

Luminescence 3D-Ordered Porous Materials Composed of CdSe and CdTe Nanocrystals

Linglu Yang,[†] Zhaohui Yang,[†] Weixiao Cao,^{*,†} Li Chen,[‡] Jun Xu,[‡] and Huizhen Zhang[‡]

College of Chemistry and Molecular Engineering and School of Physics, Peking University, Beijing 100871, China

Received: January 13, 2005; In Final Form: March 22, 2005

The luminescence porous materials of CdTe or CdSe nanocrystals (NCs) were prepared by filling the corresponding NCs into the voids of colloidal crystal by co-deposition of polymer beads and NCs. After removing the beads with tetrahydrofuran (THF), the 3D-ordered porous materials of CdTe (or CdSe) NCs were obtained. The wavelength of maximum photoluminescence of the NCs porous material shows obvious red shift compared with their aqueous dispersion. Under the excitation of high-energy electron the porous materials of CdTe and CdSe NCs will emit photons that can be collected to form a cathode luminescence (CL) image.

Introduction

The macroporous material having sub-micrometer pores with long-range ordering, known as inverse opal, have a variety of potential applications in electro- and nonlinear optics, optical and magnetic storage, catalyst, and sensors.^{1–4} The most exciting potential application of these porous materials is considered to be used for preparation of photonic crystals, which can diffract photons from a lattice of dielectric planes.^{5–7} Colloidal crystals prepared from self-organization of monodispersion latex or silica spheres are considered a promising prototype of 3D photonic crystal. After removing the colloidal crystal template by chemical etching or calcinations, the 3D-ordered porous materials are built up.^{8–10}

In recent years, semiconductor nanocrystals (NCs) with high photoluminescence quantum efficiency have shown great potential application in the fields of electroluminescence devices, thin-film light-emitting devices, and biological labels.^{11–14} Semiconductor NCs having a characteristic size in the order of the electron de Broglie wavelength (1–10 nm) exhibit unique physical and chemical properties distinctly from their corresponding individual molecules and bulk materials due to their quantum confinement effects. When semiconductor NCs are embedded into the voids of colloidal crystal, the combination of electron and photon confinements can adjust the electron and photon density within one structure.^{13,15–19}

There are some methods to introduce semiconductor NCs into the voids of colloidal crystal such as electrophoretic deposition, chemical vapor or bath deposition, and so on.^{13,17,20–26} In addition, Rogach et al. reported that the luminescence colloidal crystals are prepared with the polymer beads precoated with a CdTe NCs/polyelectrolyte layer.^{15,22} Caruso et al. obtained a composite photonic crystal composed of HgTe NC modified polymer beads and TiO₂, which was filled into the interspaces of the colloidal crystal by sol–gel method.²⁷

In this article, we filled the CdTe (or CdSe) NCs into the voids of poly(styrene-methyl methacrylate-3-sulfopropyl methacrylate, potassium salt) (P(St-MMA-SPMAP)) colloidal crystal

with co-deposition method.²⁸ After removing polymer beads, the 3D-ordered macroporous materials of CdTe (or CdSe) NCs were obtained. Furthermore, we obtain their photoluminescence (PL) spectra and cathode luminescence (CL) image and observe an obvious red shift of the PL emission as compared with the NCs filled in the voids of the colloidal crystal.

Experimental Section

Materials. Thioglycolic acid (A.R.), CdCl₂ (A.R.), selenium powder (99.95%), tellurium powder (99.999%), and NaBH₄ (A.R.) are all commercially available products.

Preparation of CdTe and CdSe NCs. The water-dispersible CdTe and CdSe NCs are synthesized according to the methods of literature.^{14,29,30} In a typical procedure, freshly oxygen-free NaHTe (or NaHSe) aqueous solution (25 μ L, 1 M) was added to 120 mL of N₂-saturated CdCl₂ solution (1.25×10^{-3} M) at pH 9.0 in the presence of thioglycolic acid (as stabilizer, 25 μ L) under stirring for 10 min at 25 °C to prepare CdTe (or CdSe) precursor. The CdTe precursor then was refluxed for 45 min to obtain CdTe NC aqueous dispersion (light pink color). The CdSe NC aqueous dispersion with yellow color was obtained when its precursor was injected into a 25 mL Teflon-lined stainless steel autoclave, then was heated to 180 °C, and maintained for 70 min.

Preparation of Monodispersed P(St-MMA-SPMAP) Spheres. The monodispersed P(St-MMA-SPMAP) latex was prepared with a soap-free method described briefly as follows: St (14.1 mL), MMA (0.78 mL), and deionized water (100 mL) were added to a three-necked flask equipped with a condenser and N₂ inlet and stirred at 70 °C. Under N₂ atmosphere a mixture composed of (NH₄)₂S₂O₈ (0.73 g), NH₄HCO₃ (0.506 g), SPMAP (0.1 g), and H₂O (10 mL) was added into the flask quickly and stirred for 3 h at 70 °C. Then a mixture composed of St (2.81 mL), MMA (0.16 mL), SPMAP (0.5 g), NH₄HCO₃ (0.1 g), and H₂O (10 mL) was added and stirred for a further 6 h to obtain the P(St-MMA-SPMAP) latex.

Preparation of CdTe and CdSe NCs Macroporous Materials. The colloidal crystal of P(St-MMA-SPMAP) fully filled with CdTe (or CdSe) NCs was prepared as follows: 3.5 mL (2.5×10^{-4} M) of CdTe (or CdSe) NCs aqueous dispersion and 35 μ L of P(St-MMA-SPMAP) latex (120 mg/mL) were mixed in a 10 mL vessel to obtain a homogeneous solution,

* Corresponding author.

[†] College of Chemistry and Molecular Engineering.

[‡] School of Physics.

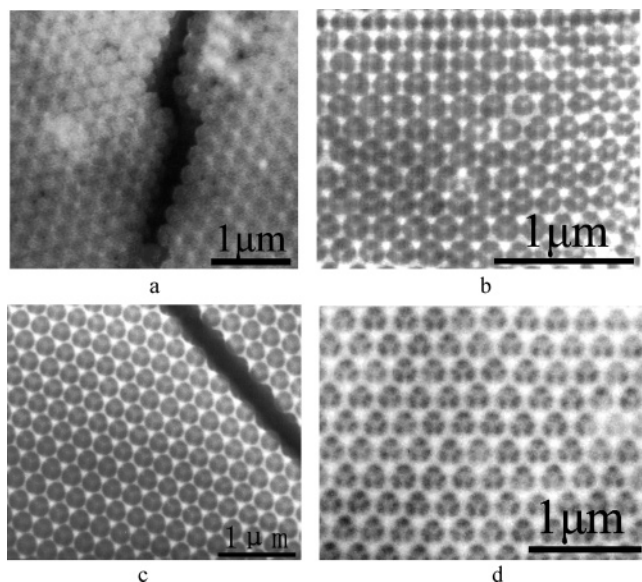


Figure 1. SEM images of the P(St-MMA-SPMAP) colloidal crystals filled with CdTe (a) and CdSe (c) NCs and the 3D porous materials of CdTe (b) and CdSe (d) NCs.

and a Si substrate ($10 \times 10 \times 1 \text{ mm}^3$) was vertically inserted. After the complete evaporation of water at $\sim 25^\circ\text{C}$, the colloidal crystal of P(St-MMA-SPMAP) filled with CdTe (or CdSe) NCs was obtained. After removing the polymer beads with THF, the 3D-ordered porous CdTe (or CdSe) NCs were obtained.

Characterization. Scanning electron microscopy (SEM) measurements were carried out on a STRATA DB 235 field-emission scanning electron microscope at 15 kV. Photoluminescence (PL) spectra were recorded on a F-4500 spectrofluorimeter (Hitachi Co.) at room temperature. CL spectra and images were collected on a Monocl Quanta 200F (Gaton Co.) equipped on an environmental scanning electron microscope (FEI) at 15 kV acceleration voltage at room temperature.

Normalized UV–vis reflectance spectra were obtained on a Shimadzu-1800 spectrometer with a reflectance spectroscopy accessory. High-resolution transmission electron microscopy (HRTEM) measurements were performed on a H-9000 NAR (Hitachi) microscope operating at 150 kV. A fluorescence micrograph was taken on an Olympus BX-60M fluorescence microscope.

Results and Discussion

The size of CdTe and CdSe NCs used to fill the interspaces of the colloidal crystal is determined by HRTEM to be ~ 3.8 and ~ 3.4 nm in average diameter, respectively (see Supporting Information). Figure 1 shows the SEM images of a P(St-MMA-SPMAP) colloidal crystal filled with CdTe (a) or CdSe (c) NCs and the corresponding porous materials of CdTe (b) or CdSe (d) NCs.

The bright regions of Figure 1a,c represent the CdTe or CdSe NCs fully filled in the voids of colloidal crystal, and the dark regions represent the polymer beads due to the different secondary electron contrast between the polymer beads and NCs. The porous materials of the NCs (Figure 1b,d) are the exact inverse replica of the colloidal crystals (Figure 1a,c). The dark regions of Figure 1b,d represent the air pores of the porous material. The oriented pore framework of them was observed clearly. A triangular pattern below every hole can be visualized because each hole just locates above the three holes of the nether layer. The diameter of the pore is about 270 nm on average. For investigating the stability of the macroporous materials of CdTe and CdSe NCs against solvents, we immerse them in dimethylformamide (DMF) and CHCl_3 for 24 h. Results show that the porous structure can be kept perfectly in the above solvents. In comparison with the composite inverse opal of NCs and polymer reported in the literatures^{25,26} the porous materials of pure CdTe and CdSe NCs prepared with co-deposition have higher refractive index and easier process.

Figure 2 shows the photoluminescence spectra (PL) of the CdTe (a) and CdSe (b) NCs dispersed in water (curve 1), filled

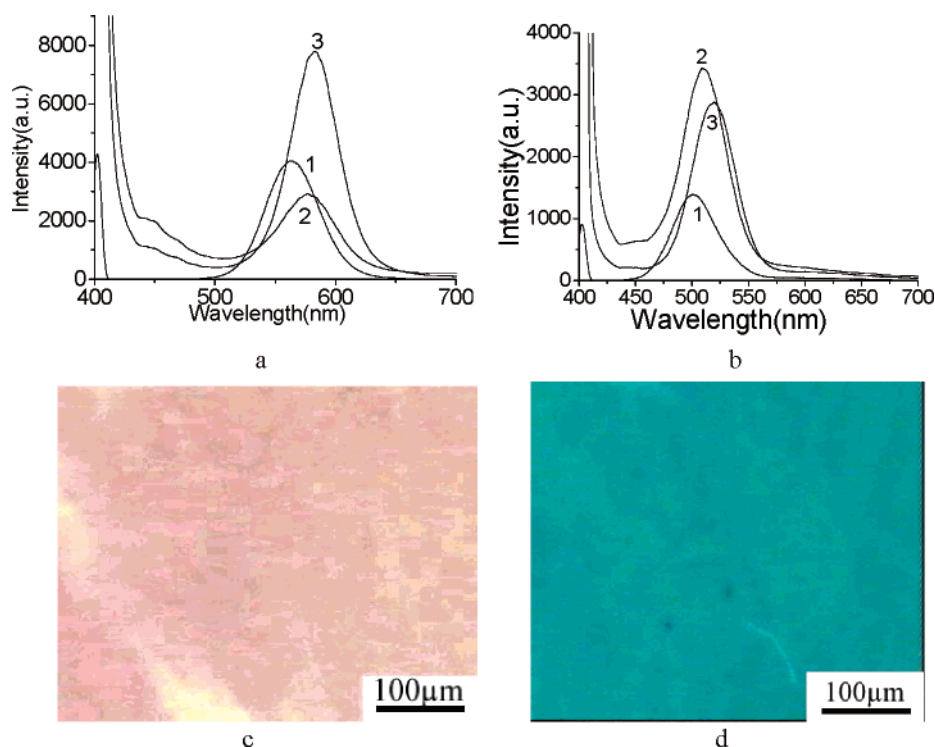


Figure 2. PL spectra of CdTe (a) and CdSe (b) NCs in water (curve 1), in the voids of the colloidal crystal (curve 2), and in the porous materials (curve 3) and the PL images of the CdTe (c) and CdSe (d) NCs porous materials.

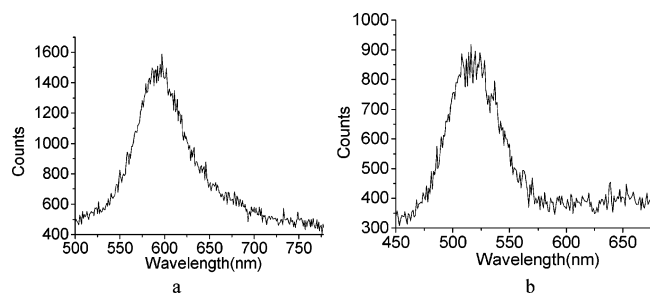


Figure 3. Cathode luminescence spectra of porous CdTe (a) and CdSe (b) NCs.

into p(St-MMA-SPMAP) colloidal crystal (curve 2), and formed porous materials (curve 3), respectively. As compared with the dispersion solution the wavelength of maximum photoluminescence of the CdTe NCs filled in the voids of the P(St-MMA-SPMAP) colloidal crystal shifts to longer wavelength, i.e., from 563 nm in water to 576 nm in voids. After removing the colloids, the wavelength shifts further to 582 nm. There is the same trend in the case of CdSe NCs. The wavelength of maximum photoluminescence shifts from 496 nm in aqueous dispersion to 510 nm in voids of the colloidal crystal and to 520 nm in porous materials of CdSe NCs. These results are in accord with those reported in the literature,^{15,20,21} which revealed an asymmetrical broadening of the emission of CdTe (or CdS) NCs and a red shift of photoluminescence of the NCs sitting in the voids of colloidal crystal. From the results we obtained and those reported in the literature, the wavelength of maximum photoluminescence of the NCs should be related with their circumstance. Therefore, the occurrence of the further red shift of emission can be ascribed to the change of refractive index of the surrounding matrix after NCs form a porous framework. Parts c and d of Figure 2 show the photoluminescence images of the porous material. It is clear that the porous materials of CdTe (Figure 2c) and CdSe (Figure 2d) NCs have homogeneous orange and green color luminescences, respectively.

Figure 3 shows CL spectra of NCs porous materials. The emission peak of CdTe (a) and CdSe (b) porous materials were detected at ~590 and ~520 nm, respectively. It indicates that the high-energy electrons from electron beam can excite the porous CdTe and CdSe NCs to emit photons.

Parts a and c of Figure 4 show CL images of the porous materials of CdTe and CdSe NCs, respectively. Parts b and d of Figure 4 show their corresponding SEM images at the same place. They are very similar, but the CL images have the worst clarity and brightness due to the lower quantum emission efficiency and the damage of the nanocrystals surface under the bombardment of a high-voltage electron beam.

The spherical colloidal particles are preferable to form face-centered-cubic (fcc) packing due to their favorable entropy. The maximum Bragg reflection wavelength (λ), i.e., the position of the band gap (PBG) of the colloidal crystal with fcc structure, can be calculated with the following equation.³¹

$$\lambda = 2[(1 - \Phi)n_{\text{walls}} + \Phi n_{\text{voids}}]d_{hkl}/m, \quad m = 1, 2, 3, \dots$$

$$d_{hkl} = 1.414D/(h^2 + k^2 + l^2)^{0.5}$$

where Φ and n_{walls} represent the volume fraction and refractive index of the wall material and n_{voids} is the refractive index of the void (or colloidal sphere). For an fcc structure the wavelength of the PBG can be predicted to occur for either all even or all odd of h, k, l indices.³¹ The main PBG of colloidal crystals doped with CdSe NCs and CdSe macroporous are at

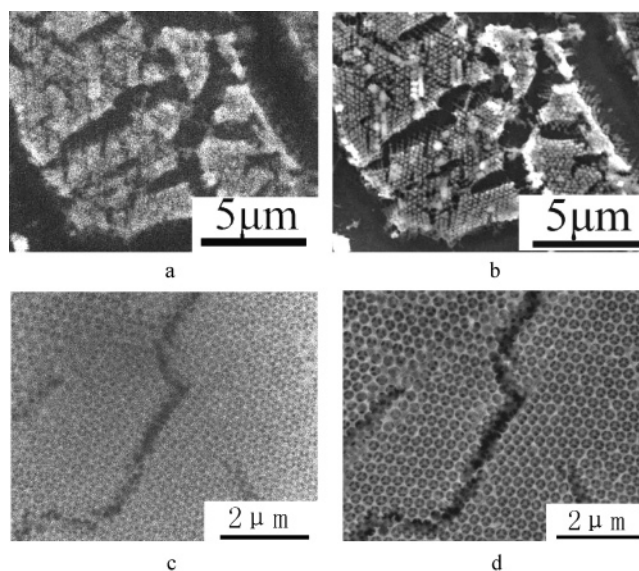


Figure 4. CL images of porous CdTe (a) and CdSe (c) NCs and SEM images of porous CdTe (b) and CdSe (d) at the same place.

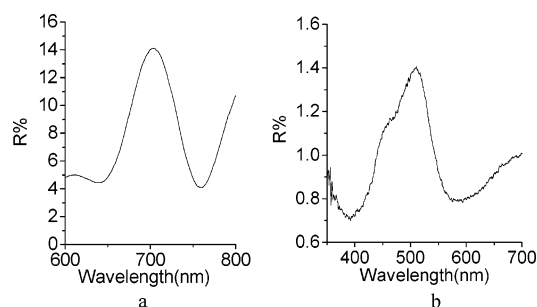


Figure 5. Normalized reflectance spectra of P(St-MMA-SPMAP) colloidal crystals filled with CdSe NCs (a) and porous CdSe NCs (b).

703 nm (Figure 5a) and 512 nm (Figure 5b), respectively. It basically accords with the calculated value at 707 nm ($\lambda_{(200)}$) and 540 nm ($\lambda_{(200)}$). The PBG appearance of both the colloidal crystals doped with CdSe and CdSe NCs macroporous materials shows that they have long-length ordered structure.

Conclusions. The porous materials of CdTe and CdSe NCs were prepared using P(St-MMA-SPMAP) colloidal crystal as a template with the co-deposition method. The SEM images show they have ordered 3D structure. The wavelength of maximum photoluminescence of the porous materials red-shifts about 20 nm compared with that of their aqueous dispersion. In addition, electron-beam bombardment can excite these materials to emit photons and generate CL images.

Acknowledgment. The authors are grateful to the NSFC for financial support of this work (Grant Nos. 20274002 and 90406018).

Supporting Information Available: HRTEM images of CdSe (left) and CdTe (right) NCs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, 386, 143.
- Velev, O. D.; Lenhoff, A. M. *Curr. Opin. Colloid Interface Sci.* **2000**, 5, 56.
- Temelkuran, B.; Ozbay, E. *Appl. Phys. Lett.* **1999**, 74, 486.
- Painter, O.; Lee, R. K.; Scherer, A.; Yariv, A.; O'Brien, J. D.; Dapkus, P. D.; Kim, I. *Science* **1999**, 284, 1819.
- Yablonovitch, E. *J. Opt. Soc. Am. B* **1993**, 10, 283–295.

- (6) Joannopoulos, J. D.; Villeneuve, P. R.; Fan, S. *Nature* **1997**, *386*, 143–149.
- (7) Special Issue on Electromagnetic Crystal Structures, Design, Synthesis, and Application. *J. Lightwave Technol.* **1999**, *17*.
- (8) Holland, B. T.; Blanford, A. S. *Science* **1998**, *281*, 538.
- (9) Wijnhoven, J. E. G. J.; Vos, W. L. *Science* **1998**, *281*, 802.
- (10) Xia, Y.; Gates, B.; Yin, Y.; Liu, Y. *Adv. Mater.* **2000**, *12*, 693.
- (11) Schlamp, M. C.; Peng, X. G.; Ailvisatos, A. P. *J. Appl. Phys.* **1997**, *82*, 5837.
- (12) Rogach, A. L.; Kotov, N. A.; Koktysh, D. S.; Susha, A. S.; Caruso, F. *Colloids and Surfaces A: Physicochem Eng. Aspects* **2002**, *202*, 135.
- (13) Blanco, A.; Lopez, C.; Mayoral, R.; Míguez, H.; Meseguer, F.; Mifsud, A.; Herrero, J. *J. Appl. Phys. Lett.* **1998**, *73*, 28.
- (14) Zhang, H.; Wang, L. P.; Xiong, H. M.; Hu, L. H.; Yang, B.; Li, W. *Adv. Mater.* **2003**, *15*, 1712.
- (15) Rogach, A. L.; Susha, A.; Caruso, F.; Sukhorukov, G.; Kornowski, A.; Kershaw, S.; Möhwald, H.; Eychmüller, A.; Weller, H. *Adv. Mater.* **2000**, *12*, 333.
- (16) Lodahl, P.; Van Driel, A. F.; Nikolaev, I. S.; Irman, A.; Overgaag, K.; Vanmaekelbergh, D.; Vos, W. L. *Nature* **2004**, *430*, 654.
- (17) Vlasov, Y. A.; Luterova, K.; Pelant, I.; Honerlage, B.; Astratov, V. N. *Appl. Phys. Lett.* **1997**, *71*, 1616.
- (18) Solov'yev, V. G.; Romanov, S. G.; Sotomayor Torres, C. M.; Müller, M.; Zentel, R.; Gaponik, N.; Eychmüller, A.; Rogach, A. L. *J. Appl. Phys.* **2003**, *94*, 1205.
- (19) Gaponik, N.; Eychmüller, A.; Rogach, A. L.; Solov'yev, V. G.; Sotomayor Torres, C. M.; Romanov, S. G. *J. Appl. Phys.* **2004**, *95*, 1029.
- (20) Romanov, S. G.; Fokin, A. V.; Alperovich, V. I.; Johnson, N. P.; De La Rue, M. R. *Phys. Status Solidi A* **1997**, *164*, 169.
- (21) Gaponenko, S. V.; Kapitonov, A. M.; Bogomolov, V. N.; Prokofiev, A. V.; Eychmüller, A.; Rogach, A. L. *JETP Lett.* **1998**, *68*, 142.
- (22) Radtchenko, I. L.; Sukhorukov, G. B.; Gaponik, N.; Kornowski, A.; Rogach, A. L.; Möhwald, H. *Adv. Mater.* **2001**, *13*, 1684.
- (23) Rogach, A. L.; Kotov, N. A.; Koktysh, D. S.; Ostrander, J. W.; Ragoisha, G. A. *Chem. Mater.* **2000**, *12*, 2721.
- (24) Vlasov, Y. A.; Yao, N.; Norris, D. J. *Adv. Mater.* **1999**, *11*, 165.
- (25) Wang, D. Y.; Caruso, F. *Chem. Commun.* **2001**, 489.
- (26) Yu, A. M.; Meiser, F.; Cassagneau, T.; Caruso, F. *Nano Lett.* **2004**, *4*, 177.
- (27) Wang, D. Y.; Rogach, A. L.; Caruso, F. *Chem. Mater.* **2003**, *15*, 2724.
- (28) Cong, H. L.; Cao, W. X. *J. Colloid Interface Sci.* **2004**, *278*, 423.
- (29) Rogach, A. L.; Kornowski, A.; Gao, M.; Eychmüller, A.; Weller, H. *J. Phys. Chem. B* **1999**, *103*, 3065.
- (30) Zhang, H.; Zhou, Zh.; Yang, B. *J. Phys. Chem. B* **2003**, *107*, 8–13.
- (31) Schroden, R. C.; Al-Daous, M.; Blanford, C. F.; Stein, A. *Chem. Mater.* **2002**, *14*, 3305.