Manipulation of luminescence from CdSe nanoparticles by three-dimensional photonic crystal

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We have demonstrated that the luminescence properties of CdSe nanoparticles can be manipulated by self-assembled silica photonic crystal. When the emitting wavelength of nanoparticles matches the stop band of the photonic crystal, the photoluminescence of the CdSe nanoparticles can be greatly enhanced by up to five times. By changing the collection angle of photoluminescence measurements, the photoluminescence intensity of CdSe embedded in photonic crystal can also be controlled. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1888042]

Yablonovitch[1] and John[2] suggested the concept of photonic crystals in 1987. Photonic crystals are macroscopic dielectric media arranged in periodic structures. They exhibit photonic band gap that is similar to the electronic band gap of the material. We therefore can control the propagation of the light by allowing it only in a certain direction at certain frequencies or localizing light in specific areas. A tremendous application in optical communication is expected. In 1989, Yablonovitch and Gmitter[3] proved the concept experimentally. Since then great attention has been paid to the fabrications and studies of artificial three-dimensional periodic dielectric structures. Many methods have been developed to fabricate the photonic crystal that include multilayer lithography,[4] multibeam holographic lithography,[5] self-assembly,[6,7] etc. Among them, self-assembly is the simplest method to fabricate three-dimensional (3D) photonic crystals. Essentially, monodisperse colloidal spheres can be spontaneously assembled into periodic arrays under certain circumstances. Blanco *et al.*[8] and Miller *et al.*[9] have gone a further step to obtain a complete band gap. They have used nanoparticle-embedded photonic crystal to improve the refractive index contrast between periodic structures. For the application of photonic crystal, silica capillaries had been stacked, fused together, and drawn down to photonic crystal fiber,[10] and then it possible to greatly widen the transmission bands by fabricating a different structure, a Kagome lattice.[11] Colombelli *et al.*[12] combined photonic and electronic band-structure engineering to create a surface-emitting quantum cascade microcavity laser. Noda and co-workers[13] have made a photonic nanostructure device which light propagating through the waveguide was trapped by the point defect and emitted to free space.

Here, we report the manipulation of photoluminescence properties of CdSe nanoparticles by silica photonic crystals. The CdSe nanoparticles were grown by modifying Peng's[14] method. CdO 0.06 g, trioctylphosphine oxide (TOPO) 5 g, and tetradecylphosphonic acid (TDPA) 0.26 g were loaded in a three neck flask. At about 300 °C, reddish CdO powder was dissolved into a colorless homogeneous solution. By cooling down to 270 °C, then an injection of 0.9-ml Se solution [1.987-g Se dissolved in 50-ml tributylphosphine (TBP)], high-quality CdSe nanoparticles were obtained. The size of the nanoparticles was evaluated by transmission electron microscopy (TEM) to be 4.6 nm±10%. The UV-VIS and photoluminescence (PL) spectra of CdSe show sharp absorption peaks that indicate the nanoparticles close to monodisperse.

Amorphous monodispersive spherical silica particles were synthesized by using the sol-gel method.[15] A 20 ml of tetraethylorthosilicate (TEOS) was dissolved in 200-ml ethanol (95%) and the solution was held and stirred with a mechanical stirrer in water bath at 30 °C for 30 min. Then 20-ml ammonia solution (ammonium hydroxide, 28–30 -wt % solution of NH_3 in water) was added into the TEOS solution and stirred for 2 h. After 2 h of the reaction, a monodispersive silica colloid solution was obtained. Then the silica colloid solution was centrifuged at 5000 rpm for 10 min to separate the silica particles from the liquid. The powder was then washed by 200-ml ethanol accompanied with ultrasonication. The washing procedure was repeated three times to ensure the complete removal of reactants. Then the silica powder was dried at 100 °C for 12 h.

The silica photonic crystal was prepared using the convective method.[7] Silica powder was redispersed in ethanol with a concentration of 1-wt % solution. Then the glass substrate was immersed into the silica colloid solution vertically. The solution was placed in an 80 °C oven for 12 h. After the evaporation of ethanol, the silica photonic crystal was self-assembled onto the vertical substrate.

Figure 1 shows the scanning electron microscopy (SEM) micrographs of silica photonic crystal infiltrated with CdSe nanoparticles. The silica photonic crystal reveals a hexagonal-type close packing. The CdSe nanoparticles are uniformly distributed inside the silica photonic crystal.

Colloidal crystals formed from monodisperse spheres exhibit a photonic crystal band gap. The photonic stop band

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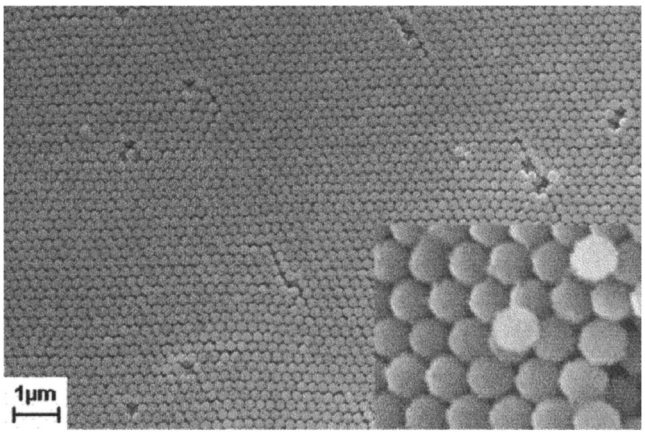

FIG. 1. SEM micrograph of silica photonic crystal infiltrated with CdSe nanoparticles. The inset shows the CdSe nanoparticles that are uniformly distributed inside the photonic crystal.

demonstrates themselves as dips in transmission spectra or as peaks in the corresponding reflection spectra. The spectra position of the stop band depends on (1) the diameter of the spheres that built photonic crystal, (2) the angle between the crystal orientation of the sample and the direction of the incident light, and (3) the refractive index constant of the photonic crystal. In this work, optical transmission spectra were measured by UV-VIS spectrometer. Figure 2 shows the transmission spectra of silica photonic crystals at normal incident of light. As expected from the calculation,[16] for the fcc lattice, the stop band λ_{max} changes with the spheres diameter D as shown in the following:

$$\lambda_{max} = 2(2/3)^{1/2} D(n^2 - \sin^2 \theta)^{1/2}, \quad (1)$$

where n is the refractive index of the assembly particles and θ is the angle between the incident light and the normal to the substrate. The absorption peaks changed with the diameters of silica spheres varied from 407–738 nm as expected.

Photoluminescence measurements were taken at room temperature under a 325-nm He–Cd laser line excitation. There is no luminescence from silica photonic crystal, thus any luminescence observed arises from the CdSe nanoparticles. By selecting the right sphere diameter that matches the

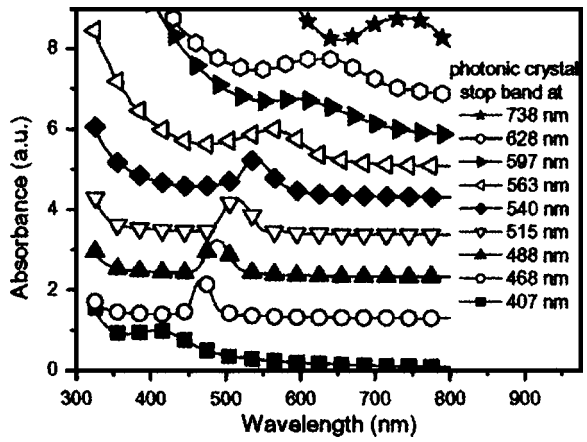

FIG. 2. Transmission spectra of nine samples of silica photonic crystals at normal incident light. The absorption peaks are changed with the diameters of silica spheres that can be varied from 407–738 nm.

wavelength of the emitting spectrum of the CdSe nanoparticles, the photoluminescence of CdSe nanoparticles can be manipulated by 3D photonic crystal.

Samples with three different arrangements of CdSe nanoparticles were used to study the manipulation of their photoluminescence by 3D photonic crystals. The sample of the first arrangement was prepared by placing the CdSe solution onto the glass slide, and then evaporated off the solvent to obtain a thin layer of nanoparticles on the glass. The photoluminescence was measured at the same side of the CdSe nanoparticles layer. The sample of the second arrangement was prepared by placing the CdSe solution onto the silica photonic crystal, and the nanoparticles were infiltrated into the photonic crystal. Then the solvent was evaporated off to obtain the sample. The photoluminescence was measured at the same side of the infiltrated CdSe. The sample of the third arrangement was prepared by placing the CdSe nanoparticles onto the glass substrate and the photonic crystal was on the other side of the glass substrate. The photoluminescence was measured at the same side of CdSe. The CdSe solution was mixed with 3 and 4.6 nm nanoparticles and exhibited photoluminescence peak at 517 and 580 nm, respectively. For a photonic crystal assembled from 234-nm silica spheres, the stop band of photonic crystal for normal incident is at about 490 nm. If the photoluminescent peak of CdSe is matched with the transmission peak of photonic crystal then a high coupling between the light emission of CdSe and the stop band of silica photonic crystal will be revealed.

The photoluminescence measurement of CdSe nanoparticles with the first arrangement was used as the blank of experiment. The CdSe is a phtoluminescent material without silica photonic crystal. The photoluminescence peak at 580 nm, which is not affected by the stopping band of silica photonic crystal, was used as an internal standard to normalize the peak intensity at 517 nm. To eliminate the effect of photonic crystal band on the photoluminescence of the CdSe at 580 nm, we selected the stopping band of the photonic crystal band at 490 nm, not at 517 nm. The photoluminescence intensity at 517 nm from the second arrangement and the third arrangement was greatly enhanced by 4–5 times to that of the first arrangement, as shown in Fig. 3. In the second arrangement, the CdSe nanoparticles covered the silica photonic crystal completely. When the CdSe nanoparticles on the surface of photonic crystal were excited by laser, it emitted the photoluminescence. The collected photoluminescence now includes the emitted radiation reflected by silica photonic crystal because the emission of CdSe nanoparticles is not allowed to travel inside the photonic crystal. Thus the intensity of the photoluminescence can be increased dramatically. The photoluminescence enhancement was also observed for the third arrangement, the mechanism is the same as that of the second arrangement. The photoluminescence of CdSe was passed through the glass slide and was reflected by the silica photonic crystal.

When the angle of photoluminescence collection was varied from 90° to 45°, the stop band of the photonic crystal was moved to lower wavelengths. Using the second arrangement, we carefully controlled the CdSe nanoparticles inside

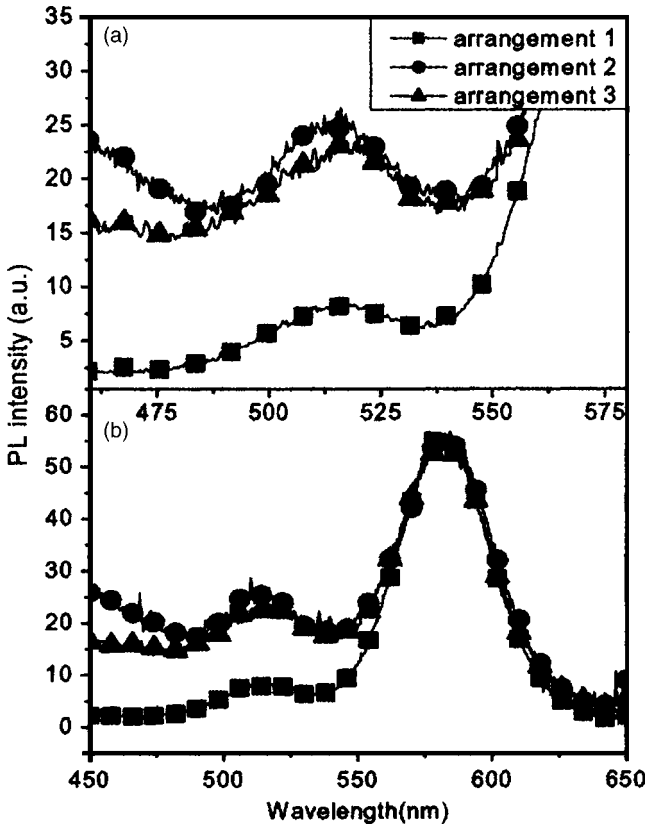

FIG. 3. Photoluminescence spectra of various arrangements of the CdSe nanoparticles with respect to the photonic crystal with stop band at 490 nm. (a) The photoluminescence intensity at 517 nm from the arrangement 2 and the arrangement 3 was greatly enhanced by 4–5 times as compared to that of arrangement 1. (b) The full spectra including the standard peak.

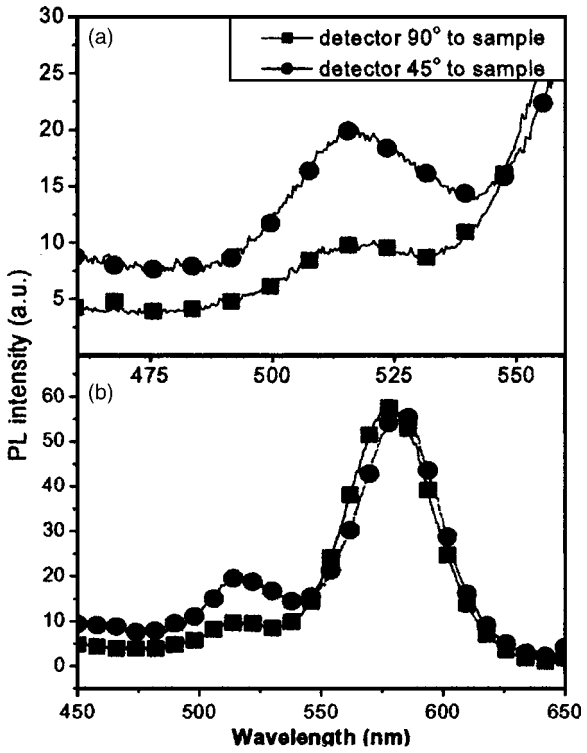

FIG. 4. Photoluminescence spectra were measured at 45° and 90° respect to the CdSe infiltrated photonic crystal with stop band at 520 nm. (a) The photoluminescence intensity of 517 nm collected at an angle of 45° is larger than that collected at an angle of 90°. (b) The full spectra including the standard peak.

the voids of silica photonic crystal that has the stop band at 520 nm. We have observed that the photoluminescence intensity of the 45° collection is two times larger than that of the 90° collection, as shown in Fig. 4. At the 90° collection, the stop band of silica photonic crystal at 520 nm inhibited the photoluminescence peak of CdSe at 517 nm. When the collection angle varied to 45°, the stop band of photonic crystal was blueshifted and the photoluminescence of CdSe nanoparticles emitted outside from the stop band of photonic crystal. In this way, one can control the intensity of the photoluminescence by changing the angle of the photonic crystal. With a complete photonic crystal band gap broad enough to overlap with the whole photoluminescence band of the nanoparticles, the total inhibition of CdSe photoluminescence will be possible.

In summary, we have demonstrated that the luminescence properties of the CdSe nanoparticles can be controlled by self-assembled 3D silica photonic crystal. When the emitting wavelength of the nanoparticles matches the stop band of photonic crystal, the photoluminescence of the CdSe nanoparticles can be greatly enhanced by up to five times. By changing the collection angle of the photoluminescence measurements, the photoluminescence intensity of CdSe embedded in photonic crystal can also be controlled.

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[1]E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).
[2]S. John, Phys. Rev. Lett. **58**, 2468 (1987).
[3]E. Yablonovitch and T. J. Gmitter, Phys. Rev. B **48**, 11265 (1993).
[4]S. Noda, MRS Bull. **26**, 618 (2001).
[5]A. J. Turberfield, MRS Bull. **26**, 632 (2001).
[6]Y. A. Vlasov, M. Deutsch, and D. J. Norris, Appl. Phys. Lett. **76**, 1627 (2000).
[7]S. H. Park and Y. N. Xia, Langmuir **15**, 266 (1999).
[8]A. Blanco, C. Lopez, R. Mayoral, H. Mÿguez, and F. Meseguer, Appl. Phys. Lett. **73**, 13,1784 (1998).
[9]M. Miller, R. Zentel, T. Maka, S. G. Romanov, and C. M. S. Torres, Adv. Mater. (Weinheim, Ger.) **12**, 1499 (2000).
[10]J. C. Knight, T. A. Birks, P. St. J. Russell, and D. M. Atkin, Opt. Lett. **21**, 1547 (1996).
[11]F. Benabid, J. C. Knight, G. Antonopoulos, and P. St. J. Russell, Science **298**, 399 (2002).
[12]R. Colombelli *et al.*, Science **32** 1374 (2003).
[13]B. Song, S. Noda, and T. Asano, Science **300** 1537 (2003).
[14]Z. A. Peng and X. Peng, J. Am. Chem. Soc. **123** 183 (2001).
[15]W. Stŏber, A. Fink, and E. J. Bohn, J. Colloid Interface Sci. **26**, 62 (1968).
[16]Y. Xia, B. Gates, and S. H. Park, J. Lightwave Technol. **17**, 11,1956 (1999).