

Fluorescence Properties of Cd(OH)₂-activated CdS and CuS-coated CdS Nanocrystals*

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Abstract CdS nanocrystals with a mean diameter 5 nm have been prepared by sol-gel method. Fluorescence (FL) properties of CdS nanocrystals modified with two different methods were studied at room temperature. Activation of CdS nanocrystals by a cadmium hydroxide precipitate leads to an enhancement of FL intensity by a factor of 15 compared with the ones without activation. We have firstly chosen CuS as a shell to coat CdS nanocrystals by ion substitution reaction, and the FL of the coated CdS/CuS was also investigated. With the modification of CuS the initial surface defect states of CdS nanocrystals was passivated, which resulted in the appearance of the direct 'band-edge' recombination of the electron-hole pair in CdS nanocrystals.

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1 Introduction

Recently, the study on the characterization of the semiconductor nanocrystals prepared by sol-gel method has been made including almost all II-VI compounds. Some III-V semiconductors^[1] and even IV-IV semiconductors^[2] also can be prepared in solution. Since quantum confinement of electrons and holes in a nanocrystal, the colloidal semiconductor nanocrystals have displayed some novel linear and nonlinear optical properties compared with the bulk materials. But as the size of nanocrystals decreases, the surface to volume ratio of nanocrystals increases and the surface effect becomes important. Especially, the interface-related defects strongly affect the FL process of nanocrystals. On the one hand the strong FL from the defects make the 'band-edge' recombination difficult to be detected, on the other hand some defect states as the nonradiative recombination centres of the

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charge carriers make FL efficiency of nanocrystals very low. In order to improve FL features of nanocrystals the surface modification techniques have been used to increase the FL quantum yields. For example, CdS has been used to produce a fully epitaxial shell around CdSe nanocrystals which displays luminescence quantum yields as high as 80% at room temperature^[3], CdSe quantum dots passivated with a ZnS layer displays strong luminescence (35 to 50% quantum yield) at room temperature^[4,5]. The coated CdSe/CdS system has been used as fluorescent probes for the study of biological materials^[6].

In this paper we present detailed studies of optical properties of colloidal CdS nanocrystals treated by surface modification with two different materials. Activating CdS with a relatively wide-bandgap Cd(OH)₂ results in a dramatic enhancement of fluorescence intensity of CdS nanocrystals, while coating CdS with a relatively narrow-bandgap CuS make the direct 'band-edge' FL of CdS nanocrystals observable.

2 Experiment

The CdS base sol was prepared by sol-gel method. 9.5 ml of 2mM Na₂S aqueous solution was slowly injected into 10 ml of 2mM Cd(NO₃)₂ aqueous solution containing 10 ml of 0.4% gelatin as the stabilizing agent under vigorous stirring. The PH of solution before the precipitation with Na₂S was adjusted to 8. The whole synthetic time was about 5 min. The analyses of TEM and ED reveal that the size of CdS nanocrystals synthesized in this method is about 5 nm, and the crystal structure is the wurtzite structure^[7]. The activation of the base sol consisted of the dropwise addition of 1M NaOH to establish a pH of 11, followed by the dropwise addition of 1.2×10^{-5} M Cd(NO₃)₂.

In order to make the coated CdS/CuS nanocrystals, to the CdS base colloid solution above, 4ml of 2mM Cu(NO₃)₂ solution is added under stirring. Because of the absence of excess S²⁻ ions in the solution, the separated CuS single nanoparticles can not be formed directly. At first, Cu²⁺ ions are attached to the surface of CdS nanocrystals, and then the Cu²⁺ ions displace Cd²⁺ in the Cd—S bond to form a Cu—S bond on the surface of CdS nanoparticles. These CdS nanoparticles with a shell of CuS on the surface are called coated CdS/CuS nanocrystals. The procedure of ion displacing is shown in Eq. 1.



Here, we selected CuS with a relatively narrow-bandgap as coat material because the solubility product of CuS is at least 16 orders of magnitude smaller compared to that of CdS, which assure that the substitution-type reaction (1) can occur.

3 Results and Discussion

Figure 1 shows the absorption (curve a) and FL spectra of CdS nanocrystals at room temperature before (curve b) and after activation (curve c) ($\lambda_{\text{exc}} = 400\text{nm}$). The absorption spectrum of CdS nanocrystals shows that the onset of absorption is near 460nm, which means the bandgap of CdS nanocrystals is about 2.70eV. Compared with the bandgap

(2.45eV) of bulk CdS there is 0.25eV blue shift, which shows evident quantum sized effect. The base soils had a weak FL band in the 500 nm to 700 nm range, which is attributed to recombination of charge carriers immobilized in traps of different energies. The low quantum yield is due to the dominating of the non-radiative recombination of the charge carriers. After activation the FL intensity have an enhancement by a factor of 15 and the FL peak position ($\lambda = 570\text{nm}$) almost does not shift. We tentatively propose that the surface of CdS nanocrystals be passivated by Cd(OH)₂. It is because during activation, SH⁻ groups of the surface of CdS nanocrystals are converted into S²⁻ ions which then bind excess Cd²⁺ ions, possibly in the form of S²⁻...Cd²⁺...OH⁻ structure. The removal of SH⁻ groups and the accumulation of Cd²⁺ ions on the surface destroy the sites

where non-radiative recombination of the charge carriers can occur, so the radiation recombination of charge carriers trapped in shallow traps is enhanced relatively. The strong FL band is close to the onset of absorption ($\lambda = 460\text{nm}$), so we can deduce that it is attributed to the recombination of charge carriers trapped in shallow traps (near band gap recombination).

The FL spectra of CdS (curve *a*) and coated CdS/CuS system (curve *b*) at room temperature are shown in Fig. 2 ($\lambda_{\text{exc}} = 400\text{nm}$). Compared *b* with *a* two features are of interest: (1) The 'band-edge' fluorescence ($\lambda = 460\text{nm}$) of CdS nanocrystals becomes evident in the coated CdS/CuS system; (2) The initial FL peak of CdS nanocrystals shifts from 570nm to 680nm. From the two features we propose that after CdS nanocrystals were coated by CuS layer the surface defect states of CdS nanocrystals were passivated by CuS layer. So the strong FL from the traps on the surface of CdS nanocrystals is extinguished and the 'band-edge' FL relatively enhances. The FL peak at 680nm was attributed to the luminescence of CuS layer formed on the surface of the CdS nanocrystals, because the FL energy is close to the bandgap (2.0eV) of CuS nanocrystals. The scheme of the band structure for explaining the FL process of coated CdS/CuS is shown in Fig. 3. As the surface of CdS nanocrystals was coated by a layer of CuS, the initial surface defect states of CdS nanocrystals was passivated and the band of CuS is formed. The FL process of coated CdS/CuS system proceeds in two ways: one is the direct 'band-edge' fluorescence of CdS nanocrystals, the other is fluorescence from CuS layer. Because FL intensity from CuS layer is much weaker than that from the surface defect states of CdS nanocrystals and FL peak position from CuS layer deviate prominently from that from 'band-edge' of CdS nanocrystals, the direct 'band-edge' FL becomes observable.

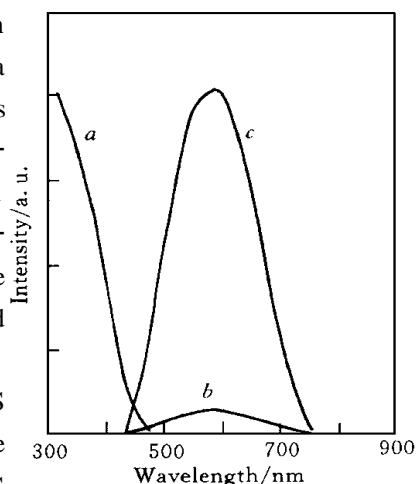


FIG. 1 Absorption (*a*) and fluorescence spectra of CdS before (*b*) and after activation (*c*)

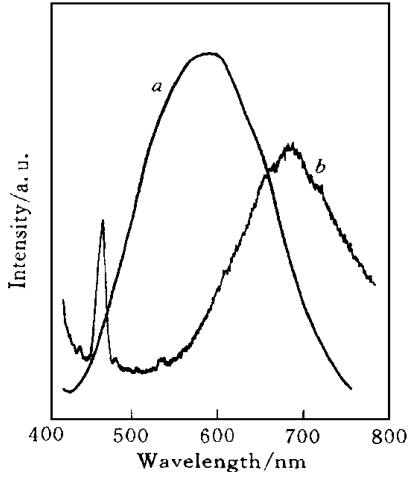


FIG. 2 Fluorescence spectra of CdS (a) and coated CdS/CuS system (b) ($\lambda_{\text{exc}} = 400\text{nm}$)

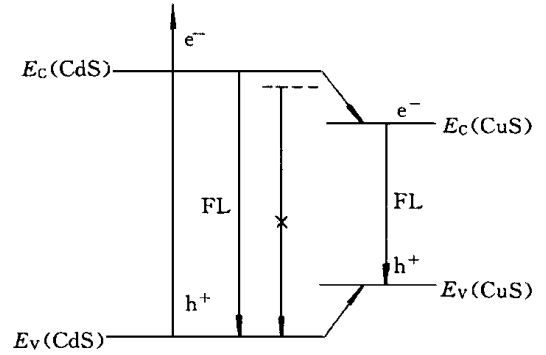


FIG. 3 Energy schemes illustrating the FL process of coated CdS/CuS system

4 Conclusion

Two different methods have been used to modify the surface of CdS nanocrystals. Cd(OH)₂-activated CdS nanocrystals have an enhancement of FL intensity as the result of surface passivation. Due to the formation of CuS layer on the surface of CdS nanoparticles, FL from the surface defect states of CdS nanocrystals is extinguished and the direct 'band-edge' FL becomes observable.

References

- [1] H. Ushida, C. J. Curtis and A. J. Nozik, *J. Phys. Chem.* 1991, **95**: 5382
- [2] J. R. Heath, *Science*, 1992, **258**: 1131.
- [3] X. G. Peng, M. C. Schlamp, A. V. Kadavanich *et al.*, *J. Am. Chem. Soc.*, 1997, **119**(30): 7019.
- [4] M. A. Hines and P. Guyot-Sionnest, *J. Am. Chem. Soc.*, 1996, **118**: 468.
- [5] B. O. Dabbousi *et al.*, *J. Phys. Chem.*, 1997, **101**: 9463.
- [6] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A. P. Alivisatos, *Science*, 1998, **281**: 2013.
- [7] H. M. Chen, X. F. Huang, H. B. Huang *et al.*, *SPIE*, 1998, **3175**: 32.