

## Multicolored luminescent CdS nanocrystals

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Received 15 July 2007; accepted 10 September 2007

**Abstract:** The observation of efficient blue, green, orange and red luminescence from CdS nanocrystals made by using a reverse micelle method was reported. The blue luminescence about 480 nm is attributed to the radiative recombination of electron-hole pairs. The red luminescence around 650 nm is due to the radiative recombination of the exciton trapped in the nanocrystal surface defect states. The combination of different portion of band-edge emission and surface trap state emission results in green and orange luminescence for the nanocrystals. The CdS nanocrystals with efficient multicolored luminescence may find potential application in full color displays and biolabelings.

**Key words:** CdS nanocrystals; reverse micelle; multicolor emission; luminescence modulation

### 1 Introduction

Semiconductor nanocrystals show unique size- or shape-dependent optical properties due to the quantum confinement effects, thus may find a wide range of applications in optoelectronic devices, photocatalysis, solar energy conversion and biological imaging and labeling[1–3]. For various aims of applications, the optical properties of semiconductor nanocrystals are required to be controllable and tailored. The tunability of optical properties of semiconductor nanocrystals is of key importance and would be beneficial to their applicability.

The II–VI semiconductor nanocrystals, such as CdSe, CdTe and CdS nanocrystals, are the group of nanostructures that have been mostly investigated[4–8] because of their high luminescence efficiency and easily adjustable luminescence from ultraviolet to near infrared region by nanocrystals sizes showing the prospective for optoelectronic devices and biological imaging and labeling applications. The synthesis of high quality CdTe and CdSe nanocrystals has been continuously reported, and their tunable emissions covering almost all visible regions have been achieved successfully. While for the

CdS nanocrystals, due to the hardness for controlling their surface situation, in most cases, the visible emission around orange region arised from the recombination of CdS nanocrystal surface trap states is inevitably observed, and their bandgap emission at blue region is hardly realized because of the trap states abundant on the nanocrystal surfaces. Recently, PENG et al[5] have reported the synthesis of high quality CdS nanocrystals, however the nanocrystals tend to give deep-trap luminescence. BAWENDI et al[4] has achieved the blue luminescence, however in order to realize it, inorganic ZnS shells are used to modify CdS cores to form a CdS/ZnS core-shell nanostructures. The blue luminescence was found that it came from CdS nanocrystalspolymer composites[9]. The direct realization of blue or even multicolored luminescence from pure CdS materials is still a challenge.

As a direct wide bandgap (2.42 eV) semiconductor, CdS nanocrystals may be potentially used in optoelectronics of nonlinear optics and light emitting diodes. It is also found CdS nanocrystals show electronically driven laser properties, which may open a pathway for using CdS nanocrystals in telecommunications and data storage areas[1]. Recently, a new simulated emission of CdS nanostructures has been

observed by several groups[10–12], and their stimulated emission properties are largely related to the surface situation and crystallization of nanocrystals. Therefore the controlling and tuning of band-edge emission and surface trap state emission of CdS nanocrystals are obviously very important to realize the tunable optical properties, and laser emission.

Previously we have reported a novel quaternary reverse micelle method for obtaining blue emitting CdS nanocrystals[13]. The method was facile and available for obtaining size tunable CdS nanocrystals. However, we did not realize tunable emission in all visible range, and the insight mechanism of emission was not fully presented. In this work, we found that by adjusting the reactant concentration and post-treatment of the obtained CdS nanocrystals, the band-edge emission and surface trap state emission of CdS nanocrystals can be leveraged, resulting in the different emissions in blue, green, orange and red colors. The proportions of band-edge emission and surface trap state emission according to surface situation and crystallization are the key factors affecting the emission properties of CdS nanocrystals. The results preliminarily show the possibility of controlling and tuning CdS nanocrystal luminescence properties.

## 2 Experimental

### 2.1 Preparation of CdS nanocrystals

The synthesis of multicolored luminescent CdS nanocrystals follows a simple reverse micelle method developed by our group. The preparative procedures are described as follows. Typically, two of reverse micelles were prepared. One contains cetyltrimethyl ammonium bromide(CTAB), hexanol, heptane and  $\text{Cd}(\text{NO}_3)_2$ , and the other consists of CTAB, hexanol, heptane and  $\text{Na}_2\text{S}$ , according to the amount of each composition listed in Table 1. Then one reverse micelle was dropwise added into the other reverse micelle at room temperature with continuous stirring. The reaction could take place upon the mixing of the two micelles with the solution turned into yellow within several seconds indicating the formation of CdS nanocrystals. The formed nanocrystals show different emitting colors of orange and red with wavelength at 605 and 650 nm respectively due to the difference of reactant concentrations. Then the refluxing

post-treatment for promoting the crystallization and removing the surface trap states was performed under protection of nitrogen by diluting the formed CdS reverse micelle solution one time using the same composition reverse micelles but with water instead of reactant aqueous. The CdS nanocrystals exhibiting orange emitting color changed into blue emitting color after 5 h refluxing post-treatment, while for the CdS nanocrystals showing red emitting color converted into green emitting color after 8 h refluxing post-treatment.

### 2.2 Characterization

The size and morphology of the CdS nanocrystals were characterized by transmission electron microscopy (TEM, 9000-NAR, Hitachi, Japan) operating at 200 kV accelerating voltage. Dry powder samples were used for the XRD (Rigaku, Dmax-2000,  $\text{CuK}_\alpha$  radiation) structural measurements. The optical property of the samples was investigated by Uv-Visible Spectroscopy (UV-3010, Hitachi, Japan) and Fluorescent Spectroscopy, (F-4500, Hitachi, Japan). X-ray photoelectron spectroscopy(XPS, ESCALab5) was used to characterize the surface structure, composition and the surface state. Fourier Transform Infrared spectrometry (FT-IR, Nicolet Magna-IR 750) was adopted to study the capping agent exchange mechanism.

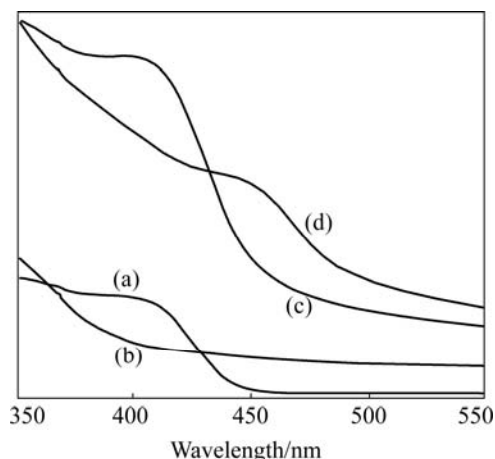
## 3 Results and discussion

### 3.1 Optical property of multicolored luminescent CdS nanocrystals

Fig.1 shows the Uv-visible absorption spectra of multicolored luminescent CdS nanocrystals. The as-prepared CdS nanocrystals obtained at lower original reactant  $[\text{Cd}^{2+}]$  or  $[\text{S}^{2-}]$  concentration ( $8.45 \times 10^{-4}$ ) have absorption onset around 450 nm (Fig.1(a)), while the CdS nanocrystals made at larger original reactant  $[\text{Cd}^{2+}]$  or  $[\text{S}^{2-}]$  concentration ( $4.23 \times 10^{-3}$ ) show a absorption feature around 475 nm due to the CdS first (1s–1s) transition[14]. The relatively sharp absorption peak indicates narrow size distribution of the nanocrystals. The larger concentration causes the fast growth of particle sizes, resulting in different absorption onsets. We performed the reflux treatment for the CdS nanocrystals made at both concentrations. After the reflux treatment,

**Table 1** Reaction conditions for preparing different emitting colored CdS nanocrystals

$m(\text{CTAB})/\text{g}$	$V(\text{Hexanol})/\text{mL}$	$V(\text{Heptant})/\text{mL}$	Reactant $\text{Cd}(\text{NO}_3)_2$ and $\text{Na}_2\text{S}$	$[\text{Cd}^{2+}]$ or $[\text{S}^{2-}]$ original concentration/( $\text{mol} \cdot \text{L}^{-1}$ )	Reflux treatment time/h	Emitting color
0.5	0.9	5.6	0.6 mL, 0.02 mol/L	$8.45 \times 10^{-4}$	0	Orange
0.5	0.9	5.6	0.6 mL, 0.02 mol/L	$8.45 \times 10^{-4}$	5	Blue
0.5	0.9	5.6	0.6 mL, 0.1 mol/L	$4.23 \times 10^{-3}$	0	Red
0.5	0.9	5.6	0.6 mL, 0.1 mol/L	$4.23 \times 10^{-3}$	8	Green

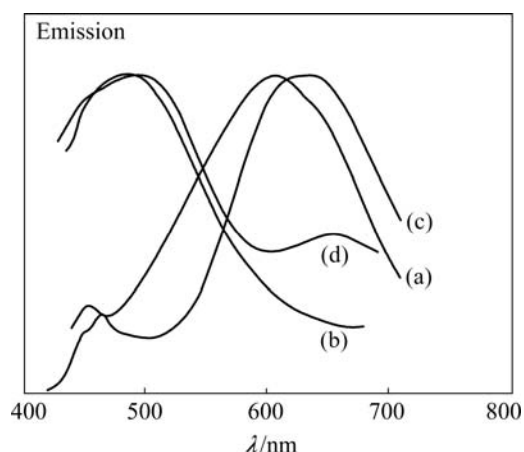


**Fig.1** Uv-visible optical absorption spectra of orange (a), blue (b), red (c) and green (d) emitting CdS nanocrystals

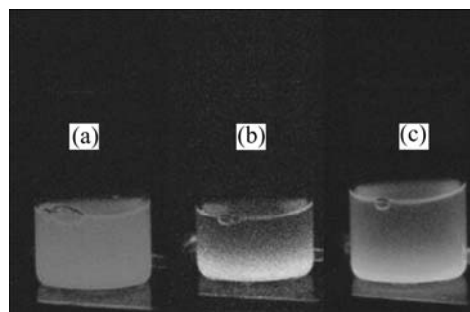
the absorption onsets of CdS nanocrystals obtained at both concentrations show a quite large red shift. The absorption onsets shift to 475 nm and 550 nm for orange and red luminescent CdS nanocrystals respectively. The red shift may be attributed to the nanocrystal growing larger under reflux treatment condition.

Fig.2 shows the room temperature photoluminescence of multicolored luminescent CdS nanocrystals. The as-prepared CdS nanocrystals at lower original reactant  $[Cd^{2+}]$  or  $[S^{2-}]$  concentration ( $8.45 \times 10^{-4}$ ) without reflux treatment show a strong emission peak around 605 nm, giving a deep orange color luminescence (Fig.2(a)). This emission peak is normally observed and derived from the recombination of the exaction trapped in the defect states localized on the nanocrystals surfaces[15–17]. A relatively small emission peak around 456 nm corresponding to blue emission is also observed. This blue emission is due to radiative recombination of an electron-hole pair as referred to band edge emission[14]. The band edge emission is much weaker than surface trap state emission, thus the blue emission is totally covered by the orange emission. The same case happens to the CdS nanocrystals prepared at larger original reactant  $[Cd^{2+}]$  or  $[S^{2-}]$  concentration ( $4.23 \times 10^{-3}$ ). The red emission with peak centered around 650 nm is evidenced, while a relatively small blue emission is observed as well (Fig.2(c)). As the orange and red emissions of CdS nanocrystals are attributed to the abundant trap states on nanocrystals surfaces, which results in poor crystallization, and in turn competes with the band edge emission. If one can control the crystallization and the trap state of the nanocrystals, i.e., the relative ratio of surface trap state emission and recombination luminescence of electron and hole pair, it may be possible to modulate the luminescent colors of the nanocrystals. Thus, we tried to leverage the band edge emission and surface trap state emission of CdS for

obtain multicolor luminescence by conducting the post-treatment by refluxing the as-prepared orange and red luminescent CdS nanocrystals. The reflux time can be controlled to obtain the CdS nanocrystals with different crystallization and trap states, which shows different proportion of band edge emission and surface trap state emission. The orange emitting CdS nanocrystals show the blue luminescence with emission peak at 480 nm after 5 h reflux post-treatment. The red emitting CdS nanocrystals have a green luminescence, which is composed of different proportion of blue emission and red emission. Therefore in this case it is possible for us to modulate the luminescent colors by combining different proportion of band edge emission and surface trap state emission to get multicolored luminescent CdS nanocrystals. The luminescence of CdS nanocrystals is brightly eye-viewable under UV irradiation, as shown in Fig.3. The quantum yield of the blue emission of CdS nanocrystals could be up to about 11%[13].



**Fig.2** Room temperature photoluminescence of orange (a), blue (b), red (c) and green (d) luminescent CdS nanocrystals



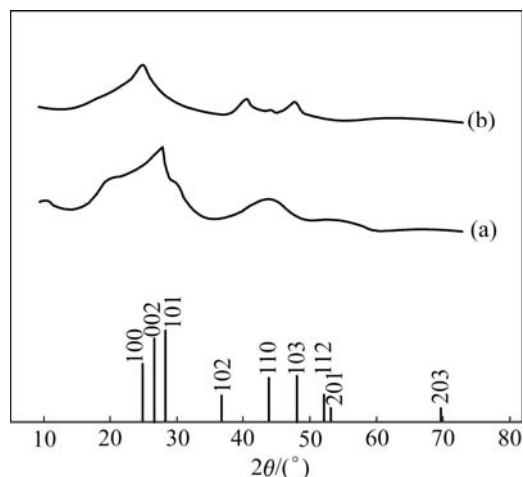
**Fig.3** Blue(a), green(b) and red(c) luminescence of multicolored CdS nanocrystals prepared by reverse micelle method under different reaction conditions

### 3.2 Luminescent color modulation mechanism

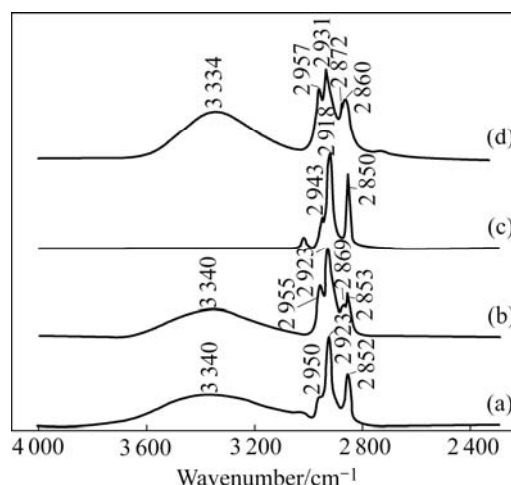
The reflux post-treatment was carried out by diluting the fresh orange and red CdS nanocrystals

reverse micelle solution one time by a same composition reverse micelle but replacing the reactant aqueous by  $H_2O$ . It has been reported that reflux treatment may improve the crystallization and eliminate the surface states[18–19], which causes the luminescence of nanocrystals changed. Normally, when reverse micelle is used for making CdS nanocrystals, the reverse micelle droplets may have the effects on confinement of CdS nanocrystal size. However, after the CdS nanocrystals formed, a small amount of water still exists inside the droplet. Reflux treatment may remove the water, ensuring the direct interaction of surface capping agents with nanocrystals. This makes the surface modification of CdS nanocrystals more effective[13]. As the small molecule of cosurfactant of hexanol has a much stronger interaction with nanocrystals in comparison with CTAB of cationic surfactant[20], by reflux treatment, the hexanol may partially replace the CTAB on nanocrystals surfaces and make the surface modification compact. This may eliminate surface trap states, causing the effective modification of CdS nanocrystals and better promotion of the crystallization. The above modification mechanism is proved by the XRD, FT-IR, and XPS. Fig.4 shows the XRD patterns of orange luminescent CdS nanocrystals before and after reflux treatment. It is suggested that after the reflux treatment the diffraction peaks of (110) and (103) of CdS nanocrystals are enhanced, and the diffraction overlap due to the peak broadening of nanoscale materials is partially eliminated. The enhancement of (100) diffraction peak at  $27^\circ$  moves to lower angle. All these changes are due to the crystallization improvement of CdS nanocrystals after the reflux treatment, which may cause the change of their luminescence.

Fig.5 shows the FT-IR spectra of CdS nanocrystals before and after reflux treatment, indicating the surface capping agent replacement process. It can be seen from



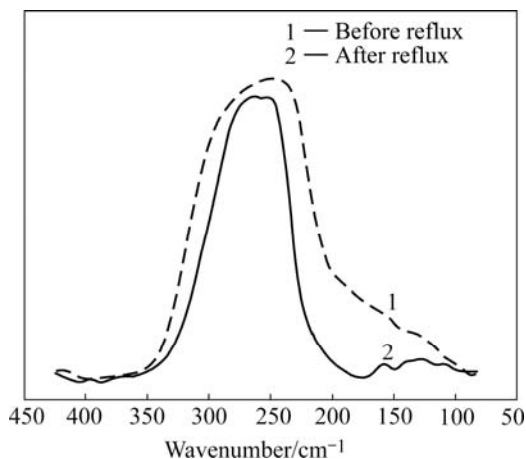
**Fig.4** XRD patterns of CdS nanocrystals before reflux (orange emitting) (a) and after reflux (blue emitting) (b)



**Fig.5** FT-IR spectra of orange (a), blue emitting CdS nanocrystals (b), CTAB (c) and hexanol (d), showing surfactant exchange mechanism

Fig.5 that the CTAB and hexanol coexist on both CdS nanocrystal surfaces before and after the reflux treatment, as the characteristic stretch vibration peaks of both CTAB and hexanol are observed in all samples. However, the wavelength and shape of IR peaks are obviously different before and after the reflux treatment. Before the reflux treatment, the IR peaks of CdS nanocrystals are mostly the same as those of CTAB in the middle IR wavelength region. The IR peaks at 2852 and 2923  $cm^{-1}$  are indexed to the symmetry and asymmetry stretch vibration of  $CH_2$  of CTAB molecule. After the reflux treatment, the wavelength and peaks of IR peaks of CdS nanocrystals are fitted well with those of hexanol molecules. The IR peaks at 2853, 2869, 2923 and 2955  $cm^{-1}$  can be indexed to the symmetry and asymmetry stretch vibration of  $CH_2$  and  $CH_3$  of hexanol molecule. The changes of IR peaks of CdS nanocrystals before and after reflux treatment suggest the surface capping agent partial replacement of CTAB by hexanol, which results in the effective surface modification and better crystallization. Moreover, the far IR spectra of CdS nanocrystals before and after reflux treatment also prove this mechanism, as shown in Fig.6. After reflux treatment, the stretch vibration of Cd-S bond of CdS nanocrystals moves to longer wavelength, implying the weakening of Cd-S interaction. This is due to the fact that hexanol has stronger interaction with  $Cd^{2+}$  in comparison with CTAB, and after the reflux treatment, the hexanol molecules partially replace the CTAB molecules on CdS nanocrystal surfaces, resulting in strong interaction of surface capping agent with  $Cd^{2+}$ , which in turn weakens the Cd-S interaction. This evidence further confirms the surface capping agent replacement modification mechanism. In addition, during the reflux treatment, a small amount of CTAB separating out on the

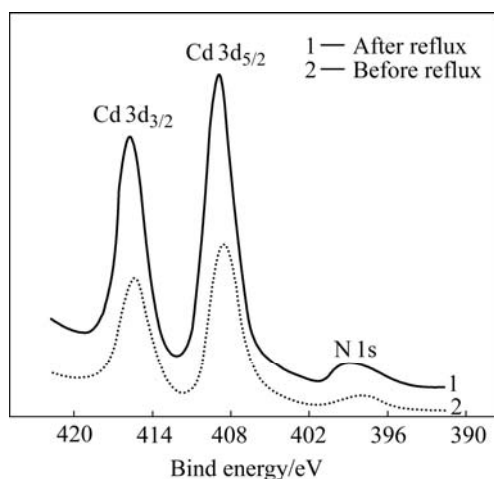
vessel wall also indirectly proves this mechanism. The surface capping agent replacement modification dominates the surface state situation, thus finally results in the luminescence discrepancy.



**Fig.6** FT-IR spectra of CdS nanocrystals before reflux (orange emitting) and after reflux (blue emitting)

Fig.7 shows the difference of surface situation before and after reflux treatment. The accumulation of peak area indicates the molar ratio of Cd to S on nanocrystals surface is around 1:1. The binding energy of Cd 3d<sub>3/2</sub> and Cd 3d<sub>5/2</sub> shifts a little to higher energy, which is normally attributed to the oxidation of CdS nanocrystals or nanocrystals surface state changes. In our experiment, the reflux treatment was conducted under the nitrogen protection and there are surface capping agents on nanocrystals surfaces, so the binding energy may not be due to the oxidation, but because of the surface state changes of the nanocrystals, which was caused by enhanced modification come from hexanol partially replacing CTAB [20].

In summary, the luminescence changes of CdS



**Fig.7** XPS spectra of CdS nanocrystals before reflux (orange emitting) and after reflux (blue emitting)

nanocrystals are ascribed to the changes of surface state situation and crystallization of CdS nanocrystals after reflux treatment. The surface state situation is largely associated with the surface capping agents. Therefore, by changing the surface capping situation, it is possible to leverage the band-edge emission and surface trap state emission of CdS nanocrystals to achieve multicolor luminescence covering from blue to red wavelength region.

## 4 Conclusions

1) A series of CdS nanocrystals with blue, green, orange and red luminescence were prepared via a reverse micelle method.

2) The luminescence of CdS nanocrystals is largely affected by the reactant concentration and post-treatment. The blue luminescence achieved by reflux treatment of orange luminescent CdS nanocrystals is attributed to the band-edge emission with a 32 nm blue shift in comparison with its bulk materials due to quantum effect confinement; while the green luminescence achieved by reflux treatment of red luminescent CdS nanocrystals are the combination of different portions of surface trap state emission and band edge emission.

3) The modulation of multicolor luminescence of CdS nanocrystals is due to surface capping agent replacement mechanism and crystallization improvement during the reflux treatment

4) This study may provide a feasible way for making multicolored CdS nanocrystals potential for full color displays and biolabelings applications.

## References

- [1] DUAN Xiang-feng, HUANG Yu, AGARWAL R, LIEBER C M. Single-nanowire electrically driven lasers [J]. *Nature*, 2003, 421: 241–245.
- [2] FUHRER M S, NYGARD J, SHIH L, FORERO M, YOON Young-gui, MAZZONI M S C, CHOI H J, IHM J, LOUIE S G, Z A, MCEUEN P L. Crossed nanotube junctions [J]. *Science*, 2000, 288: 494–497.
- [3] CHAN W C W, NIE S M. Quantum dot bioconjugates for ultrasensitive nonisotopic detection [J]. *Science*, 1998, 281: 2016–2018.
- [4] STECKEL J S, ZIMMER J P, COE-SULLIVAN S, STOTT N E, BULOVIC V, BAWENDI M G. Blue luminescence from (CdS)ZnS core-shell nanocrystals [J]. *Angew Chem Int Ed*, 2004, 43: 2154–2158.
- [5] YU W W, PENG X G. Formation of high-quality CdS and other II-VI semiconductor nanocrystals in noncoordinating solvents: Tunable reactivity of monomers [J]. *Angew Chem*, 2002, 41: 2368–2371.
- [6] GAPONIK N, TALAPIN D V, ROGACH A L, HOPPE K, SHEVCHENKO E V, KOMOWSKI A, EYCHMULLER A, WELLER H. Thiol-capping of CdTe nanocrystals: An alternative to organometallic synthetic routes [J]. *J Phys Chem B*, 2002, 106: 7177–7185.
- [7] JOLY A G, CHEN W, MCCREADY D E, MALM J O, BOVIN J O.

- Upconversion luminescence of CdTe nanoparticles [J]. *Phys Rev B*, 2005, 71: 165304–165312.
- [8] CHEN W, ZHANG J, WESTCOTT S L, JOLY A G, MALM J O, BOVIN J O. The origin of X-ray luminescence from CdTe nanoparticles in CdTe/BaFBr:Eu<sup>2+</sup> nanocomposite phosphors [J]. *J Appl Phys*, 2006, 99: 034302–034306.
- [9] ZHAO P Q, WE X L, FAN J Y, CHU P K, SIU G G. Enhanced and tunable blue luminescence from CdS nanocrystal-polymer composites [J]. *Scripta Materialia*, 2006, 55: 1123–1126.
- [10] AGARAL R, BARRELET C J, LIEBER C M. Lasing in single cadmium sulfide nanowire optical cavities [J]. *Nano Lett*, 2005, 5: 917–920.
- [11] PAN A L, WANG S, LIU R B, LI C, ZOU B S. Optical waveguide through CdS nanoribbons [J]. *Small*, 2005, 1: 980–983.
- [12] PAN An-lian, LIU Rui-bin, YANG Qing, ZHU Yong-chun, YANG Guo-zhen, ZOU Bing-suo, CHEN Ke-qiu. Stimulated emissions in aligned CdS nanowires at room temperature [J]. *J Phys Chem B*, 2005, 109: 24268–24272.
- [13] ZHANG Jun, SUN Ling-dong, LIAO Chun-sheng, YAN Chun-hua. Size control and photoluminescence enhancement of CdS nanoparticles prepared via reverse micelle method [J]. *Solid State Communications*, 2002, 124: 45–48.
- [14] FENDLER J H. Atomic and molecular clusters in membrane mimetic chemistry [J]. *Chem Rev*, 1987, 87: 877–899.
- [15] PEDONE L, CAPONETTI E, LEONE M, MILITELLO V, PANTO V, POLIZZI S, SALADINO M L. Synthesis and characterization of CdS nanoparticles embedded in a polymethylmethacrylate matrix [J]. *Journal of Colloid and Interface Science*, 2005, 284: 495–500.
- [16] LIN Y, ZHANG J, SARGENT E H, KUMACHEVA E. Photonic pseudo-gap-based modification of photoluminescence from CdS nanocrystal satellites around polymer microspheres in a photonic crystal [J]. *Appl Phys Lett*, 2002, 81: 3134–3136.
- [17] WUISTER S F, MEIJERINK A. Synthesis and luminescence of (3-mercaptopropyl) trimethoxysilane capped CdS quantum dots [J]. *Journal of Luminescence*, 2003, 102/103: 338–343.
- [18] HAN M Y, GAN L M, HUANG W, CHEW C H, ZHOU B S, OUEK C H, XU G Q, JI W, ZHANG X J, NG S C. Characterization and third-order optical nonlinearities of uniform surface-modified CdS nanoparticles [J]. *Talanta*, 1998, 45: 735–738.
- [19] HAN M Y, GAN L M, HUANG W, CHEW C H, ZHOU B S. Enhancement of photocatalytic oxidation activity by surface-modified CdS nanoparticles of high photostability [J]. *Chemistry Letter*, 1997, 8: 751–752.
- [20] CURRI M L, AGOSTIANO A, MANNA L, MONICA M D, CATALANO M, CHINARARONA L, SPAGNOLO V, LUGARA M. Synthesis and characterization of CdS nanoclusters in a quaternary microemulsion: The role of the cosurfactant [J]. *J Phys Chem B*, 2000, 104: 8391–8397.

(Edited by LI Xiang-qun)