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Enhanced and tunable blue luminescence from CdS nanocrystal–polymer composites

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CdS nanocrystals were synthesized by a hydrothermal procedure and dispersed in an aqueous solution. CdS nanocrystal–polystyrene composites were produced by adding the CdS colloids into a toluene solution that contains dissolved polystyrene and casting the mixed solution onto a Si wafer. The photoluminescence from the composites was wavelength-tunable in the blue and its intensity was enhanced sixfold compared to that from the original solution. Raman results give unequivocal information about the origin of the intensity enhancement.

Keywords: Nanocomposites; Fabrication; Luminescence

Group II–VI semiconductor nanocrystals have received considerable attention due to their unique size-dependent chemical and physical properties [1,2]. As a typical direct band gap (2.42 eV at room temperature) semiconductor and a prototype zero-dimensional quantum-confined material, CdS nanocrystals have been extensively investigated. Various synthetic methods, including reverse-micelle [3], colloidal [4] and arrested precipitation [5], have been developed to fabricate monodispersed CdS nanocrystals. These luminescent CdS nanocrystals have wide potential applications in optical switches, sensors, electroluminescent devices, lasers and biomedical tags [6–8].

In recent years, polymers that contain special functional groups have been used as specific stabilizers for the solution synthesis of CdS nanocrystals and preparation of nc-CdS–polymer films with different properties [4,5,9–12]. Compared to other bulk materials, these polymer/nanocrystal composites possess unique characteristics. Firstly, the polymer can enhance the stability of nanocrystals, control their size range and improve their surface structure [13,14]. Secondly, polymer films possessing the optical characteristics of semiconductor nanocrystals can be produced, and such materials facilitate optical measurements. However, the synthesis of single well-dispersed or monodispersed CdS nanocrystals with adjustable sizes and protected from photo-oxidation is a big challenge. In particular, it is difficult to generate greatly enhanced luminescence in such polymer/nanocrystal systems. In this paper, we report the syntheses of (i) ultra-small CdS nanocrystals dispersed in an aqueous solution and (ii) transparent nc-CdS–polystyrene composite films. Luminescence from the CdS crystallites encapsulated in the polymer is greatly enhanced and better stability is achieved from the composite compared to the aqueous solution. The wavelengths of the emission from the two kinds of samples can be continuously tuned within the blue range. Detailed analyses of the Raman spectra have enabled us to identify the origin of the enhanced luminescence from the nc-CdS–polymer films [4,15,16].

The CdS nanocrystals were synthesized via a hydrothermal method at room temperature; these conditions improve the crystallinity and are convenient for forming nc-CdS–polymer films. The reactants were 0.05 M $Cd(CA)_2 \cdot 2H_2O$ and 0.005 M $C_3H_7NO_2S \cdot HCl \cdot 2H_2O$. In order to accelerate the dissociation of sulfur ions from $C_3H_7NO_2S \cdot HCl \cdot 2H_2O$, several drops of 0.12 M NaOH aqueous solution were added to the mixed aqueous solution, which contained 1.2 ml $Cd(CA)_2 \cdot 2H_2O$ and 5.6 ml $C_3H_7NO_2S \cdot HCl \cdot 2H_2O$.

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The final solution was diluted to 20 ml and then injected into a stainless steel autoclave, sealed and maintained at 130 °C for 4 h to form a white-yellow aqueous solution containing CdS nanocrystals. After spectral examinations, the aqueous solution containing the CdS nanocrystals was added to the toluene suspension which contains dissolved polystyrene, followed by gentle circular stirring from center to edge. The mixed solution was then cast onto a Si wafer where the nc-CdS–polystyrene composite film formed after evaporation of the solvents.

The micrographs were recorded using a JEOL JEM-2010 transmission electron miscroscope at an accelerating voltage of 200 kV. The photoluminescence (PL) spectra were acquired using a FluoroMax-2 fluorescence spectrometer. The Raman spectra were recorded with a T64000 triple Raman system with a backscattering geometry using the 514.5 nm line of an Ar^+ laser as the excitation source. All the measurements were performed at room temperature.

Typical high-resolution transmission electron microscopy (HR-TEM) images of the CdS crystallites from the solution are displayed in Figure 1. The particles mostly resemble clubs with lengths of 3–6 nm and widths of 0.5–3 nm (Fig. 1a). Some comma- and gourd-shaped particles with cross-sectional widths of about 4 nm can also be observed (Fig. 1(b) and (c)). The HR-TEM images show two sets of lattice fringes with lattice spacings of 0.193 (Fig. 1a) and 0.134 nm (Fig. 1b and c), corresponding to the {2 2 0} and {3 3 1} planes of CdS [16–18], respectively. The particles are highly crystalline and have a cubic phase.

The PL spectra from the CdS nanocrystals dispersed in the aqueous solution are shown in Figure 2. The emission band peak shifts continuously from ~400 to ~500 nm as the excitation wavelength increases from 300 to 440 nm, above which no emission can be observed. The PL spectra are smooth and do not show any substructures. The full width at half maximum (FWHM) of the PL peak is 100–125 nm. These results

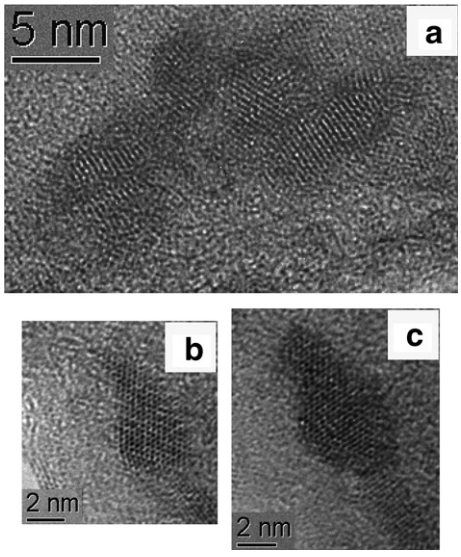

Figure 1. HR-TEM images obtained from the CdS nanoparticles on a graphite grid. The particles are shaped like: (a) dots, (b) rods or (b, c) commas.

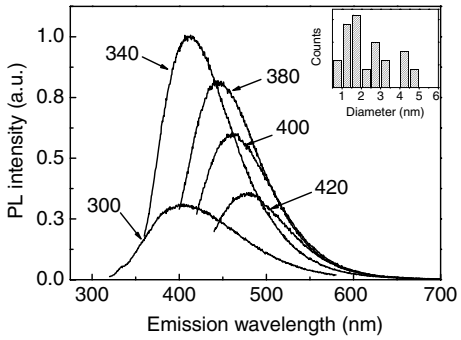

Figure 2. PL spectra acquired from the CdS nanoparticles in an aqueous solution excited by the 300, 340, 380, 400 or 420 nm lines. The inset shows the histogram of the size distribution of the particles.

suggest that the luminescence originates from band edge recombination of carriers considering that the bulk band gap of CdS is 2.42 eV (512 nm) [19,20]. The inset in Figure 2 shows the histogram of the size distribution of the CdS particles averaged from 14 HR-TEM micrographs taken from different areas. The diameter of the particles ranges from 0.5 to 4.5 nm and the most probable diameter is 1.63 nm, which is well below the Bohr radius of bulk CdS where strong quantum confinement effects may appear [21]. The maximum intensity in the PL spectrum acquired from the CdS aqueous solution is at ~411 nm when excited by the 340 nm line of a Xe lamp (Fig. 2). This arises from emission from particles with the most probable diameter. This diameter, d, can be calculated by substituting E for 3.02 eV (411 nm) in the following equation [22]:

$$E - E_g = \frac{2\hbar^2\pi^2}{d^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{3.536e^2}{\varepsilon d}, \quad (1)$$

where m_e and m_h are the effective masses of electron and hole, and ε is the high-frequency dielectric constant of bulk CdS. The calculated value of d is 1.65 nm, which is in good agreement with the experimental value of 1.63 nm. It further confirms the band edge recombination mechanism for the luminescence.

PL with peak wavelength smaller than 425 nm has rarely been observed from CdS nanocrystals except in some recent experiments [4,21], in which only a sharp and constant emission band centered at 400 nm was detected. These results are quite different from the wide and smooth emission bands induced by the quantum confinement effect. The origin of this kind of luminescence band is currently unclear. Our TEM results show that in order to obtain deep-blue emission (below 400 nm), the CdS particles must be smaller than 1.6 nm.

Generally, emission from nanoparticles in solutions is unstable [9]. We have observed that the emission intensity from an aqueous CdS solution diminishes dramatically after several days. Therefore, in order to achieve stable blue emission from the CdS nanocrystals, we prepared the nc-CdS–polystyrene composite film (see above). The nc-CdS–polystyrene film shows very strong emission with two distinct features. Firstly, the emission wavelength from the same region on the film is almost constant when excited by different wavelengths.

Secondly, the emission wavelengths are different from different regions on the film. Several typical PL spectra of one nc-CdS–polystyrene film are depicted in Figure 3a. The PL peak wavelength shifts from 437 to 496 nm, corresponding to different locations on the film (all excitation wavelengths have been selected to generate maximum emission intensity at each excited region). In fact, the emission wavelength can be almost continuously tuned from ~437 to ~496 nm by moving to different parts of the film. To explore the origin of the variable emission, we fabricated another nc-CdS–polystyrene composite with the mixed solution being sonically processed before casting onto a Si wafer. This yielded a composite film in which the CdS particles were more uniformly distributed. The PL peak wavelength is almost the same across the entire surface of this film. Taking into account these observations, and the fact that the original polystyrene and toluene show no emission in the visible range, the emission from the film appears to originate from band edge recombination. The variable emission wavelengths from different locations on the film fabricated without sonic treatment arise from unevenly distributed particles with different sizes. It should be noted that the PL from the nc-CdS–poly- styrene film (Fig. 3a) shows a redshift relative to the most intense emission peak from the CdS solution (centered at 411 nm, see Fig. 2). It can be induced by aggregation of some CdS nanocrystals during incorporation into the polymer. The PL spectral line corresponding to small emission wavelengths is not very smooth but becomes smoother with increasing excitation wavelength. This may be due to a small deviation in the size distribution of the CdS particles in the composite film from the original continuous one in the solution.

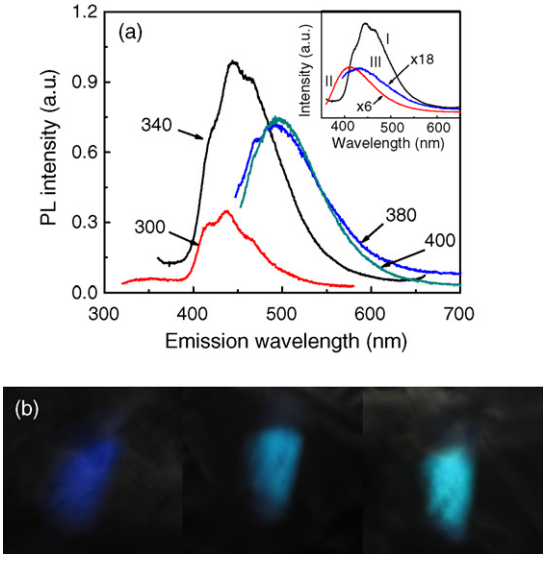

Figure 3. (a) PL spectra obtained from different regions on one nc-CdS–polystyrene film. The inset shows the PL spectra acquired from the (I) nc-CdS–polystyrene film, (II) freshly prepared film and (III) aged solution at an excitation wavelength of 340 nm. (b) Fluorescent images of the composite film which correspond to the three PL spectra shown in Figure 4(a) with emission wavelengths of about 437, 465 and 492 nm, from left to right.

We compare the variations of the PL intensities from different samples. The inset in Figure 3(a) shows the PL spectra acquired from the freshly prepared (curve II) and aged (for 3 days) (curve III) CdS aqueous solution as well as the nc-CdS–polystyrene film (curve I). The 340 nm line of a Xe lamp was used to obtain these spectra. The PL intensity from the CdS aqueous solution decreases by about a factor of three after exposure to air for 3 days, indicating the poor stability of the luminescent CdS solution. This mainly originates from aggregation of the CdS crystallites. In contrast, the PL intensity is enhanced by about a factor of six if the CdS colloids (curve II) are incorporated into a polymer (curve I). In most other cases, the PL intensity has been observed to diminish drastically when nanocrystalline particles are encapsulated by a polymer. The highly enhanced emission observed from the nc-CdS–polystyrene composites here may be explained as follows. Firstly, the wide band gap of polystyrene [about 4.78 eV (260 nm) obtained from its absorption spectrum] confines the carriers in the CdS nanocrystals. Secondly, the photoexcited electrons in the polystyrene can move from their higher lowest unoccupied molecular orbital (LUMO) to the lower LUMO via nonradiative transitions. The photoexcited holes can also be transferred in a similar manner. These photoexcited carriers then recombine in the CdS crystallites through band-to-band radiative transition via resonant electron or energy transfer, thereby greatly enhancing the PL. Finally, polystyrene is transparent to visible radiation. It can provide good passivation for the surfaces of CdS nanocrystals and thus suppress the nonradiative recombination processes of carriers excited from the CdS cores via surface states. As a result, the PL intensity is further enhanced [1,23] and very bright luminescence can be visually observed from the nc-CdS–polystyrene film. Figure 3(b) displays several emission photos (taken with a digital camera) that correspond to the PL spectra shown in Figure 3(a). The colors vary from deep blue to cyan.

To further unravel the mechanism of the emission enhancement from the nc-CdS–polystyrene composite

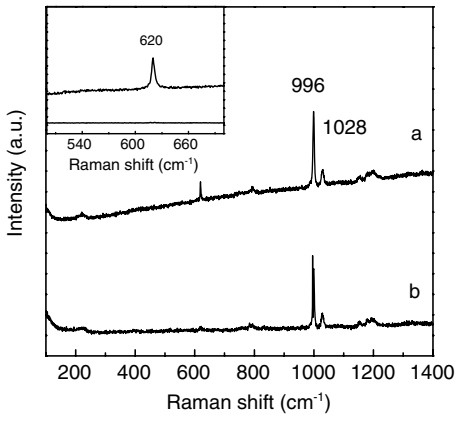

Figure 4. Raman spectrum obtained from the nc-CdS–polystyrene film (curve a) and pure polystyrene film (curve b) excited by the 514 nm line of an Ar^+ laser. The inset displays the Raman bands between 500 and 700 cm^{-1} observed from the nc-CdS–polystyrene and pure polystyrene films.

film, Raman spectroscopy, a conformation-sensitive technique, was employed. Figure 4 displays the Raman spectra of the nc-CdS–polystyrene composite (curve a) and pure polystyrene film (curve b) excited by the 514 nm line of an Ar^+ laser. Except for the vibration band at 620 cm^{-1}, which does not belong to the characteristic Raman bands of CdS nanocrystals [24], all the other vibration bands are identical in peak frequency and intensity in curves a and b, and can be assigned to the characteristic Raman spectral bands of singly substituted benzene in polystyrene [25]. The 620 cm^{-1} band clearly exists in curve a, but almost disappears in curve b (see inset). This feature indicates that the 620 cm^{-1} Raman band arises from an interaction between the CdS nanocrystals and the surface polystyrene molecules, namely, dot–matrix interactions. The interaction results in strain-induced deformation of the phenyl ring and makes it possible to transfer electrons from polystyrene molecules to CdS nanocrystals. This changes the effective polarizability of the polystyrene molecules and leads to the strong enhancement of the 620 cm^{-1} vibration band. Therefore, the Raman results support our explanation regarding the PL enhancement mechanism as discussed in the above paragraph.

In conclusion, we have synthesized ultra-small CdS nanocrystals in an aqueous solution and subsequently fabricated transparent nc-CdS–polystyrene films that exhibit enhanced emission. The emission wavelengths vary over a wide spectral range due to the different CdS particle sizes. The nc-CdS–polystyrene composites yield high-intensity and stable luminescence, thereby making the materials suitable for solid emitters used in color displays and microelectronic devices.

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