

Hollow Silica Nanospheres: In situ, Semi-In situ, and Two-Step Synthesis

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Sophisticated functional nanostructures could be building blocks for potential future applications. We have prepared hollow silica nanospheres from luminescent semiconductor/silica core/shell nanoparticles. Different synthesis strategies enable various applications of these particles, whereas the progression of the reaction can be monitored by the luminescence (and vanishing of luminescence) of the functional nanoparticles. Furthermore, we succeeded in preparing extremely small and monodisperse hollow nanoparticles.

Introduction

Inorganic hollow nanospheres with well-defined architectures are of interest because of their low density, low toxicity, large surface area, high chemical and thermal stability, and surface permeability. Such hollow capsules can pave the way for applications in catalysis, as the stationary phase for selective separation, controlled (drug) delivery, artificial cells, light fillers, low-dielectric-constant prosthetic materials, or photonic crystals.^{1–4} Recently, a growing interest has also been directed toward the exploration of porous silica as gas and heavy metal ion adsorbents, as well as inorganic carriers for enzyme immobilization.^{5–11}

Extensive research has been undertaken into the synthesis of inorganic hollow microspheres over the past decade. There are a variety of pathways for synthesizing hollow particles of various compositions. Hollow inorganic particles were mostly made by removing a core material from core/shell nanoparticles, by either annealing at high temperature or dissolving the core with acids, alkalis, or an appropriate

organic solvent.^{12–16} Additionally, hollow silica spheres have been made by templating routes, which make use of vesicles, emulsion systems, acoustic cavitations, or electrically forced liquid jets.^{17–24}

In contrast to the above-mentioned synthesis methods, we describe a novel, room-temperature, and mild synthesis process for hollow silica nanoparticles using luminescent CdSe/ZnS nanoparticles as templates. Silica encapsulation and dissolution of the core particles can be done simultaneously (in situ) by modification of the reaction conditions. The size and shape of the hollow spheres can be controlled by the dimensions of the core nanoparticles. The reaction can be monitored by detection of the luminescence of the cores. Furthermore, the fact that the CdSe/ZnS nanoparticles luminesce enables potential future applications, for instance, as optical nanosensors.

Two classes of techniques have been developed for silica particle formation: sol–gel and microemulsion methods.

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Patrick proposed a sol-gel technique, in which acidic gelation of a sodium silicate solution causes silica formation.²⁵ Later, Ströber et al. produced silica by hydrolysis of tetraethyl orthosilicate (TEOS) in a basic solution containing ethanol and ammonium hydroxide. Particles produced by Ströber's method were 200–1500 nm in diameter.²⁶ Osseo-Asare and Arrigada carried out Ströber's reaction in a water-in-oil microemulsion to form smaller silica particles about 25–70 nm in diameter.²⁷

Experimental Section

Chemicals. All of the chemicals were used as received from Aldrich without further purification. Polyethylene glycol nonylphenyl ether (Synperonic NP 5) was purchased from Fluka; ammonia aqueous solution (33 wt %), dimethylamine (40 wt %) cyclohexane, acetone, butanol, propanol, and ethanol were from internal sources.

Preparation. The CdSe/ZnS/SiO₂ particles were prepared by means of a modified water-in-oil microemulsion method at room temperature. Typically, 10 mL of cyclohexane, 1.3 mL of NP-5 as surfactant, 400 μ L of a solution of as-prepared luminescent CdSe/ZnS NCs (8.72×10^{-7} mol/L) in chloroform, and 80 μ L of TEOS (tetraethyl orthosilicate) as a precursor for silica formation were added in a flask under vigorous stirring. Thirty minutes after the microemulsion system was formed, 150 μ L of ammonia aqueous solution (33 wt %) was introduced to initiate the encapsulation process. Subsequently, the reaction mixture was aged for 24 h at room temperature. After the reaction was completed, the nanoparticles were precipitated from the microemulsion using acetone and centrifuged; the resulting precipitate of CdSe/ZnS/SiO₂ composite particles was washed in sequence with butanol, propanol, ethanol, and water to remove any surfactant and unreacted educts. Finally, aqueous dispersions of the composite particles were obtained.

Characterization. The products have been characterized by transmission electron microscopy (TEM) and energy-dispersive X-ray analysis (EDX) (results not shown here). TEM studies, combined with EDX, were carried out on a Zeiss LEO 912 Omega instrument operating at 120 kV. TEM specimens were made by evaporating one drop of reaction solution onto carbon-coated copper grids. Grids were blotted dry on filter paper and investigated without further treatment.

Results and Discussion

Out of the many techniques to prepare nanoparticles, the water-in-oil microemulsion is one most widely used to prepare nanomaterials of small size.^{28–30} This method exploits two useful properties of reverse microemulsions: the capacity to dissolve reactants in the water core and the constant exchange of the aqueous phase among micelles. In this method, reverse micelles are formed, i.e., water nanodroplets are formed in an organic medium, and used as nanoreactors for the formation of nanoparticles. The water:oil ratio can be carefully adjusted to control the particle size. Therefore, fabrication of nanoparticles within microemulsions

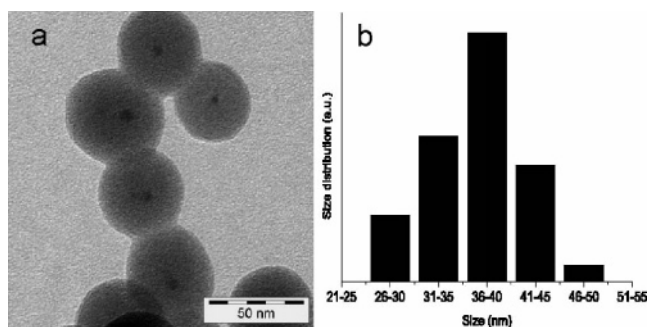


Figure 1. (a) TEM micrograph; (b) size distribution histogram of CdSe/ZnS/SiO₂ nanoparticles synthesized with optimum conditions.

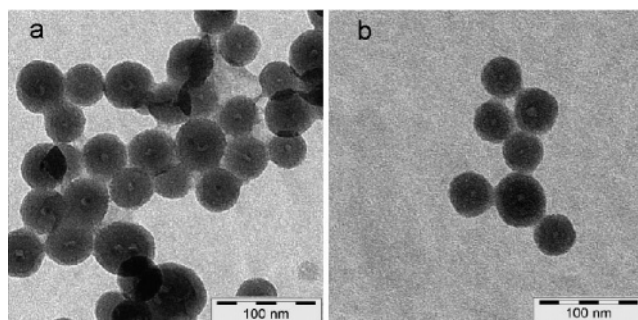


Figure 2. TEM micrographs of core/shell-structured CdSe/ZnS/SiO₂ particles prepared under different initial amounts of ammonia solution: (a) 200 and (b) 250 μ L.

has been shown to be a convenient route to monodisperse particles of controllable size.

Figure 1a depicts a transmission electron microscopy (TEM) micrograph of CdSe/ZnS/SiO₂ nanoparticles, which were synthesized with optimum conditions as described in one of our recent papers (Experimental Section).³¹ Because the electron density of CdSe/ZnS is significantly higher than that of silica, darker and lighter parts of the particles correspond to CdSe/ZnS and silica, respectively. The TEM micrograph shows, that each silica nanoparticle contains one CdSe/ZnS core and that homonucleation was effectively prevented. The mean diameter of the CdSe/ZnS/SiO₂ nanoparticles was calculated from the transmission electron micrograph by averaging more than a few hundred nanoparticles. The average diameter was 38 nm for core/shell particles (histogram depicted in Figure 1b).

When the initial amount of ammonia solution was increased from 150 to 200 μ L, most of the core particles were incompletely dissolved (Figure 2a). With a further increase in ammonia to 250 μ L, a spherical hollow was observed inside of the silica nanoparticles (Figure 2b). There was no evidence of fractured, deformed, coalescence, extensive cracking, or collapsed structures among the hollow silica particles.

Another parameter that was studied for the synthesis of hollow silica particles (in situ process) was the duration of the silica encapsulation of the core particles. Incompletely dissolved core/shell structures were found after 3 days (Figure 3a); hollow silica particles were obtained after 5 days of stirring. The luminescence of the cores vanishes instantly,

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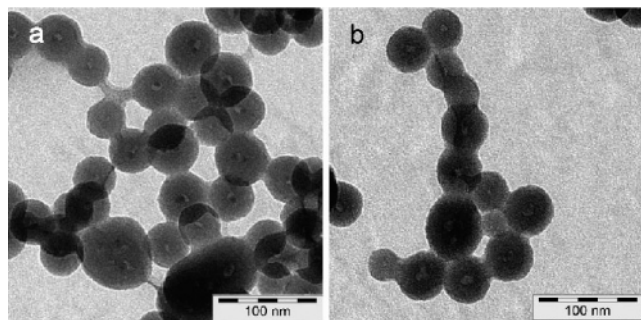


Figure 3. TEM micrographs of core/shell-structured CdSe/ZnS/SiO₂ particles obtained after different reaction times: (a) 3 and (b) 5 days.

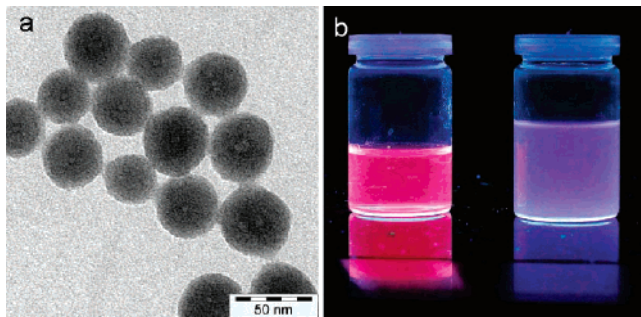


Figure 4. (a) TEM micrograph of hollow silica nanoparticles; (b) photograph of final product under UV lamp before (left) and after (right) dissolution of the luminescent cores.

when the ammonia approaches the CdSe. Therefore, the dissolution process can be followed only by means of TEM. TEM micrographs show that the central parts of the spheres are light and the edges are dark (Figure 3b), which indicates that the spheres become hollow along with the removal of the core particles. The obtained products were polydisperse after reaction times of more than 1 day, most likely as a result of Ostwald ripening.

We were able to prepare hollow silica particles by means of a semi-in situ process (dissolution of the luminescent cores prior to the washing step). An additional 100 μ L of ammonia solution was added to the reaction under optimum synthesis conditions 1 h before the reaction was terminated. Because the silica shells prepared by this method are usually porous, ammonia molecules could diffuse to the cores and dissolved them subsequently. The silica pore size was estimated by diffusion/chemisorption of differently sized organic luminescence “quenchers” to the core’s surface. An average pore size of 3 \AA was roughly estimated. Dissolved ions diffused gradually out of the shell, and finally left hollow silica spheres (Figure 4a). The luminescence of the core particles vanished on the addition of ammonia (Figure 4b).

Finally, hollow silica nanospheres were obtained by dissolving the cores using nitric acid with a two-step process. After preparation of the CdSe/ZnS/SiO₂ nanoparticles, 1 mL of nitric acid (65 wt/wt) was added to a solution of the particles in 5 mL of water. The reaction mixture was stirred for 30 min, and the resulting product was repeatedly rinsed with water. Figure 5a depicts the resulting hollow silica particles, which did not show any deformation or shrinking. The silica spheres had an inner hole diameter of about 6.5 nm (Figure 5b). The size distribution of the inner diameter

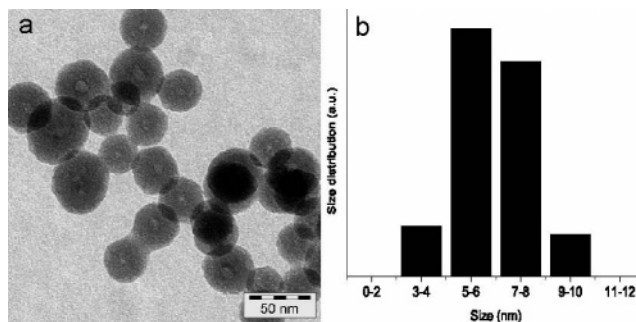
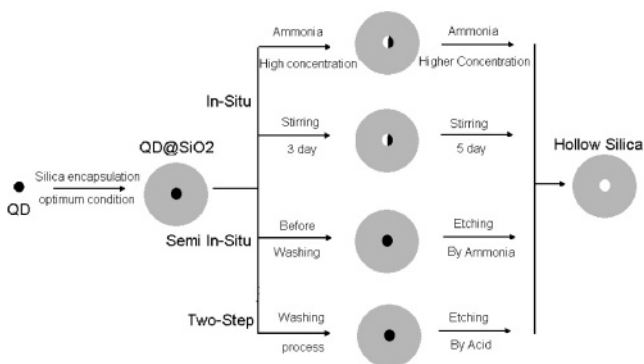


Figure 5. (a) TEM micrograph and (b) size distribution of inner diameter of hollow silica nanoparticles.

Scheme 1. Schematic Diagram of the Formation of the Hollow Silica Spheres with Different Processes



has been determined from the histogram obtained by statistically measuring the sizes of more than one hundred individual nanoparticles on a TEM grid.

Scheme 1 displays the various options to prepare monodisperse hollow silica nanoparticles. When the concentration of ammonia is above the optimum conditions, the core particles start to dissolve incompletely. Perfect hollow spheres were obtained with an increasing concentration of ammonia (in situ). A similar result could be reached with increasing reaction time: incomplete dissolution was observed after 3 days, whereas hollow nanoparticles were obtained after 5 days (the nanoparticles were not as monodisperse as with the first method, most likely due to Ostwald ripening). High concentrations of ammonia, added prior to the washing process, resulted in hollow silica spheres, as well as addition of an acidic solution after workup of the core/shell nanoparticles (two-step process). The amorphous nature of the shell and mesopores in the shell wall provide sufficient open channels to enable the inorganic components of the core to be released from the spheres. Because these new methods get by without any high-temperature treatment, the silica structure is perfectly kept after the etching process.

Conclusion

In summary, porous hollow silica nanoparticles with hole diameters of about 6.5 nm and wall thicknesses of 15 nm were prepared with a novel synthesis method, using luminescent CdSe/ZnS cores as templates. Ammonia was used as catalyst for the polymerization of silica and to dissolve the CdSe/ZnS cores at once. The decision of whether core/shell nanoparticles or hollow spheres are obtained is governed

by the concentration of ammonia and reaction duration. The yielded hollow silica spheres were of superior quality regarding their size and monodispersity. The produced hollow spheres are envisioned to have applications in areas ranging from medicine to pharmaceuticals and materials science, because the silica surface can be easily functional-

ized with different groups and can be attached to a variety of biological species.

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