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Reduced photo-instability of luminescence spectrum of core-shell CdSe/CdS nanocrystals

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Coated CdSe/CdS nanocrystals have been synthesized through a new reaction routine in micelle solution. High resolution transmission electron microscope image demonstrated the monodispersity and core-shell structure of CdSe/CdS nanocrystals. Photooxidation experiments shown that by coating with a wider bandgap material CdS, the surface states of CdSe cores could be decreased and the photo-instability of their luminescence spectrum could be reduced. This phenomena were temporary interpreted that lack of carriers at the outlayer surface reduced photooxidation degradation of CdSe/CdS nanocrystals.

1. Introduction

Semiconductors of nanometer size show interesting electrical and optical properties due to their large quantum-sized effect. Because semiconductor nanocrystals such as CdSe and CdS can emit tunable lights which depend upon their sizes, they has many potential application in optoelectronic devices. However, bare nanocrystals CdS or CdSe are unstable in luminescence spectrum when exposed to air and light due to photooxidation at their surface. This has placed some limits on the use of the nanocrystals. To control the nanocrystal surface and reduce the photochemical instablility of II–VI nanocrystals, great efforts have been made. Inorganic passivation is mostly used methods. By coating nanocrystal with a wider bandgap material the surface of core nanocrystal can be electronically passivated, which can boost the amount of luminescence and reduce photochemical degradation.

Many inorganic passivation systems of II–VI nanocrystals have been studied, such as CdSe/ZnS [1], CdSe/CdS [2] and HgS/CdS [3] and have been shown improved luminescence properties.

In this paper we focus the study on reducing the photo-instability of CdSe core by coating with a shell of CdS. We used a new reaction routine to produce CdSe and coated CdSe/CdS nanocrystals in micelle solution. HRTEM observation confirmed the core-shell structure of CdSe/CdS nanocrystals. Photooxidation experiments demonstrate that photochemical stability of luminescence spectrum of core-shell CdSe/CdS is enhanced as compared to the CdSe cores.

2. Experiments

2.1. Synthesis of CdSe and CdSe/CdS

CdSe nanoparticles in micelles were prepared according to following reaction [4]:

$$Cd^{2+} + 2\,OH^- + SeSO_3^{2-} \rightarrow CdSe + SO_4^{2-} + H_2O \tag{1}$$

Two separate solutions were prepared by dissolving surfactant AOT (sodium dioctyl sulfosuccinate) in heptane. Then deionized water was added to above two solutions. Stirring gave two homogeneous micelle solutions with $W = 2$–5 ([H_2O]/[AOT]). Under quickly stirring a standard solution of Cd^{2+} was added to one of above micelle solutions, while a $SeSO_3^{2-}$ solution was added to another micelle solution. Then the Cd^{2+} micelle solution was transferred slowly to $SeSO_3^{2-}$ solution and this procedure resulted in a orange or red CdSe solution. The size of CdSe nanocrystals could be controlled by changing the Cd^{2+} concentration, $SeSO_3^{2-}$ concentration and W value of the micellar solution.

To prepare coated CdSe/CdS nanocrystals, micelle solution containing Na_2S aqueous solution and heptane were added dropwise to above starting CdSe micelle solution (with a Cd/Se molar ratio of 1.5/1.0) under stirring. S^{2-} ions could react with Cd^{2+} ions on the surface of the CdSe core forming layers of CdS on the CdSe cores.

3. Results and discussion

3.1. Core-shell structure

Average sizes of CdSe cores and CdSe/CdS nanocrystals can be determined by TEM images. We surveyed of approximately 300 nanoparticles of CdSe and CdSe/CdS respectively. This yielded the histograms shown in Fig. 1 curve a and curve b. The average diameter of CdSe is about 2.1 nm, and the particles have a narrow size distribution. When the CdSe sample were treated with 0.5 mM Na_2S. The average diameter of coated CdSe/CdS nanocrystals increased to about 3.1 nm (see Fig. 1 curve b), and those particles have a slightly broader distribution.

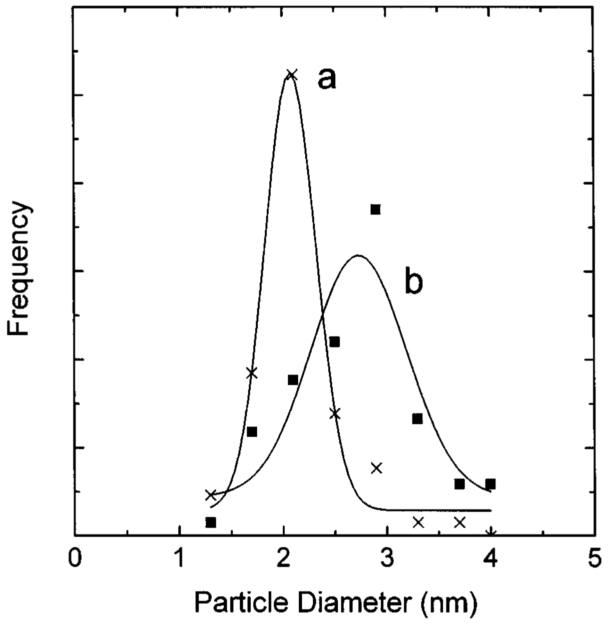

Figure 1 Particle size histograms of CdSe (×) and CdSe/CdS nanocrystals (■).

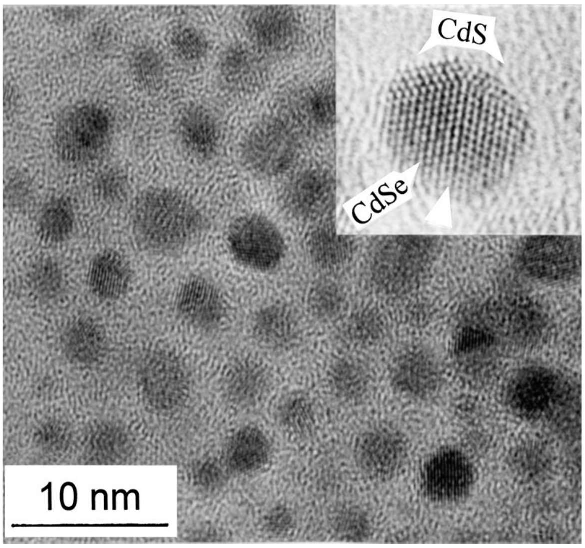

Figure 2 HRTEM micrograph of coated CdSe/CdS nanocrystals. The sample was prepared by coating nanocrystals from 0.6 mM CdSe in micelle solution.

A JEM-4000EX electron microscope operating at 400 KV was used for HRTEM observation. Fig. 2 is a HRTEM micrograph of CdSe nanocrystals coated by CdS. As shown in the inset of Fig. 2, for a single CdSe/CdS nanocrystal, two parts with different contrasts were observed. A darker core areas of strong absorption of the electron beam is believed to be CdSe and a brighter shell areas of less absorption is believed to be CdS. The CdSe core areas with a triangular structure is viewed along the [001] zone axes. The core area shows a hexagonal shape due to faceting along (100) surface planes of CdSe. (In the middle of the core area arrowhead indicates a edge dislocation which was formed by two attached nanocrystals [5].) It is clearly shown that on those (100) surface planes several layers of semiconductor CdS has been grown. As it grows, an flat and ordered interface appear. Because CdS has a lighter atomic weight than CdSe, the shell parts of CdS absorbs more electron beam and appear brighter than CdSe core does.

The increase of the mean diameter and HRTEM micrograph of the CdSe/CdS nanocrystals confirmed that core-shell CdSe/CdS nanocrystals were formed using this type of preparation.

3.2. Photo-instability in CdSe core due to surface traps

To investigate the photochemical stability of CdSe/CdS nanocrystals, photooxidation experiments were carried out. CdSe or CdS nanocrystals in micelle dissolved and degraded in aerated solutions upon a strong sunlight illumination at $T = 300$ K [6]:

$$\mathrm{CdS} + \mathrm{O_2} \overset{h\nu}{\rightarrow} \mathrm{Cd^{2+}} + \mathrm{SO_4^{2-}}$$

Fig. 3 shows the absorption and PL spectra of bare CdSe solution with different illumination time, the sample was prepared with a Cd/Se molar ratio of 1.0/1.0.

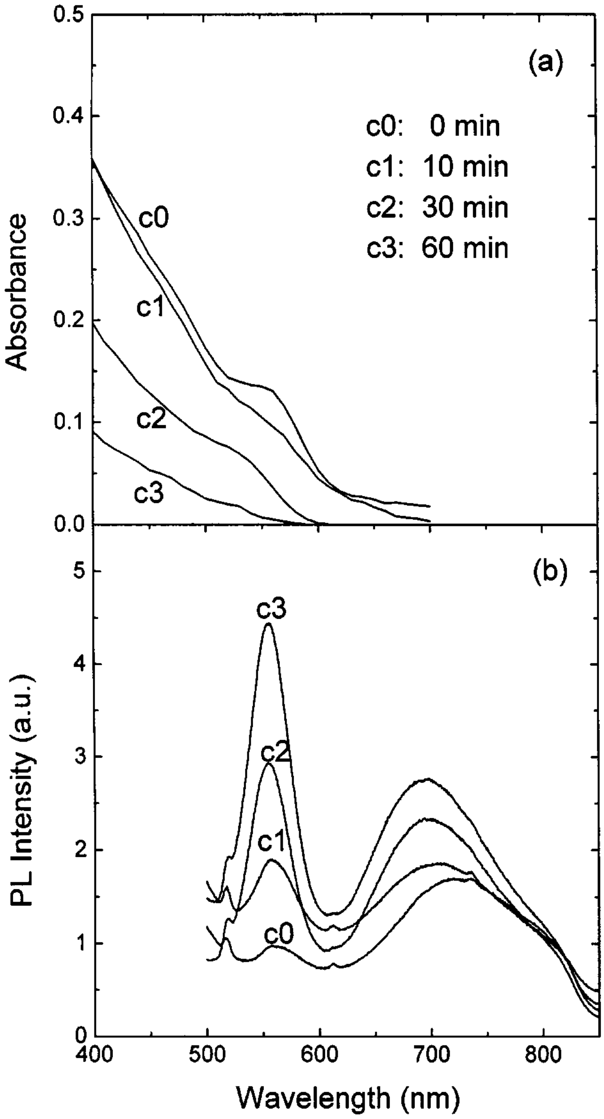

Figure 3 Ultraviolet-visible absorption spectra and PL spectra of bare CdSe nanocrystals in micelle solution after different times of sunlight illumination ($\lambda_{\mathrm{exc}} = 450$ nm).

As shown in Fig. 3a, with times increasing the nanocrystals became smaller, the absorption edge as well as the 1s-1s transition peaks was shifted to shorter wavelength due to quantum-sized effect (curves c1 to c3). The PL spectra in Fig. 3b also show the process of photooxidation and instability of the nanocrystals. In generally there are two PL peaks: a narrow one due to band-edge emission and a broad lower energy peak attributable to the recombination of the surface trapped carriers. As seen in curve c0, before illumination most carriers recombine through surface traps, the intensity of band-edge peak is lower than that of surface state peak. After illumination, as size of the nanocrystals decreasing, both peaks shift to shorter wavelength. Besides, the intensity of two peaks also increase. We thought this is due to the activation of bare CdSe nanocrystal by a $Cd(OH)_2$ precipitate [6]. Cd^{2+} ions which formerly had been released by photooxidation reacted with the OH^- ions in the solution and formed a $Cd(OH)_2$ shell at the CdSe nanocrystal surface, which activated the particle and enhanced the luminescence peaks dramatically.

The photo-instability of CdSe core is reasonable because the photooxidation reaction requires the presence at the nanocrystal surface of oxygen and carriers [6]. In bare CdSe nanocrystals, electrons and holes are trapped by surface states (as seen in curve c0). So when these nanocrystals were exposed to oxygen and a strong sunlight they dissolved and degraded rapidly through photo-oxidation reaction.

3.3. Reduced photo-instability in luminescence spectrum of CdSe/CdS

By coating with a shell of CdS we can reduce the photo-instability of CdSe core. Fig. 4 shows the absorption and PL spectra of CdSe/CdS nanocrystals before and after sunlight illumination. Firstly, we could see clearly that the CdSe/CdS nanocrystals exhibit a more sharp band-edge emission in luminescence spectrum (see curve s0). This is interpreted as a removal of recombination centers during the formation of CdS layers on the CdSe core, which improved the luminescence properties of the CdSe/CdS nanocrystals. As compared to CdSe cores in Fig. 3, the intensity and position of the PL peaks of CdSe/CdS change little and the

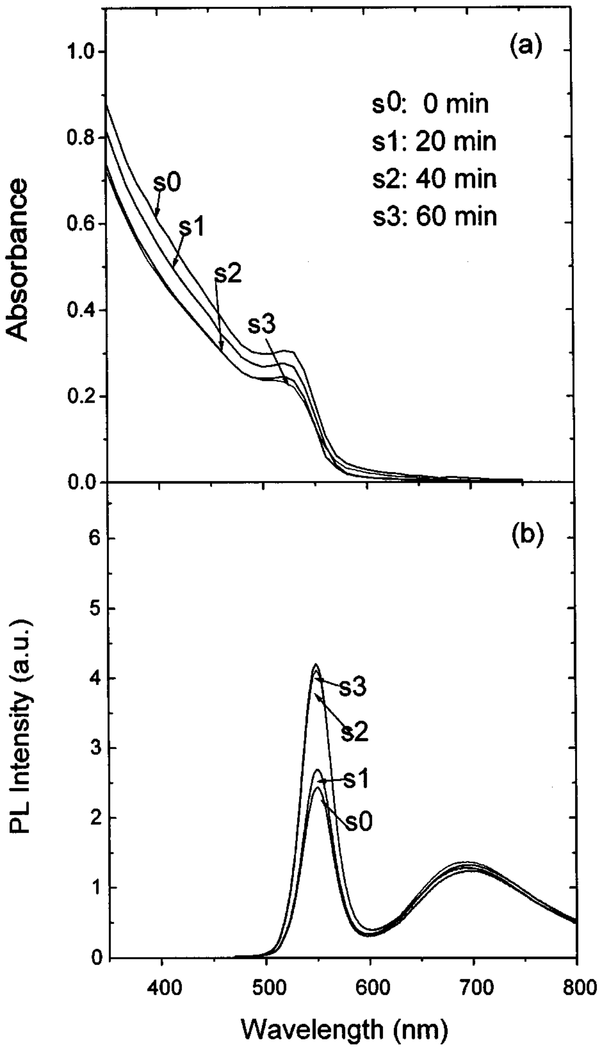

Figure 4 Ultraviolet-visible absorption spectra and PL spectra of coated CdSe/CdS nanocrystals in micelle solution after different times of sunlight illumination ($\lambda_{exc} = 450$ nm).

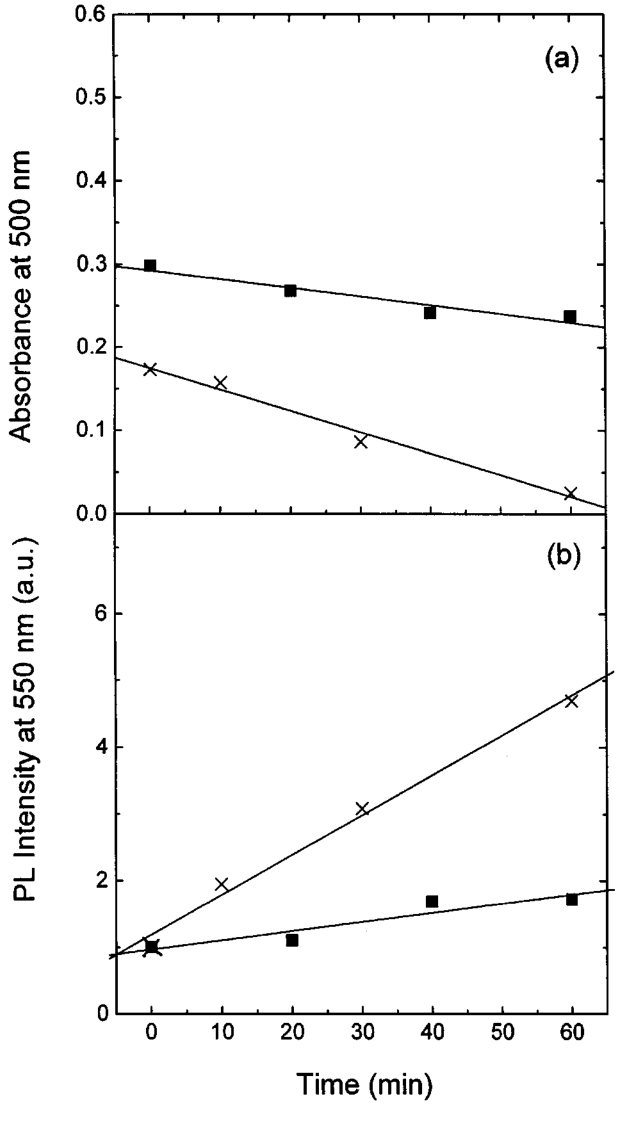

Figure 5 Comparison of photooxidation stability of CdSe and coated CdSe/CdS nanocrystals. (a) Absorbance at 500 nm, (b) PL intensity at 550 nm as a function of illumination time. CdSe (×) and CdSe/CdS nanocrystals (■).

1s-1s transition peaks as well as the absorption edges in absorption spectra also show little shifts (see curve s1 to s3) during the illumination time of 1 hour.

We compared the photostability of CdSe core and CdSe/CdS nanocrystals using the optical absorbance at 500 nm and PL intensity at 550 nm. The results is shown in Fig. 5. It shows clearly that during illumination times of about 1 hour, CdSe/CdS nanocrystals were more stable than CdSe core.

The reduced photo-instability in luminescence spectrum of core-shell CdSe/CdS could be interpreted that: By coating CdSe core with a wider bandgap material CdS, both holes and electrons will experience a potential which confine them away from the outlayer surface. Then the lack of carriers at the coated nanocrystal surface reduced photooxidation degradation of core-shell CdSe/CdS nanocrystals.

4. Conclusions

In the present paper coated CdSe/CdS nanocrystals can be synthesized through a new reaction routine in micelle solution and they show a reduced photo-instability in luminescence spectrum. HRTEM images give us detailed structural information about these system. The results show the CdS shell of several layers in thickness have been grown on CdSe core.

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