

Preparation of CdSe nanocrystals in organic system and electroluminescence characteristics of the devices^{*}

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CdSe nanocrystals were prepared by a colloidal chemical approach using CdO and Se powder as precursors in an organic system of TOPO/TOP, and a multilayered electroluminescence device was fabricated with CdSe as emitting layer. The results show that the photoluminescence spectra of the CdSe nanocrystals almost cover the whole visible region and the full width at half maximum (FWHM) is appropriately 200 nm. The electroluminescence spectrum of the multilayered device at different voltages was investigated. The electroluminescence intensity is enhanced with increasing operating voltage, and the CIE coordinates of the device change from (0.34, 0.37) at 6 V to (0.44, 0.46) at 20 V as the operating voltage increases, which indicates that the colors of the device could be tuned by the operating voltage.

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Semiconductor nanocrystals have attracted wide interests in the last few years because they have high luminescence efficiency and size-tunable band gap characteristics. The semiconductor nanocrystals could be functionalized using various surfactants to make them soluble in polar or non-polar solvents, and could be well dispersed organic/inorganic solvents. Therefore, the semiconductor nanocrystals are suitable for optoelectronic applications^[1-7]. Recently, the use of inorganic semiconductor nanocrystals in combination with polymers in the manufacture of LEDs has been reported^[3-7]. However, the reports about the broad emission from semiconductor nanocrystals are relatively few. In this paper, we prepared CdSe nanocrystals in TOPO/TOP systems following the method by Peng *et al.*^[8]. A multilayered device was fabricated using CdSe nanocrystals as an emitting layer. The EL spectrum of the device and the PL spectrum of CdSe nanocrystals exhibited broadband emission, and the EL intensity of the device increased as the operating voltage increased. By calculation, the CIE coordinates of the device at different operating voltages were changed, which suggested that the luminescence of the device could be tuned by changing the operating voltage. The broad emission from the device shows the great potential for use in white light emitting applications.

The experiment was operated under high pure nitro-

gen atmosphere. CdO was dissolved in lauric acid at 150°C, then trioctylphosphine oxide (TOPO) was added. The mixture was heated to 300°C, TOPSe stock solution (Se powder dissolved in trioctylphosphine) was injected into the mixture. The solution was kept at this temperature for 10 minutes, and the CdSe nanocrystals formed. Anhydrous methanol was added to the mixture to precipitate the CdSe nanocrystals. The precipitated CdSe nanocrystals were washed 3 times with anhydrous methanol to remove unbound surfactant, then re-dissolved in chloroform.

The chemical structures of the materials used in the device are shown in Fig. 1. The PEDOT:PSS was used to improve the holes transport by facilitating hole-injection. ITO-coated glass substrates with a sheet resistive of $60\Omega/\gamma$ were cleaned consecutively in ultrasonic baths containing DI-water, ethanol and acetone. The solution of PEDOT:PSS and the CdSe QDs in chloroform solution were fabricated by spin-coating method. 2,9-dimethyl-4,7-diphenyl-1,10-phe-nanthroline (BCP) (10nm) and 8-tris-hydroxyquinoline aluminium (Alq₃) (10 nm) were deposited onto the CdSe QDs layer by the thermal evaporation method. Then the cathode layer of Al was used as the top electrode, and a summary of the device is shown in Fig. 1.

As shown in Fig. 2, the transmission electron microscope(TEM) image of the specimens indicates that the CdSe nanocrystals aggregate with a low crystalline matter so that the image is unclear. This is because the TOPO molecules coalesced following the elimination of the solvent in the TEM vacuum chamber^[9].

The absorption and photoluminescence spectra of CdSe in chloroform solution are shown in Fig. 3 .

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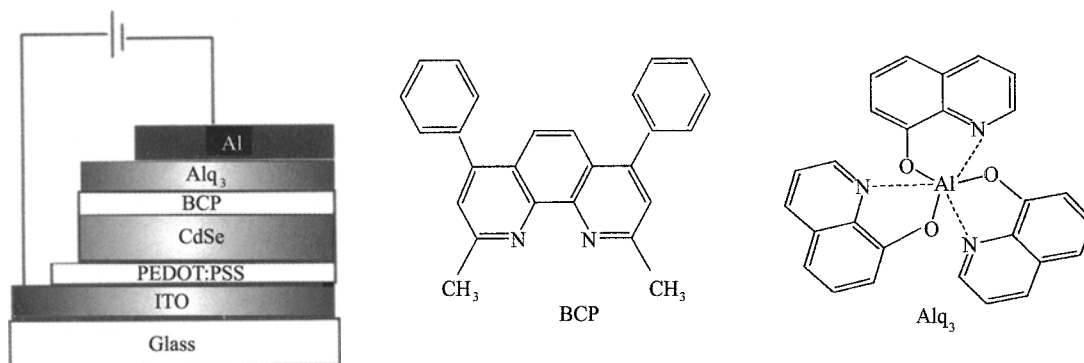


Fig. 1 Configuration of the device and chemical structure of the materials used in this experiment

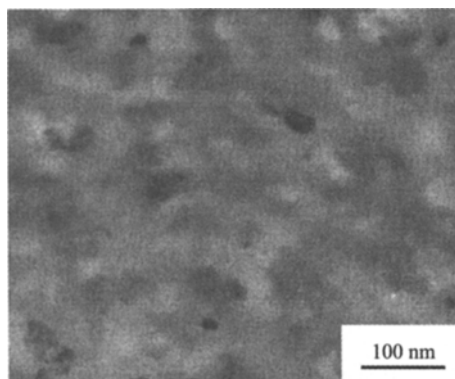


Fig. 2 TEM image of TOPO capped CdSe nanocrystals

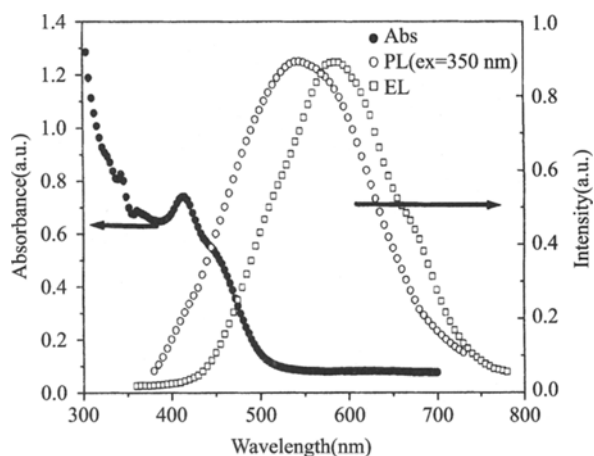


Fig. 3 Absorption spectrum and photoluminescence of CdSe nanocrystals and electroluminescence for the device

As can be seen from Fig. 3 that the absorption peak is located at about 416 nm. It is also seen in Fig. 3 that the PL spectrum of CdSe nanocrystals and EL spectrum of the device cover the visible region range from 380 nm to 780 nm, and a full width at half maximum (FWHM) is

appropriate 200 nm. The EL spectrum of the device shifts to the longer wavelength compared with the PL spectrum. The reasons can be attributed to the following: 1) when the carriers inject into the smaller nanocrystals under electric field, the potential becomes bigger because of quantum confinement effect, so most of the carriers can inject into the bigger nanocrystals. 2) energy transfer from the smaller nanocrystals to the bigger nanocrystals^[1]. The broad emission possibly comes from charge recombination from particle surface defects that arise from the presence of non-coordinated surface selenium sites and the deep trap sites at the particle surface. Also, the broad particle size distribution may contribute to the inhomogeneous broadening^[6,7].

Fig. 4 gives the EL spectra of the device at different operating voltages. It is seen that the EL intensity increases as the operating voltage increases, and this is because the electric fields increase and the probability of the electron-hole composite increases when the operating voltage is higher than the turn-on voltage. This leads to the enhancement of the luminescence intensity. The connection between the CIE coordinates of the device and the operating voltage is shown in Fig. 5. When the operating voltage increases from 6 V to 20 V, the CIE coordinates changes from (0.34, 0.37) to (0.44, 0.46), which suggests that the colors of the device can be tuned by changing the operating voltage. This can be interpreted as follows: as the operating voltage increases, the holes between the interface of CdSe and BCP can leak into Alq₃, which leads to the luminescence of Alq₃. However, the genuine reason has not been clarified.

Fig. 6 shows the energy level diagram of the device. The work functions of ITO, PEDOT:PSS and Al electrodes, and the electron affinities (EA) and ionization energies (IE) of Alq₃, BCP and CdSe nanocrystals are taken from previous experimental data^[3,4,10]. In the device, holes are considered to be injected from the ITO electrode through PEDOT:PSS layer into the CdSe nanocrystals. Similarly, the electrons are considered to be in-

jected from the Al electrode into Alq₃ electron transporting layer and BCP hole blocking layer, and are eventually transported to the CdSe nanocrystals. Because of the offset between the HOMO of CdSe nanocrystals and BCP is 1.6 eV, the potential between CdSe and BCP is formed by introduction of the BCP, which blocks the transfer of the holes so that the holes aggregates the interface between the CdSe nanocrystals and BCP. This accelerates the combination of the holes and the electrons. However, the holes can not be transported into the electron transporting layer Alq₃ effectively^[10].

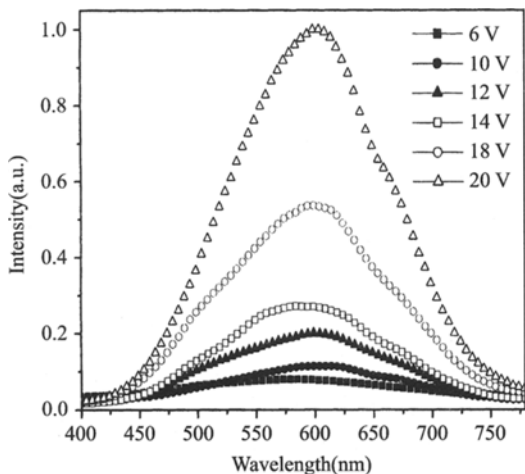


Fig. 4 Electroluminescence spectra of the device at different operating voltage

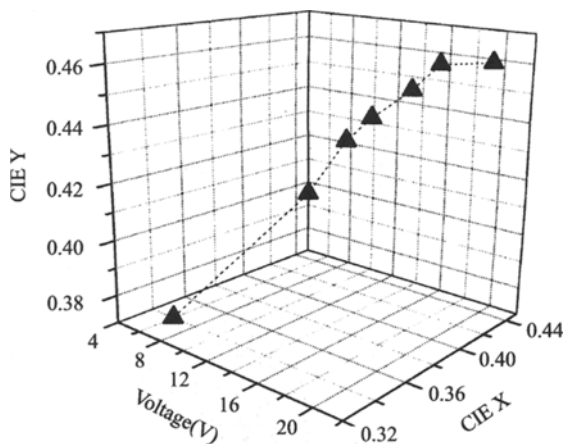


Fig. 5 Variation curve of CIE coordinates of the device with the applied voltage

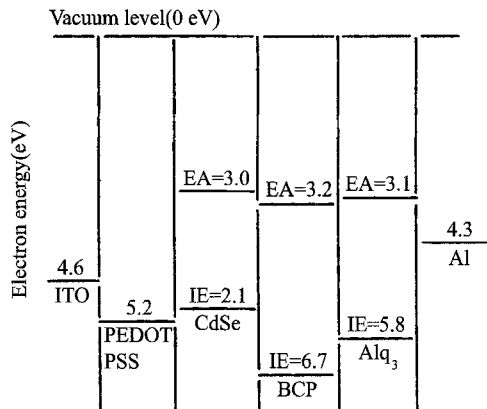


Fig. 6 Energy diagrams of the multilayered device

In summary, we have synthesized CdSe nanocrystals in TOPO/TOP organic system, and have fabricated EL devices with CdSe nanocrystals as emitting layer and Alq₃ as electron transporting layer. The PL spectrum of CdSe nanocrystals and EL spectra under different voltages are investigated, and it is found that the PL spectrum and the EL spectra cover almost the visible region with the full width at half maximum of 200 nm. Moreover, the CIE coordinates of the device change from (0.34, 0.37) at 6 V to (0.44, 0.46) at 20 V, which suggests that the luminescence of the device can be tuned by changing the operating voltage.

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