Stability Investigation of PbSe and PbSe/CdSe Nanocrystals

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Introduction

Colloidal IV-VI semiconductor nanocrystals (NC) are of increasing interest in potential applications such as telecommunication, photoelectronic device, and biomedical labeling. The band gap of bulk PbSe is only 0.28 eV at room temperature, and its exciton Bohr radius is 46nm as a strong confinement effect material.

In the past decade, several approaches have been developed to prepare the PbSe nanocrystals with uniform size and high emission efficiency[1-4]. However, because the PbSe nanocrystals are unstable in the air condition[5-7], several ways have been used to stabilize it. PbSe/PbS[8] and PbSe/SiO_2[9] core/shell structures have been developed but with excessive loss of quantum efficiency. Hollingsworth group developed an ion exchange method to use Cd to replace Pb in outlayer of large PbSe core nanocrystals to form core/shell PbSe/CdSe core/shell structure[10]. The limitation of this method is it is difficult to growth thick CdSe layer and damage lattice structure of PbSe nanocrystals. Although many approaches have been studied, the stability of PbSe remains a critical issue preventing widespread commercial applications. In this letter, we employ the successive ion layer adsorption and reaction[11] (SILAR) to form the air-stable PbSe/CdSe nanocrystals with high quantum yield. The thickness of the CdSe layer can be well controlled.

Experimental Section

Materials

Lead (II) oxide (99.99%), 1-octadecylamine (ODA, 98%), and cadmium cyclohexanebutyrate were purchased from Alfa Aesar. Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), tributylphosphine (TBP, 97%), and selenium (100 mesh, 99.99%) were obtained from Aldrich. Oleylamine (OLA, 98%) was purchased from City Chemical. Acetone, chloroform, methanol, toluene, and tetrachloroethylene were purchased from VWR.

Synthesis of PbSe Core Nanocrystals

PbSe nanocrystals were synthesized on the basis of our previously reported approach[2]. In detail, 0.892 g (4.00 mmol) of PbO, 2.260 g (8.00 mmol) of OA, and 12.848 g of ODE were loaded into a three-neck flask and heated to 180°C to dissolve PbO powder under N_2 flow. The temperature was then set to 170°C, and 6.400 g of 10% Se-TBP solution was swiftly injected into the vigorously stirred solution. After the injection, the temperature quickly dropped and was then kept at 140°C for the growth of PbSe nanocrystals.

Injection Solutions

The cadmium injection solution (0.04 M) was prepared by dissolving cadmium cyclohexanebutyrate (0.1804 g) in OLA (8.13 g) at 60°C under N_2 flow to obtain a clear solution. The selenium injection solution (0.04 M) was prepared by dissolving selenium (0.0316 g) in ODE (7.88 g) at 220°C under N_2 flow to obtain a clear yellow solution. Then, both injection solutions were allowed to cool to room temperature.

Synthesis of PbSe/CdSe Nanocrystals

PbSe nanocrystals (4.8 nm in diameter, 1.01×10^{-4} mmol of particles) dissolved in 5 mL of hexanes were loaded in a 25 mL three-neck flask and mixed with 1.500 g of ODA and 5.000 g of ODE. A mechanical pump was employed at room temperature for 30 min to remove the hexanes from the system. Subsequently, the reaction mixture was heated to 120°C. For each injection, a predetermined amount of the cadmium and selenium solutions were injected into the three-neck flask with a syringe using a standard air-free procedure. The reaction was stopped by the injection of toluene and followed by a methanol extraction. Then, the nanocrystals were dissolved in chloroform to precipitate them with acetone to remove excess amines.

Result and Discussion

Figure 1 and 2 shows the evolution of absorption and photoluminescence (PL) spectra of the PbSe/CdSe NQDs upon the growth of 2.1 nm CdSe shell over 4.8 nm PbSe cores in a typical reaction. A consistent red shift of the peak wavelength was observed from both the absorption and PL spectra. Similar wavelength shifts were also mentioned by Li *et al.*[11] and Xu *et al.*[8] in their synthesis of CdSe/CdS and PbSe/PbS core/shell NQDs respectively. It is realized that the increase of CdSe layers reduced the quantum

confinement on the electronic transitions in PbSe nanocrystals because of the relatively low barrier height at the PbSe/CdSe interface and renders the spreading of the carriers' wavefunctions out of the core regions, which in turn leads to the observed red shift of the optical transition with respect to the plain core samples.

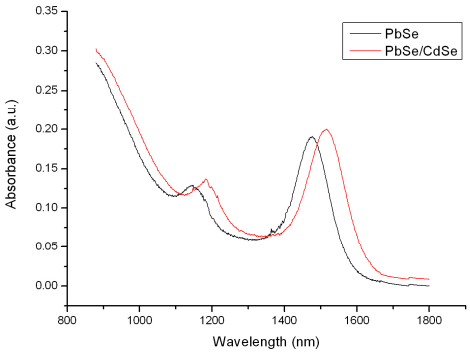

Fig.1: The evolution of the absorption spectra of 4.8 nm PbSe cores with 2.1 nm CdSe shell.

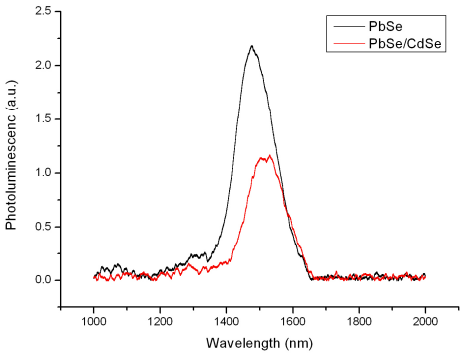

Fig.2: The evolution of the photoluminescence spectra of 4.8 nm PbSe cores with 2.1 nm CdSe shell

CdSe shells leaves PbSe cores effectively separated from the ambient conditions. Previously the PL spectra were observed to be unstable. The stability of PbSe nanocrystals is tremendously enhanced under ambient conditions with CdSe shell. A shell of CdSe extends the useful life of PbSe NQDs under ambient conditions from a few days to at least several months, during which time the emission efficiency almost doesn't decline. The normalize quantum yield (QY) data is shown in Table 1. Compared with QY of PbSe nanocrystals, QY of PbSe/CdSe nanocrystals is stable under ambient conditions.

Table 1: QY of PbSe and PbSe/CdSe nanocrystals under ambient conditions

Time	PbSe	PbSe/CdSe
Fresh NCs	1.00	0.82
11 days	0.06	0.81

Conclusion

The SILAR technique was used in the synthesis of PbSe/CdSe core/shell nanocrystals. The stability of PbSe nanocrystals was tremendously enhanced under ambient conditions.

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