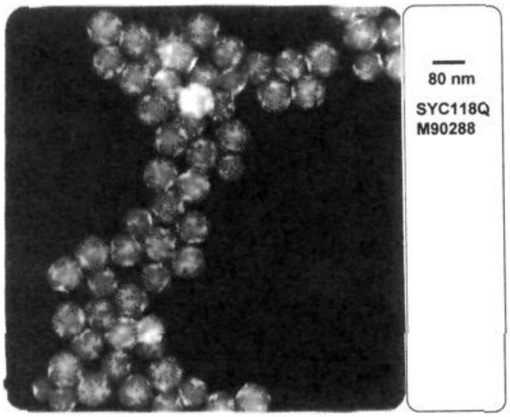


Figure 5. TEM micrograph of silica–CdS nanocomposite spheres with CdS patches within and on the sphere surface.

cadmium sulfide patches on the surface and within the interior. These nanocomposite spheres were prepared by injecting a larger amount of the Cd and S microemulsions at each injection while utilizing fewer injections.

The CdS core silica particles (Figure 6) were prepared by first synthesizing 6-nm CdS cores in the microemulsion with $w = 3$, $h = 4.8$ and subsequently growing silica spheres around the cores to a final 39-nm diameter. To synthesize the CdS cores, two Igepal microemulsions containing the Cd and S ions were slowly injected into an identical Igepal microemulsion. The total amount of Cd and S added depended upon the desired size of the CdS core. We injected a total of 2.2 mmol of Cd and S over a period of 2 h. We then added 5 mL of TEOS within 10 min. The reaction was completed over a period of 20 h.

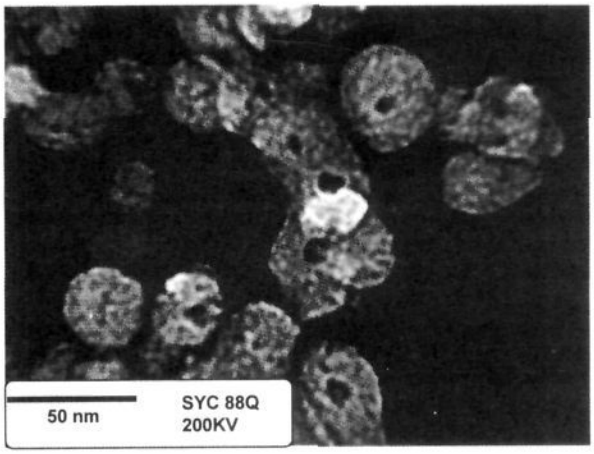


Figure 6. TEM micrograph of *ca.* 39-nm silica particles with *ca.* 6-nm CdS cores. The photograph shows these silica particles after acid dissolution of the CdS cores. This results in *ca.* 6-nm voids at the sphere centers.

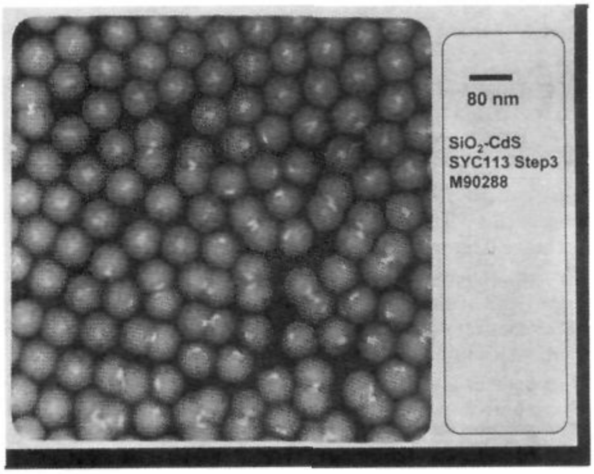


Figure 7. TEM micrograph of doublet and triplet silica spheres welded by CdS inclusions.

Spherical shells of CdS were grown around the silica spheres by first synthesizing the silica cores, followed by addition of Cd and S microemulsions, followed by another step of silica growth. These sandwiches can be visualized only by etching away the CdS layers, as shown in the accompanying paper.[17] If desired, additional layers of CdS and TEOS can be added. In principle, numerous layered shells could be prepared using this method to allow multidecker silica–CdS sandwiches.

Silica spheres synthesized with CdS quantum dot surface inclusions were prepared by using thioacetamide, which reacts more slowly with cadmium nitrate in the water nanodroplets. For example, we prepared 54-nm silica spheres with CdS particle surface inclusions of sizes ranging between 4 and 7 nm by using alcohol-free Igepal microemulsions with 5 mM thioacetamide with $w = 3$, $h = 4.8$. The $Cd(NO_3)_2$ microemulsion was injected in a pulsed mode over a period of 24 h.

Sphere doublets and triplets, where two or three silica spheres are joined by CdS quantum dot welds (Figure 7), were grown by a three-step growth process. The initial synthesis fabricated a 45-nm CdS coated silica sphere with large CdS caps on the surface.

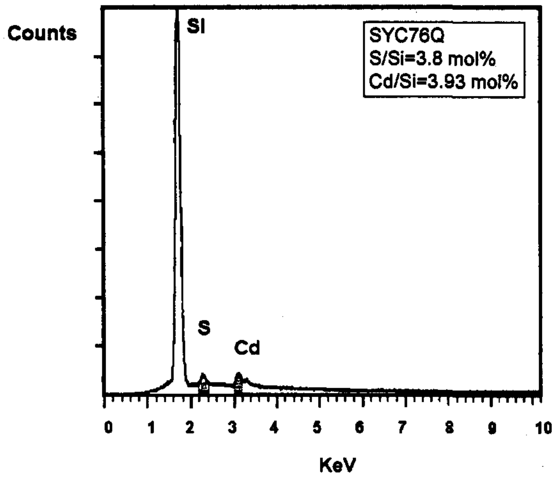


Figure 8. SEM/EDS elemental analysis of silica–CdS nanocomposite.

Table 2. Results of SEM/EDS Analysis on Silica–CdS Nanocomposites

	determined		expected	
sample	S/Si, mol %	Cd/Si, mol %	S/Si, mol %	Cd/Si, mol %
SYC76Q	3.8 ± 0.2	3.9 ± 0.1	8	8
SYC82Q	8.5 ± 0.1	11.5 ± 0.1	10	10
SYC92Q	8.8 ± 0.5	8.5 ± 0.2	7.9	7.9

These core particles were synthesized over a period of 20 h in an Igepal CO-520 microemulsion with $w = 3$, $h = 4.8$. The initial reaction microemulsion contained 0.14 M Igepal. $Cd(NO_3)_2$- and $(NH_4)_2S$-containing microemulsions were added after an initial reaction period of 6 h after the TEOS injection, in order to localize the CdS patches on the surface. The Cd and S microemulsions were added by pulsed injection over a period of 14 h. The final CdS concentration was 5 mol % of that of the silica.

In the second step, additional Igepal (0.025 mol), TEOS (0.18 mol) and NH_4OH solution (0.52 mol) were added to 100 mL of the above solution in order to increase the sphere size to 75 nm. The $h = 4.8$ value was maintained to be identical to that above. This reaction microemulsion was rapidly stirred for an additional 12 h. TEM micrographs show formation of doublets and triplets at the end of step 2.

In the third step, additional Igepal (0.042 mol), TEOS (0.022 mol), and NH_4OH solution (0.17 mol) were added, and the reaction continued with rapid stirring for an additional 50 h. The final microemulsion had $w = 4$. These reactions resulted in a complex colloid containing mainly 90-nm diameter silica spheres. However, many of the spheres formed doublets and some triplets in which the spheres were attached by CdS welds, as observed in Figure 7.

The formation of these welded spheres during the synthesis probably occurred due to collisions between spheres with CdS patches during step 2. Since the patches are sparse, most collisions were elastic, and the spheres repelled one another due to their surface charge and due to constraints imposed by the microemulsion water droplet size. Collisions where the CdS patches fortuitously touched caused adhesion. Further condensation of silica irreversibly fixed the doublets and triplets.

Chemical Composition and Structure. We determined the elemental composition of the CdS–SiO_2 sphere composites by using SEM/EDS. Figure 8 shows a typical spectrum, where the separate peaks from the Si, Cd, and S were used to determine the relative atomic concentrations. Table 2 tabulates the results for three homogeneously distributed silica–CdS sphere composites. Good agreement is generally found between the calculated and expected CdS concentrations. However, some preparations did not incorporate all of the CdS added, as indicated for sample SYC76Q, where less than half of the 8 mol % originally added was incorporated.

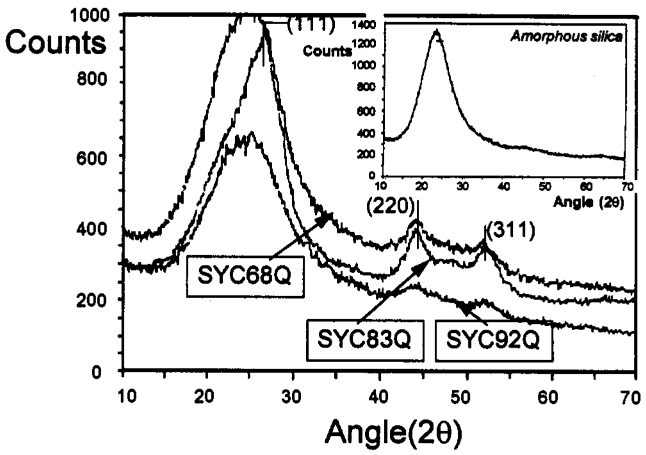


Figure 9. Typical X-ray powder diffraction spectrum of silica spheres and silica–CdS nanocomposite spheres.

Table 3. BET Specific Surface Area Measurements of Selected Silica and Silica–CdS Nanocomposites

sample ID	particle diameter (nm)	specific surface area (m^2/g)
	Plain SiO_2	
SYC60	62	105
SYC66	74	117
SYC98	60	78
SYC89	61	82
	SiO_2–CdS Nanocomposite	
SYC68Q	62	104
SYC83Q	46	112
SYC99Q	71	113
SYC92Q	62	183

The broad X-ray diffraction of the silica spheres indicates that the SiO_2 is amorphous (Figure 9). The silica–CdS sphere composites show sharper peaks for the CdS inclusions (Figure 9b), which indicates that the CdS inclusions are in a cubic phase[21,22] of a Hawleyite structure.[23]

The CdS diffraction peaks are relatively broad due to the small size of the inclusions (*ca.* 25 Å from the TEM micrographs). We use the Scherrer diffraction formula relating diffraction angular width, β, to the domain size, D, to get an independent measure of the CdS inclusion size:

$$D = k\lambda/\beta \cos \theta$$

where $k = 1$ for the CdS cubic structure, λ is the X-ray wavelength (1.541 Å), and θ is the diffraction angle. We calculate a 25-Å CdS diameter.

Particle Properties. The surface charge of the silica–CdS nanocomposites differs from that of the pure silica particles. The isoelectric point of our silica–CdS sphere composites is pH 2.5, while that of the silica spheres is 3.8.

Table 3 lists the BET surface area measurements of our particles. The particles show surface areas approximately 2 times larger than those calculated to result from their spherical outer surface areas, assuming a particle density of 1.9 g/mol.[26] There are typically large variations in the surface areas of Stöber synthesized silica spheres since the porosity depends strongly on the preparation conditions.[24,25] Although some variation exists between our preparations, the porosities of the silica–CdS nanocomposite spheres are similar to those of the pure silica spheres.

Quantum Confinement. CdS quantum dots show blue shifts of their band edges due to quantum confinement effects associated with the small size of the particles which limit the volume occupied by the electron and the electron hole pair formed. Figure 10

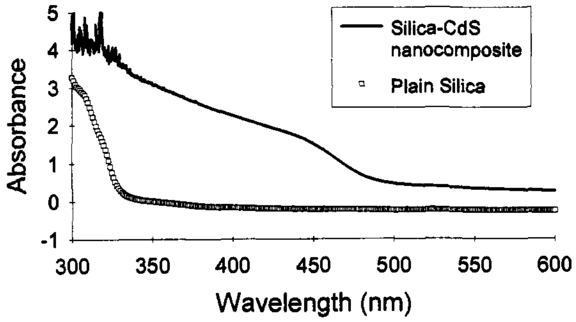


Figure 10. UV-visible absorption spectrum for pure silica and silica-CdS nanocomposite spheres.

shows the UV-visible absorption spectrum of 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 scattering is evident at shorter wavelengths. For the silica-CdS composites, the CdS band edge occurs at *ca.* 430 nm; the existing experimental correlation of band edge and quantum dot size[27] can be used to estimate an inclusion size of *ca.* 24 Å, which is close to that estimated from both the TEM photographs and the X-ray diffraction peak width measurements.

Conclusions

We have demonstrated new methods to grow silica-CdS sphere nanocomposites which allow us to produce colloidal particles with a variety of morphologies. We can easily modify the recipe to synthesize silica particles of various sizes. This process for forming monodisperse silica spheres between 30 and 150 nm is superior to the Stöber process because the uniformity is better and larger spheres can be grown by continuing the growth of previously grown small monodisperse silica spheres.

This synthesis in a water-in-oil microemulsion can be combined with the 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 center or on the surface. In addition, the CdS particulates can be used to weld together the silica spheres to form dimers and trimers. The 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. The accompanying paper demonstrates the fabrication of a 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 matrixes for catalysis support applications.

Acknowledgment. The authors would like to express their thanks to Professor Jean Blachere for his help on SEM/EDS and X-ray measurements and Mr. Thomas Harper and Mr. Cole van Ormer for their help in the TEM measurements. The authors gratefully acknowledge support for this work from the Materials Science Center of the University of Pittsburgh, which is supported by the Air Force Office of Scientific Research through Grant No. AFOSR-91-0441, and from an Air Force Office of Scientific Research grant, No. F49620-93-1-0008, to S.A.A.