Confined growth of CdSe quantum dots in colloidal mesoporous silica for multifunctional nanostructures

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We report a new and convenient strategy for incorporating fluorescent semiconductor nanocrystals into silica hosts for the synthesis of multifunctional nanostructures. Mesoscale porosity was first created in conventional Stöber silica spheres by chemical etching under the protection of polymeric ligands. Uniform and highly luminescent CdSe nanocrystals were then directly grown in the porous silica network by reacting the silica spheres in a growth solution at high temperature. The confinement of silica network led to slower nanocrystal growth and subsequently smaller CdSe dots with blue shifted fluorescence compared with those without confinement. The loading number of CdSe nanocrystals can be easily tuned by changing the degree of porosity of the silica. The advantages of this strategy include simplicity as no special surface treatment processes are needed, general applicability to silica hosts of various shapes and sizes, high flexibility in tuning the dimensions of both the active nanocrystals and host particles, and ample opportunities for incorporating multiple functionalities. With the demonstration of a porous $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CdSe}$ composite structure with combined magnetic and optical properties, we believe this strategy may provide a platform for the fabrication of a large variety of multifunctional composite nanostructures.

INTRODUCTION

Colloidal semiconductor nanocrystals—so called quantum dots (QDs)—are widely used nanoscale fluorescent probes in biomedical applications due to their unique optical properties, such as size-dependent band gaps, extremely bright emission, a wide range of accessible colors, and remarkable photo-stability comparing to the organic dyes [1–7]. In order to enhance fluorescent response, decrease toxicity, and enable multi-functionalities, the quantum dots are frequently incorporated into a host matrix such as polymer or silica microspheres [7–18]. Among all the host materials, silica has been intensively investigated and broadly utilized, which is believed to benefit from its low reactivity, colloidal stability, biological compatibility and easy surface modification. Conventionally, semiconduct-

ing QDs are synthesized first and then incorporated into silica microspheres through impregnation or other methods [19–26]. Often the silica microspheres are very large (several micrometers), which may increase the loading of QDs to some extent, but on the other hand may limit their application in biomedical field.

Loading nanoparticles to silica microspheres is of general interest to many fields as it allows the production of colloidal composites with multiple functions. Here, we introduce a new and reliable process for creating porosity in silica spheres and then loading them with functional nanoparticles, by using CdSe QDs as an example. In conventional methods, porosity is created in silica spheres during their synthesis by using surfactants as templates (porogens), which makes it difficult to extend to silica spheres of smaller dimensions. In our approach, silica spheres are synthesized using regular Stöber process which allows large variation in size, and then etched to produce desired porosity. Instead of incorporating the pre-made QDs into host silica spheres, our process directly grows CdSe QDs inside the silica pores, producing composite spheres with relatively high loading of QDs. We also show that the growth of QDs is limited by the confinement of the pores so that they emit at shorter wavelength than those without confinement. The advantage of our process is that other functional materials can be easily incorporated in the silica spheres before loading of QDs, making it easier to create multifunctional materials. This feature was demonstrated by synthesizing $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{CdSe}$ composite structures that display both fluorescence and magnetic responses.

EXPERIMENTAL

Chemicals

Tetraethyl orthosilicate (TEOS, 98%), sodium hydroxide (98.8%), ammonium hydroxide aqueous solution (28%), and isopropanol (denatured) were purchased from Fisher

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Scientific. Poly(vinylpyrrolidone) (PVP, $M_w=10,000$), trioctylphosphine oxide ($(C_8H_{17})_3P=O$ or TOPO, 99%), trioctylphosphine ($(C_8H_{17})_3P$ or TOP, 97%), oleylamine ($C_{18}H_{37}N$, Tech., 70%), stearic acid ($C_{18}H_{36}O_2$, 99%), selenium (Se, 99.99%), and cadmium oxide (CdO, 99.5%) were obtained from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of porous silica spheres

Silica spheres were prepared through the well-known Stöber method [27]. In a typical process for producing samples with an average diameter of 450 nm, 100 mL isopropanol was first mixed with 20 mL ammonium hydroxide aqueous solution and 5 mL distilled water under vigorous stirring. After ~2 min, 5 mL of TEOS was added to the mixture which was kept under stirring for another 2 h at room temperature. The silica spheres were collected by centrifugation and washed with water for three times, and then etched by NaOH solution under protection of PVP [28,29]. Typically, the silica particles were re-dispersed in 60 mL water, mixed with 6 g of PVP powder, and refluxed for 3 h. After cooling to room temperature, 20 mL of the silica solution was mixed with a 30 mL NaOH solution (finally 0.04 g mL^{-1} of NaOH in 50 mL mixture) under continuous stirring. The resulting porous silica spheres were separated from the solution through centrifugation, washed 3 times with water, and finally dried at room temperature for 12 h.

Synthesis of porous $Fe_3O_4@SiO_2$ structures

Superparamagnetic Fe_3O_4 particles with a diameter of ~100 nm were synthesized and then coated with SiO_2 using a procedure developed previously in our group [30,31]. Then the product $Fe_3O_4@SiO_2$ was dispersed in a solution containing 20 mL of H_2O and 1 g of PVP, followed by refluxing for 3 h. Finally, the mixture was cooled down to which 5 mL of NaOH solution (0.2 g mL^{-1}) was added to induce selective etching of the silica spheres. The final porous $Fe_3O_4@SiO_2$ structures were collected and washed with the procedure described above.

Growth of CdSe within porous silica spheres

The growth of CdSe nanocrystals in porous silica spheres was adapted from a literature procedure [31]. In a typical process, 25 mg porous silica or $Fe_3O_4@SiO_2$ porous structures was added into a Se-TOP solution containing 0.158 g (2 mmol) of Se and 1.1 mL TOP (2.4 mmol), and stirred at 90°C for about half an hour until the silica spheres dispersed well in the solution. In a separate flask, CdO (0.0127 g), stearic acid (0.114 g), and TOPO (1.94 g) were

mixed in a 50 mL flask and heated to 150°C under vacuum. After adding 1 mL of oleylamine, the reaction system was heated to 320°C to form an optically clear solution under Ar protection, to which the porous silica-Se-TOP stock solution prepared above was injected. The temperature was then set at 290°C for the growth of QDs. At different time intervals, 1.5 mL reaction mixture was collected by a glass syringe and diluted by toluene for sampling. The QD-loaded porous silica spheres were separated from free CdSe nanocrystals by centrifugation at 6000 rpm for 5 min, and washed with toluene for 2 times.

Measurement of quantum yield of porous $SiO_2/CdSe$ composite structures

A standard dye Rhodamine 6G was chosen as a comparison to quantify the quantum yield of the porous $SiO_2/CdSe$ composites [32,33]. At the excitation wavelength of 488 nm, the photoluminescence (PL) spectra of the solutions of the composites and the dye were measured. The PL quantum yield of the composite samples were finally obtained by comparing the integrated PL intensities of the composites and the corresponding dye, assuming the quantum yield of the standard dye is 100%.

Estimation of CdSe loading number per sphere

The number of CdSe incorporated in each porous silica sphere was estimated by the number ratio of CdSe nanocrystals to SiO_2 beads in the solution. Briefly, the number of SiO_2 was calculated by the amount of precursor TEOS, the density of normal colloidal SiO_2 (2.2 g cm^{-3}), and the average size of SiO_2 beads characterized by transmission electron microscope (TEM) images. On the other hand, the number of CdSe QDs was determined by the Beer-Lambert law. The size-dependent absorption coefficients of CdSe QDs were obtained from reference [34].

Characterization

The size and morphology of nanostructures were investigated using a Philips Tecnai 12 transmission electron microscope (TEM) operated at 120 keV. The composition and elemental distribution of the hollow structures were mapped through energy dispersive X-ray spectroscopy (EDS) by displaying the integrated intensity of each element as a function of the beam position. Both high-angle annular dark-field (HAADF) imaging and elemental mapping were recorded on a scanning transmission electron microscope (STEM, JEOL 2100F equipped with Oxford INCA energy dispersive spectrometer (EDS), Gatan's electron energy loss spectrometer (EELS) and Digiscan II STEM controller). UV-vis absorption measurements

were carried out using a Varian Cary 50 spectrophotometer. During the measurements, all nanocrystal and dye solutions were placed in quartz cuvettes with a 1-cm path length. The fluorescence emission spectra were measured by a Spex Fluorolog Tau-3 fluorescence spectrophotometer with a xenon arc lamp source.

RESULTS AND DISCUSSION

In order to create mesoscale porosity, the silica spheres were etched by NaOH in the presence of PVP which served as a polymeric capping ligand that can bind to the silica surface [28]. After refluxing in distilled water for 3 h, the surface of Stöber silica colloids was covered by PVP, which prevented a complete dissolution of the silica by NaOH in subsequent etching step, leaving behind a mesoporous silica framework. The porosity can be controlled by the extent of etching. The porous silica spheres were then transferred to a Se-TOP stock solution and formed a good dispersion. TOP molecules were found to play an important role in this modification, as they intensively coordinated with the oxygen from the silanol groups and rendered the silica particle hydrophobic characteristics and ensured particle dispersity in the solution [35,36]. Such coordination also took place on the mesopore framework, which helped to stabilize the Se precursors within the mesopores. Finally, the Se-loaded silica spheres were swiftly injected into the reaction flask containing cadmium precursor at high temperature ($\sim 320^{\circ}\text{C}$) to initiate the growth of CdSe. Samples taken out at different reaction time were washed by toluene, centrifuged to remove the free CdSe nanocrystals generated during the growth. Finally pure CdSe loaded silica spheres were collected and dispersed in toluene.

Fig. 1a shows a typical TEM image of the porous silica spheres with diameter about 450 nm after etching for 2 h. The overall size did not decrease obviously during the etching process because of the PVP protection; while the rough

surface and the low contrast of the spheres can be clearly observed, indicating the porous nature of the spheres. Following the incorporation of CdSe, the silica spheres collected by centrifugation became reddish, providing the first evidence of entrapment of CdSe QDs. As shown in Fig. 1b, regular bright field TEM image of the sample cannot clearly reveal the presence of CdSe QDs, although the contrast of the spheres seemingly increases and the spheres especially near surface regions becomes denser after loading with CdSe QDs. A better evidence is provided by the HAADF image in Fig. 1c, which shows a small portion of a composite sphere [37]. As the contrast of HAADF imaging is highly sensitive to the atomic-number of the materials, one can clearly appreciate the uniform size of CdSe dots (bright spots) and their homogeneous distribution inside the porous silica matrix.

The composition and elemental distribution of the composite nanostructures were mapped through EDS by displaying the integrated signal intensity as a function of the beam position when operating the TEM in the scanning mode. Mapping of elements including Si, O, Cd, Se, and P against composite spheres indicated that CdSe nanocrystals and the surfactant TOPO were uniformly distributed in the silica matrix. As shown in Fig. 2a, the SiO_2 sphere contains a hollow interior due to extensive surface-protected etching. The CdSe nanocrystals appears to distribute mainly in the SiO_2 porous network, but not in the hollow region at the center. On the other hand, porous SiO_2 spheres without hollow interior can be also produced with less etching, and the CdSe nanocrystals are found to be distributed evenly throughout the corresponding composite spheres, as shown in similar elemental mapping analyses included as the Supplementary information. Although the element P also displays a uniform distribution, careful inspection suggests that the distribution of P followed the signals of Si and O. The integrated EDS spectrum of a single compos-

Figure 1 (a) TEM image of porous silica spheres produced by etching with NaOH with the protection of PVP. (b) TEM image of porous silica spheres containing CdSe nanocrystals. (c) High angle annular dark-field image of a portion of a composite sphere, showing uniformly distributed CdSe QDs (white dots) inside the porous silica matrix.

Figure 2 (a) Elemental mapping of Si, O, Cd, Se, and P against a typical SiO₂/CdSe composite sphere through EDS, confirming uniform distribution of CdSe in the silica matrix. A hollow silica sphere is intentionally chosen to show that CdSe dots are trapped in the porous silica network, not the hollow interior. The first image is a conventional TEM image. (b) Integrated EDS spectrum of a single composite sphere. The strong signal of C and weak signal of Cu are originated from the supporting carbon film and the copper grid.

ite sphere displayed in Fig. 2b further clearly confirms the composition of Si, O, Cd, Se, and P. The strong signal of C and weak signal of Cu were originated from the supporting carbon film and the copper grid from the TEM substrate, although it is believed that the surfactant TOPO might also contribute to the overall C signal. On the basis of above measurements, one can conclude that the CdSe nanocrystals have been uniformly loaded to the porous network of the SiO₂ spheres.

We then characterized the optical properties of SiO₂/CdSe composite particles. A series of porous silica beads collected at different growth stages were shown in Fig. 3. The SiO₂/CdSe composites in solution are highly luminescent (Fig. 3a). The quantum yield of the red sample could reach 40% compared with standard dye of rhodamine 6G. This remarkable brightness here can be attributed to the large number CdSe incorporated and extra protection provided by silica walls. PL and UV-vis absorption spectra of the samples corresponding to various growth time of 8, 15, 45 and 120 s are shown in Fig. 3b, with emitting peaks at

530, 550, 580 and 595 nm. True color fluorescence images of silica beads containing different single-color CdSe are also shown in Figs 3c–f, revealing that the beads are significantly brighter than the constituting single QDs, which proves the high loading amount of CdSe nanoparticles again.

After separating the mixture using centrifugation, two parts of the product were obtained: the free CdSe QDs dispersed in the supernatant and the SiO₂/CdSe composite spheres as precipitates. Interestingly, the fluorescent colors of these two parts were different under UV light and the corresponding PL spectra further proved the shifts of the PL peak positions. As shown in Fig. 4, the solid curves stand for the free CdSe QDs, and the broken curves represent SiO₂/CdSe composite structures. Very obvious blue shift was observed for all the composite spheres, indicating that the particle size of CdSe within the porous silica was smaller than the outside one. This difference becomes smaller with the time prolonged: the SiO₂/CdSe composites with green color has the largest shift, and the red ones shifts very slightly (Figs 4a–d). It demonstrates that the confinement of the porous silica structures to the growth of CdSe does exist, most likely due to the limited diffusion of the growing species to the pores. As reaction time prolonged, such a difference becomes smaller because the growth of the particles outside slows down dramatically due to the decrease in specific surface energy, while those inside can catch up. On the other hand, the PL spectra of the composite structures have no obvious broadening in contrast to the free CdSe, indicating that the porous silica structure acts as a matrix to spatially separate the embedded CdSe nanocrystals.

The degree of porosity could be easily controlled by tuning the etching time, and the transmittance spectra were used to monitor the etching process [29]. We collected two kinds of porous silica spheres at different etching time, with transmittance at 1000 nm of ~50% and ~80% in the spectrum, as shown in Fig. 5a. For convenience, these two different porous silica spheres are named as PSS1 and PSS2, respectively. The degree of etching apparent in the optical transmission measurements is fully consistent with the TEM characterization. Fig. 5b shows TEM images of these two corresponding silica spheres. When the transmittance is about 50%, the silica spheres become porous, with an obvious rough surface. After the etching time was prolonged and transmittance reached 80%, silica spheres with higher porosity PSS2 were obtained. Some of them have very low contrast in the center, indicating their hollow structures. Fig. 5c compares the loading abilities of PSS1 and PSS2 to CdSe nanocrystals. About 600 CdSe nanocrystals are doped

Figure 3 (a) Digital photo of a dispersion containing fluorescent SiO_2/CdSe composite particles under the illumination of UV light with a wavelength of ~ 365 nm. All the samples were collected from the same reaction system but at different growth stages: from left to right, 8, 15, 45 and 120 s after initiation of the reaction. The solutions only contain SiO_2/CdSe composite particles as free CdSe nanocrystals have been removed by centrifugation. (b) Absorption and emission spectra of the composite particles collected at 8, 15, 45, and 120 s (from bottom to top). (c–f) Fluorescent micrographs of the composite particles in (b) dispersed on a glass cover slip.

Figure 4 The confinement of porous silica to the growth of CdSe: PL spectra of the products collected at (a) 8, (b) 15, (c) 45, and (d) 120 s after initiation of the reaction. (The solid curves stand for the free CdSe QDs, and the broken curves were CdSe/ SiO_2 spheres.)

Figure 5 (a) The transmittance and (b) corresponding TEM images of different porous silica spheres that have been etched for different time, with higher transmittance and more porous structures at longer etching time. The blue line is with ~50% of transmittance at wavelength of 1000 nm, and red line with 80% of transmittance. (c) The loading number of CdSe nanoparticles estimated by the optical absorption of the composites with different degrees of porosity.

in PSS1 in contrast to several thousands of the nanocrystals in the PSS2. Obviously, PSS2 can entrap more CdSe nanocrystals due to the more porous structures caused by longer etching time. Interestingly, during the growth process, the number of CdSe in PSS1 nearly kept the same. Two reasons may explain this phenomenon. First, the pores in PSS1 are relatively close to the sphere surface, which makes it not an issue for the diffusion of growing species. As a result, the number of CdSe in the silica spheres is considerably low and does not increase as the reaction prolonged. Second, the porous silica matrix prevents the CdSe seeds from aggregating with each other so that the number of CdSe QDs in PSS1 remains almost unchanged. In PSS2, the pores are not limited to the surface of the spheres, which allows more precursors to penetrate into the center of the spheres. However, the diffusion time of the growing species to the pores in the centre of PSS2 cannot be ignored in this case, as a result, in the first 60 s after injection, the number of CdSe nanocrystals continuously increased, from ~1400 to ~3500 nanocrystals per PSS2 sphere. After that, the number of CdSe QDs kept the same and the size increased with

the reaction time prolonged by consuming the growing species provided from the solution. The nearly unchanged number of CdSe at the later stage of growth again proved that the porous silica matrix kept the individual CdSe QDs well separated.

The size control of the porous SiO_2/CdSe composites could be easily achieved by adjusting the initial size of the silica spheres; and the loading amount of QDs in each SiO_2 sphere were related to the porosity degree of the sphere which can be tuned by varying etching times. Moreover, the ability to directly grow the nanoparticles in normal silica opens the door to the fabrication of a large variety of multifunctional composite nanostructures. Additional functional materials can now be incorporated as cores inside normal silica first, which can then form porous structures by surface-protected etching and entrap functional nanoparticles by the direct-growth method. Here, we have demonstrated this advantage by preparing $\text{Fe}_3\text{O}_4@ \text{SiO}_2/\text{CdSe}$ composite structures. First, superparamagnetic Fe_3O_4 particles with a diameter of ~100 nm were prepared, followed by coating a layer of SiO_2 with the thickness about

Figure 6 (a) TEM image of porous $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell composite particles containing CdSe nanocrystals. (b) Fluorescent micrograph showing linear structure of the $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{CdSe}$ composite structures assembled under a magnetic field.

180 nm. After surface-protected etching, CdSe QDs were directly grown in the porous structures. Fig. 6a shows the TEM image of porous $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell structures containing CdSe nanocrystals. The dark area in the centre is the Fe_3O_4 core, and the outer layer with lower contrast is porous silica layer. Again, the CdSe particles cannot be easily identified in the silica matrix due to the similar contrast of silica domains. However, the strong fluorescent property of the composites proves the high loading amount of the CdSe QDs. Fig. 6b shows an optical microscopy image of the $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{CdSe}$ core-shell composites when they were subjected to an external magnetic field and UV light irradiation. The core-shell spheres can be self-assembled into linear chain structures, which demonstrate high magnetic sensitivity of the composite structures. Moreover, the observed strong green emission from the chain structures proves the high PL intensity. The combined magnetic-optical properties may endow the composites with many

important technological applications.

CONCLUSION

In conclusion, we developed a new strategy for incorporating luminescent QDs to silica microspheres with controllable loading amounts. In comparison to embedding nanocrystals to conventional porous silica or polymer beads, this new system has several key features. First, the CdSe nanocrystals are directly nucleated and grown within the porous silica spheres so impregnation is not needed. Second, the pores have confinement effect on the growth of CdSe which leads to blue shift of PL spectra compared with the free ones. Third, the size of the silica spheres can be tuned by adjusting the original size of silica spheres, and as a result, uniform and size-tunable QD-loaded composites can be readily produced. Forth, by taking advantage of the easy control of porosity by etching time, the loading amount of CdSe nanocrystals can be conveniently adjusted. Fifth, functional materials can be incorporated as cores inside normal silica before loading QDs, which potentially opens a door to the fabrication of a large variety of multifunctional composite nanostructures.

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Author contributions Yin Y designed and supervised the project; Li C performed the experiments and wrote the paper; Lu Z, Zhang Q, Ge J and Shi Z contributed to the general discussion and reviewed the manuscript; Aloni S contributed to the TEM analysis.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Dark-field image and elemental mapping of the composite spheres are available in the online version of the paper.

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中文摘要 本文报道了一种新颖且便捷的将荧光半导体纳米晶包覆到二氧化硅球中进而制备多功能纳米结构的方法. 从溶胶凝胶法合成二氧化硅微球开始, 在聚合物配体保护下进行化学刻蚀从而获得介孔级孔道, 然后将带有孔道的二氧化硅微球投入到制备CdSe量子点的高温反应体系中, 就可以直接在二氧化硅微球的孔道中生长尺寸均匀且具有高荧光产率的CdSe纳米晶. 研究发现二氧化硅微球中的孔道对于CdSe量子点的生长有一定的抑制作用, 因此与自由生长的量子点比较其荧光光谱会发生蓝移, 二氧化硅微球中负载CdSe量子点的数量可以通过选择不同刻蚀程度的二氧化硅微球来实现. 这种纳米结构优点在于: 不需要特殊的表面处理工艺, 对于不同形貌及尺寸的二氧化硅微球具有普适性, 对于纳米晶与主体材料的尺寸调控具有较高的灵活性, 并且可以同时包裹其他功能材料, 比如将磁性纳米粒子引入到该体系, 合成了兼具磁学与光学性能的 $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{CdSe}$ 复合纳米结构材料. 该方法为制备多功能复合纳米结构材料提供了一个平台.