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Core/Shell Structured Noble Metal (Alloy)/Cadmium Selenide Nanocrystals

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Heterogeneous nanostructures have become increasingly important, because they often exhibit multifunctional capabilities with tunable or enhanced properties.[1] Core/shell structure fabrication represents one of the most fundamental approach for creating heterostructured smart nanodevices.[2,3] Many core/shell structured nanoparticles including CdSe/CdS,[4] CdSe/ZnS,[5] Pt/Pd,[6] Pt/Fe_2O_3,[7] $FePt/Fe_3O_4$,[8] etc., have been synthesized.

Because of their excellent optical, electrical, magnetic, and catalytic properties, noble metal (alloy) nanoparticles and cadmium chalcogenide nanocrystals such as Au,[9] FePt,[10] CdSe,[11,12] FePt-CdS,[13,14] FePt-CdSe,[14] Au-CdSe,[15,16] Au-CdS,[17] Pt-CdS,[1a] NiPt-CdS,[1a] and CoPt-CdS,[1a] especially those heterogeneous nanostructured[13−15] are of special interest for ultrahigh density data storage, sensing, diagnostics, biolabeling and detection, and other applications.

Here we demonstrate a general synthesis of core/shell structured noble metal (alloy)/cadmium selenide nanocrystals, in which a FePt,[18] NiPt,[19] or Au[20] core is coupled with a shell of CdSe[21] controllable in thickness. The synthesis procedure is as described below. A mixture of noble metal (alloy) nanoparticles, cadmium stearate and oleylamine (OAm), hexadecylamine (HDA), or octyl ether (OE) and 1,2-hexadecandiol (HDD) was heated to 290−300 °C, then injected swiftly with Se precursor solution, followed by reacting for 10 s to 20 min before being cooled to room temperature (RT). The products were purified by size-selective precipitation/washing steps, and finally dispersed in n-hexane (see the Supporting Information for experimental details).

Images A and B in Figure 1 show the HRTEM images of the formed core/shell structured FePt/CdSe nanocrystals using OAm as a solvent. The clear crystal structures were indicative of the cores and the shells. The cores (about 4.0 nm in size) were coated by shells with a thickness of 2.2 or 3.3 nm. By increasing the thickness, the shells gradually became incomplete because of the incompatibility of the lattices of the core and the shell and surface tension.[13] Energy-dispersive X-ray spectroscopy (EDX) indicated that the core/shell structured nanocrystals contained elements of Fe, Pt, Cd, and Se (Figure 1C), the cores were mainly composed of Fe and Pt (see Figure S1A in the Supporting Information), whereas the shells mainly of Cd and Se (see Figure S1B in the Supporting Information). Powder X-ray diffraction (XRD) patterns (see Figure S2 in the Supporting Information) of core/shell structured FePt/CdSe nanocrystals exhibited diffraction peaks that could be indexed to face-centered cubic (fcc) FePt and hexagonal CdSe.

Core/shell structured NiPt/CdSe nanocrystals can also be prepared in the same manner. As shown in images D and E in Figure 1, the crystal structures in the HRTEM images indicated that the cores were nanocrystals of about 5.0 nm in size and the shells were nanocrystals of 2.0 or 3.5 nm in thickness. EDX microanalysis confirmed that the products consisted of elements of Ni, Pt, Cd and Se (Figure 1F), the cores of Ni and Pt (see Figure S3A in the Supporting Information), whereas the shells of Cd and Se (see Figure S3B in the Supporting Information). The XRD measurements (see Figure S4 in the Supporting Information) show that the patterns of core/shell structured

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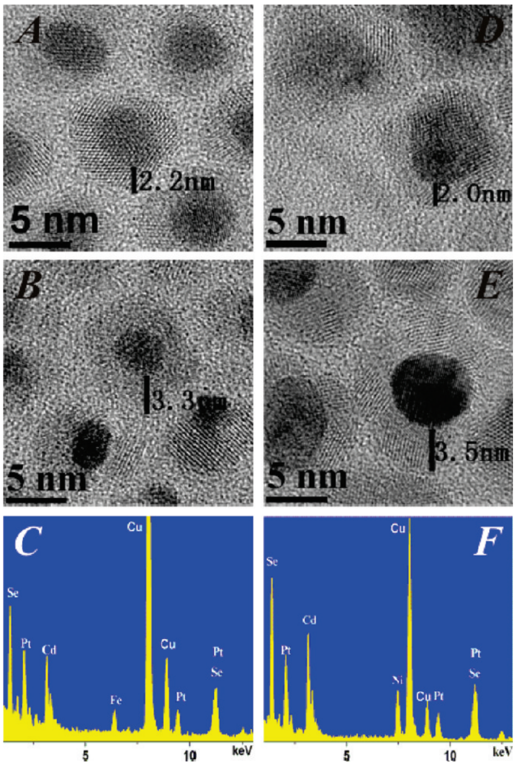

Figure 1. HRTEM images and EDX spectra of the as-prepared (A–C) FePt/CdSe and (D–F) NiPt/CdSe nanocrystals. FePt/CdSe nanocrystals with shell thicknesses of (A) 2.2 and (B) 3.3 nm; NiPt/CdSe nanocrystals with shell thicknesses of (D) 2.0 and (E) 3.5 nm.

NiPt/CdSe nanocrystals agreeed well with fcc NiPt and hexagonal CdSe.

Besides, Au/CdSe core/shell structures could also be fabricated by coating an Au core with a CdSe shell in OAm. Images A and B in Figure 2 show the HRTEM images of the products. The core had a diameter of about 6.0 nm and the shell sizes could be changed from 1.8 to 3.0 nm. The XRD patterns (Figure 2C) verified the presence of crystalline Au and CdSe. EDX shows the presence of elements of Au in the core and Cd and Se in the shell in the products (panel D in Figure 2, and panels A and B in Figure S5).

To understand the possible mechanism for formation of core/shell structured nanocrystals, we selected CoPt[22] nanoparticles as an example of noble metal alloys, and trioctylphosphine oxide (TOPO), OE, and HDA as solvents. Figure 3A–C shows the HRTEM images of products prepared in different solvents, such as TOPO (Figure 3 A), OE (Figure 3B), and HDA (Figure 3C). Only in HDA could core/shell structures be formed. As described earlier in the text, core/shell structures could also formed in OAm. As well-known, HDA and OAm are both primary amines. They can react with stearate to form the corresponding amide, leading to the precipitation of cadmium oxide,[23] whereas TOPO and OE cannot because they cannot react with stearate. Our previous results[24] also suggested that Cd could

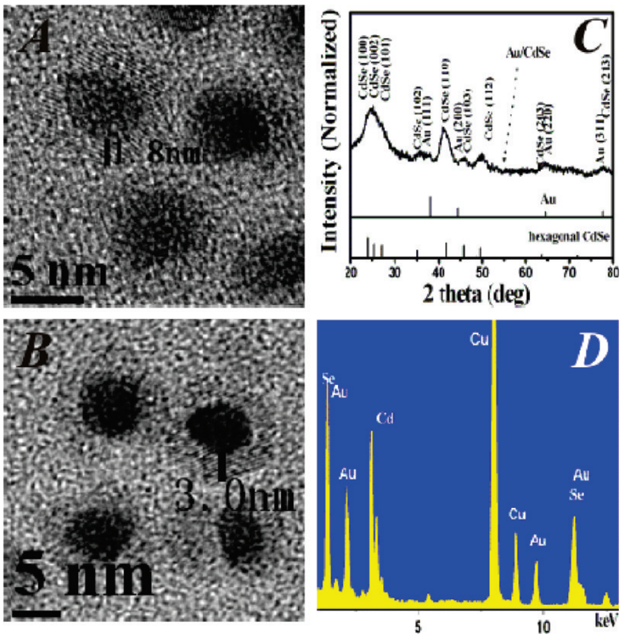

Figure 2. (A, B) HRTEM images, (C) XRD pattern, and (D) EDX spectrum of the as-prepared Au/CdSe nanocrystals with a (A) 1.8 nm thick and (B) 3.0 nm thick shell.

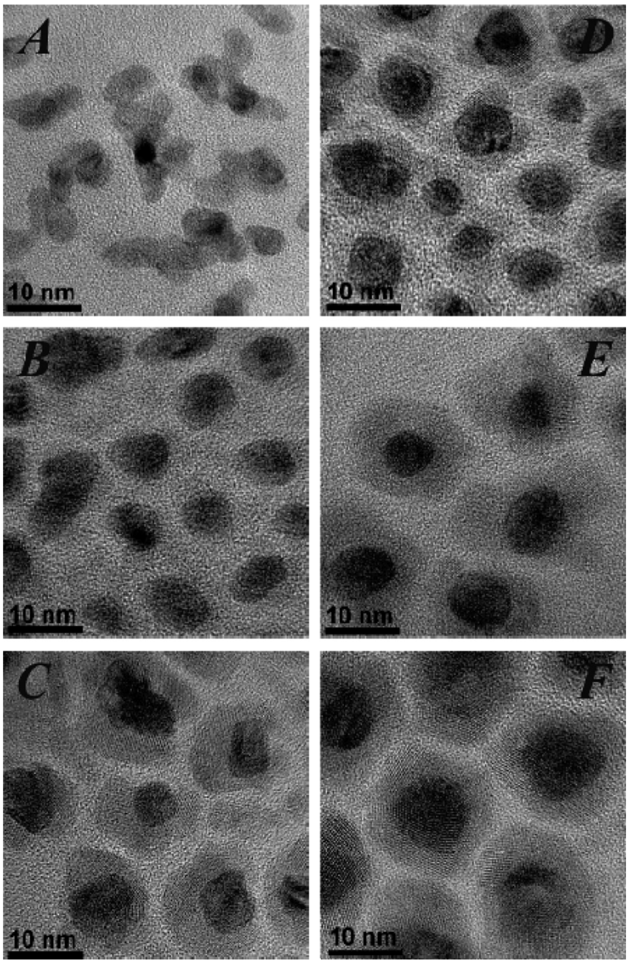

Figure 3. HRTEM images of (A–D) CoPt-CdSe, (E) CoPt/CdS and (F) NiPt/CdSe in different solvents. Growing (A) in TOPO at 300 °C for 15 min, (B) in OE at ca. 290 °C for 1 min, (C) in HDA at 300 °C for 10 min, (D) in OE with some HDD added at ca. 290 °C for 1 min, (E) in OAm at 300 °C for 5 min, and (F) in OE with some HDD added at ca. 290 °C for 5 min.

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precipitate onto the core in some fashion in OAm before injecting Se precursor, also supported by the control experiment of the formation of core/shell structured CoPt/CdS (Figure 3E) in OAm after injecting S precursor. To further understand whether the stripping off of the stearate ligands facilitated the formation of core/shell structures, we used OE as a solvent together with some amount of HDD added. As shown in Figure 3D, clear core/shell structures could be observed, suggesting that HDD could facilitate the formation of core/shell structure because its hydroxyl groups could also react with stearate to form the corresponding ester, as can be also confirmed by the formation of core/shell structured NiPt/CdSe (Figure 3 F) in OE with some HDD added. Overall, reagents capable of reacting with the carboxyl of fatty acids of cadmium precursors would strip off fatty acid ligands to make Cd precipitate onto the core, followed by formation of core/shell structure.

In conclusion, we have developed a versatile approach for preparing core/shell structured noble metal (alloy)/cadmium selenide nanocrystals with different shell thicknesses. FePt/CdSe, NiPt/CdSe, and Au/CdSe were synthesized, which are of particular interest for fabricating heterostructured smart nanodevices applicable in fields such as fluorescent-magnetic resonance multimodal imaging, biosensing, photocatalysis and magnetic applications, etc.

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Supporting Information Available: Experimental details and supplementary figures (PDF). This material is available free of charge via the Internetat http://pubs.acs.org.