

Fabrication of CdS/PMMA core/shell nanoparticles by dispersion mediated interfacial polymerization

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CdS/PMMA core/shell nanoparticles were synthesized using dispersion-mediated interfacial polymerization, and the transparent PMMA shell not only maintained the optical properties of CdS core but effectively protected the CdS core from environmental perturbation.

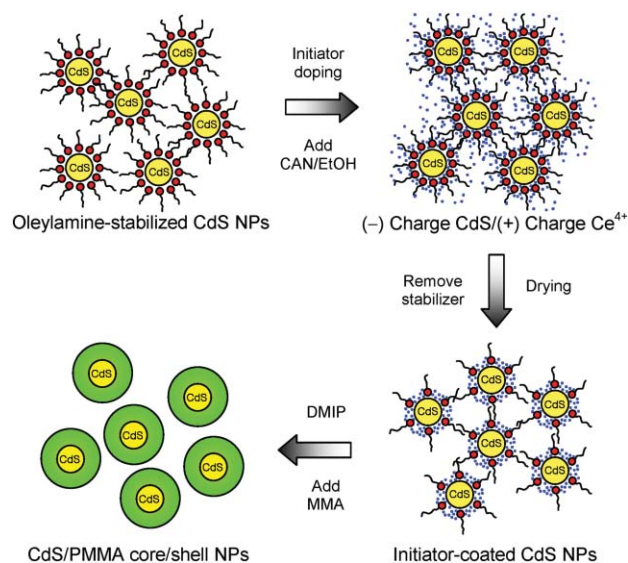
Highly luminescent II–VI semiconductor nanoparticles (NPs) have been extensively studied for the past two decades.¹ Due to the quantum confinement effect,² nanocrystals show unique size-dependent physical, chemical and optical properties, which are different from the bulk materials.³ In addition, II–IV semiconductor NPs have attracted much attention because of their various applications in areas such as biological labeling, light-emitting diodes, single-electron transistors, solar cells, photocatalysts and photonic crystals.⁴

High-quality CdS NPs synthesized by the high-temperature thermal decomposition of precursors exhibit narrow size distribution and excellent luminescent property.⁵ However, the problems in this synthetic method lie in the aggregation and degradation under the atmosphere when the organic solvent (capping agent) is removed.⁶ Compared with CdS NPs, CdS/polymer core/shell NPs provide a unique combination of improved thermal stability and photostability as well as maintaining enhanced dispersity after the removal of organic ligand or the capping agent.⁷ In addition, polymer-coated inorganic nanoparticles have several advantages over the single-component materials from the viewpoint of their potential applications. The uniform coating of organic polymers onto inorganic particles can endow the raw materials with beneficial electrical, optical and catalytic functions. In conventional solution-based methods, there have been found difficulties in controlling the coating of polymer layers on the nanocrystals without aggregation at the nanoscale. Recently, extensive studies have been performed for the encapsulation of II–IV semiconductor NPs with various polymers, which include emulsion polymerization, atomic transfer radical polymerization, layer-by-layer self-assembly of polyelectrolyte, and graft polymerization on the particle surface.⁸ However, these methods have some intrinsic problems such as intricate synthetic procedures and high cost. Therefore, it is still a challenging task to develop facile and novel methods to fabricate nanoparticle/polymer core/shell structures.

Herein, we describe the fabrication of CdS/poly(methyl methacrylate) (PMMA) core/shell nanoparticles using dispersion-mediated interfacial polymerization (DMIP). This work represents

the novel demonstration of luminescent NP-embedded polymer nanoparticles synthesis without any nanoparticle aggregation using charge–charge interactions between the CdS surface and initiator. PMMA was employed due to its optical transparency. In addition, the PMMA shells played a role in protecting the surface of CdS cores from oxidation in the environmental conditions. Our synthetic methodology includes a number of advantages over the other solution-based techniques, such as the formation of polymer layers with uniform thickness, high yield of the product, and simple fabrication steps.

The overall synthetic procedure of PMMA-coated CdS NPs is illustrated in Scheme 1. First, spherical CdS nanoparticles were synthesized from the reaction of CdCl₂ and sulfur powder in oleylamine. The molar ratio of cadmium to sulfur was 1 : 1. CdCl₂ (1×10^{-3} mol) was mixed with oleylamine (10 mL) and then the temperature was raised to 160 °C. Subsequently, sulfur powder dissolved in oleylamine (5 mL) was added dropwise to the hot solution. The mixture was kept at 160 °C for 20 h under vigorous stirring. Afterwards, the solution was cooled to room temperature, and the resulting CdS nanoparticles were washed with ethanol to remove any residual precursor. Although most of oleylamine is removed by this procedure, oleylamine remains on the surface of CdS NPs, exclusively. Therefore, the particle stability of CdS is maintained during the post-treatment such as surface modification of CdS or polymerization of PMMA. In order to polymerize the



Scheme 1 Schematic diagram of the fabrication of CdS/PMMA core/shell nanoparticles.

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MMA monomer on the surface of CdS nanoparticles, CdS nanoparticles were pretreated by ceric ammonium nitrate (CAN). Typically, 0.2 g of CAN (excess amount with respect to the CdS core) was added into the CdS/EtOH solution. The positively charged ceric ion can be attached onto the CdS nanoparticles by charge-charge interaction because the surface of CdS has negative charge.⁹ The calculated weight ratio of ceric ion to the CdS NPs is approximately 0.2. The CAN-coated CdS NPs (0.1 g) were dispersed in hexane (30 mL) and then the mixture was heated to 65 °C. The MMA monomer (1 mL) was injected to the CAN-coated CdS/hexane solution. The CAN adsorbed on CdS NPs plays a role in oxidant, and the MMA radical is produced when the medium is heated to 65 °C.¹⁰ Therefore, the radical polymerization is initiated from the surface of CdS, and the MMA can be exclusively polymerized on the surfaces of the CdS NPs.

Fig. 1(a) represents the transmission electron microscopy (TEM) image of spherical CdS NPs synthesized with CdCl₂ and sulfur in oleylamine. The CdS NPs were highly monodisperse and their average diameter was 5.4 nm. The TEM image of the CdS/PMMA core/shell NPs is displayed in Fig. 1(b). The diameter of CdS/PMMA core/shell nanoparticles was ca. 20 nm. It is clearly shown that the CdS/PMMA core/shell nanoparticles maintain their uniform dispersity after removal of capping agent. The magnified TEM image reveals the core/shell nanostructures with the shell thickness of ca. 7 nm. The hydrodynamic radii of CdS NPs and CdS/PMMA core/shell NPs measured by dynamic light scattering were 5.4 and 19.4 nm, respectively, which was in good agreement with the TEM observation. The polydispersity index of the CdS core and CdS/PMMA core/shell nanoparticles were 0.18 and 0.34, indicating that the particle size distribution was reasonably narrow without serious aggregation. After the polymerization, some disordered shapes of core/shell NPs were observed in the TEM image. During the radical polymerization, MMA monomer might be initiated at each ceric ion site on the CdS surface, and grows randomly in all directions. In a particular case, a propagating MMA chain could recombine with another Ce⁴⁺ or MMA radical, and early termination can occur compared with other propagating sites. Therefore, the irregular sphere shape of CdS/PMMA core/shell species could be formed after the radical polymerization.

Fig. 2 shows the Fourier-transform infrared (FT-IR) spectra of CdS cores and CdS/PMMA core/shell nanoparticles. The FT-IR spectrum of oleylamine-stabilized CdS nanoparticles revealed the CH₂ stretching of oleylamine at 2924 and 2853 cm⁻¹, indicating

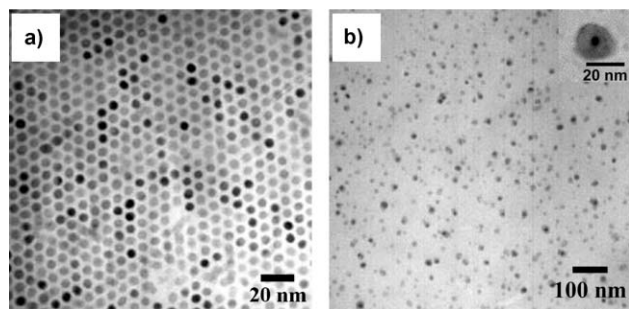


Fig. 1 TEM images of (a) CdS NPs fabricated with CdCl₂ and sulfur in oleylamine stabilizer and (b) CdS/PMMA NPs (inset: a magnified TEM image of a single core/shell NP).

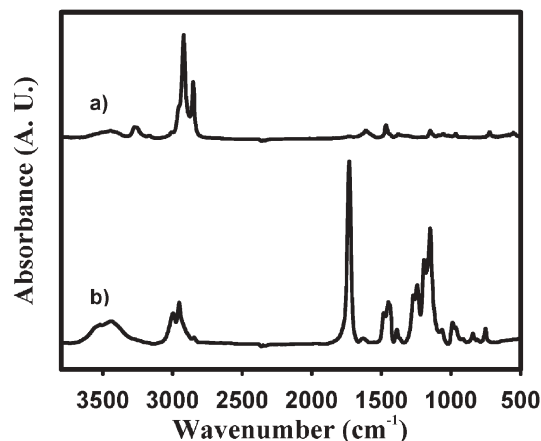


Fig. 2 FT-IR spectra of (a) CdS and (b) CdS/PMMA core/shell NPs.

that the oleylamine still remains after the washing procedure. In the FT-IR spectrum of the CdS/PMMA core/shell nanoparticles, the C–O stretching peaks of PMMA appeared at 1150, 1195, 1241 and 1277 cm⁻¹. The peak at 1731 cm⁻¹ related with C=O stretching of PMMA was also observed. Moreover, there is no band at 1640 cm⁻¹, which would originate from the double bond of MMA monomer. Judging from these data, it could be confirmed that the PMMA was successfully polymerized on the CdS surface.

UV-Vis absorption and photoluminescence (PL) spectra of CdS NPs are shown in Fig. 3. The UV-Vis of CdS NPs have a maximum absorption peak at 436 nm (Fig. 3(a)). The PL of sphere-shaped CdS NPs exhibited a sharp peak at 467 nm (excited at 436 nm), markedly blue shifted (510 nm) related to that of bulk CdS.¹¹ Bulk CdS has been reported to have a broad emission with the emission maximum in the 500–700 nm region of the luminescence spectrum. The quantum yield of CdS is measured as ca. 12%, which is in good agreement with the previous reports.^{5,12} The PL spectrum of CdS/PMMA core/shell NPs is also shown in Fig. 3(c). In the case of CdS/PMMA core/shell NPs, the quantum yield is approximately 8%. While the PL and quantum yield of CdS NPs showed higher intensity than that of CdS/PMMA core/shell NPs, the emission maximum of the spectra was

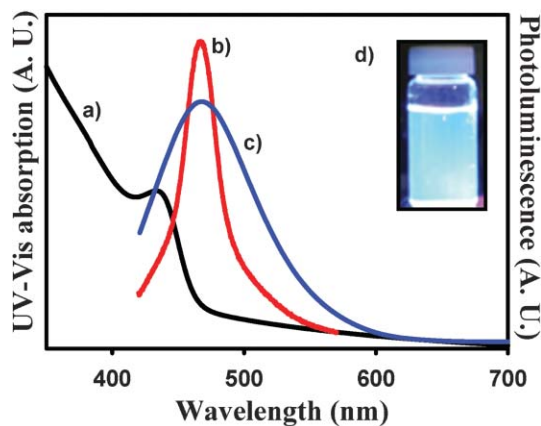


Fig. 3 (a) UV-vis absorption CdS core, (b) PL spectrum of CdS core, (c) PL spectrum of CdS/PMMA core/shell NPs, and (d) emission photograph of CdS/PMMA core/shell NPs.

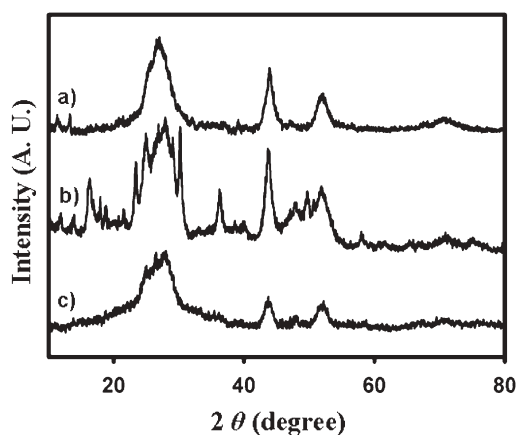


Fig. 4 X-Ray diffraction patterns of (a) as-prepared CdS NPs, (b) CdS NPs after one month, and (c) CdS/PMMA core/shell NPs after one month.

quite similar to each other. This result obviously suggests that the nano-sized PMMA shell around the CdS core does not affect the optical property of the CdS core due to its optical transparency.¹³ Fig. 3(d) shows an emission photograph of CdS/PMMA core/shell NPs. The sample was irradiated by a UV-lamp of 365 nm, and a blue color was observed from CdS NPs, which is well matched with the PL spectra.

Fig. 4 illustrates the X-ray diffraction (XRD) pattern of the as-prepared CdS NPs, CdS NPs after one month under air, and CdS/PMMA core/shell NPs after one month under air. The XRD pattern of as-prepared CdS nanoparticles indicates the characteristic peaks of cubic crystal structure corresponding to (111), (220) and (311) reflections.¹⁴ As can be seen from Fig. 4(b), the XRD pattern of CdS nanoparticles after one month was different from that of the as-prepared CdS nanoparticles. The CdS nanoparticles had been degraded, so that their original crystal structure was lost. Judging from this result, the surfactant as a stabilizer does not provide CdS nanoparticles with long-term stability and crystallinity under air and against photooxidation. Fig. 4(c) presents the XRD pattern of CdS/PMMA core/shell nanoparticles after one month. The diffraction peaks of Fig. 4(c) were identical with those of Fig. 4(a), which were designated with the cubic crystal system. Therefore, it could be concluded that the CdS nanoparticles were successfully encapsulated by PMMA layers. In addition, the PMMA-coated CdS nanoparticles maintained their surface stability against photooxidation and oxidation under air.

In conclusion, CdS/PMMA core/shell NPs were fabricated using DMIP. The PMMA shell effectively protects the surface of the CdS core from photooxidation and oxidation under air. In addition, the CdS/PMMA core/shell structure maintained the optical properties of the CdS NPs due to the optical transparency of PMMA. Dispersion-mediated interfacial polymerization provided a facile route to prepare the polymer shell on the inorganic core, and can be expanded to the fabrication of various inorganic/polymer and polymer/polymer core/shell structures.

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