Interfused semiconductor nanocrystals: brilliant blue photoluminescence and electroluminescence†

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We describe a method for producing blue light-emitting interfused CdSe//ZnS (QE up to 60%) nanocrystals and report the good performance of an electroluminescent device which uses them (external quantum efficiency ~1.5 cd A^{-1}).

Attempts to synthesize semiconductor nanocrystals in solution phase have made good progress for more than 10 years.[1] The applications of high quality nanocrystals in bio-imaging, multi-color light-emitting diodes (LED), and photovoltaic devices have become currently important technological issues.[2] The CdSe/ZnS core/shell quantum dots are well-defined, outstanding materials for various applications because of their high photoluminescent (PL) quantum efficiency (QE ~ 50%).[3] However, it is still difficult to produce pure blue light-emitting materials with high efficiency because of the limit in size control of the CdSe core.[4] Blue light-emitting alloy nanocrystals were made by heating prepared core/shell nanocrystals.[5] Since the shell layer is mixed with the core, alloy nanocrystals lack a passivation layer for quantum confinement. In this report, we introduce a method for preparing nanocrystals with an interfused structure (CdSe//ZnS), which emit strong blue light with more than 60% QE from 420 nm. Also, we report the performance of an electroluminescent (EL) device which uses the prepared nanocrystals as blue light emitters and exhibits excellent efficiency and wonderful color purity.

The general synthesis is carried out in two steps.‡ The CdSe core was prepared by the addition of Se in trioctylphosphine (TOP) to the mixture of CdO and *n*-octadecylphosphonic acid (ODPA) in trioctylamine (TOA). The separated CdSe core was injected into the mixture of zinc acetate and oleic acid in TOA at 300 °C, and then *n*-octanethiol was added drop-wise. With the lapse of reaction time, the PL wavelength shifted to shorter wavelength and the QE was improved. Fig. 1 (a) shows three nanocrystal solutions collected at different reaction times (1 h, 40 min, and 20 min) and 9,10-diphenylanthracene in ethanol (reference dye, QE 91%)[6] under 365 nm UV light. The QEs of the nanocrystals were measured as 440 nm and 56%, 53% and 62% for CdSe//ZnS-1 h ($PL_{\max}$ = 440 nm), CdSe//ZnS-40 min ($PL_{\max}$ = 464 nm), and CdSe//ZnS-20 min ($PL_{\max}$ = 476 nm), respectively. The original PL emission of the CdSe core appeared at 494 nm, and the QE was 7%. The diameter of the CdSe core is about 2.0 nm [Fig. 1(b)] and that of the CdSe//ZnS-1 h is 4 nm ± 0.5 nm [Fig. 1(c)] in the TEM image of Fig. 1, which demonstrates that particle size of the interfused nanocrystals increased by about 2.0 ~ 2.5 nm. The XRD pattern of the CdSe core and CdSe//ZnS-1 h showed an hexagonal structure for CdSe and ZnS respectively (Fig. S1†). Commonly, the coating procedure for core/shell nanocrystals has been performed using highly active precursors such as diethyl zinc and bis-trimethyl silylsulfur at a lower temperature than 160 °C because Ostwald ripening or dissolution of the cores can take place above this temperature.[7] In this investigation, the coating process was carried out at 300 °C using less active ZnS precursors. Therefore, the slowly grown ZnS layer on the CdSe core can diffuse into the core at high temperature and make an alloy phase. The degree of the blue shift from the original energy band gap was easily controlled by core material, core size, coating material, the ratio of core to coating material precursor, reaction temperature, reaction time, and so on.

The UV-Vis and PL spectra (excited at 365 nm, optical density ~0.1) of the nanocrystals are shown in Fig. 2 at each reaction step. The initial CdSe core showed a PL peak at 494 nm (FWHM ~26 nm) and first absorption maximum at 478 nm. For the ZnS growth, the core solution was injected into the Zn precursor solution at 300 °C. After 1 min, nanocrystals in the Zn precursor solution hardly showed any PL emission. However, the absorption appeared at a blue shifted position (464 nm) compared to the initial core. The ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) analysis for the nanocrystals at this stage showed that the ratio of Zn to Cd was about 0.1. Since the first absorption shifted by 14 nm to higher energy, it might be due to the diffusion of the Zn element into the CdSe core to cause PL blue-shift. However, the PL property was not as good as the previously reported alloy CdZnSe.[5] *n*-Octanethiol was added at 300 °C as a sulfur precursor, and the PL efficiency was improved in 5 min because the S precursor reacted with Zn to form a ZnS passivation layer. The first absorption maximum (470 nm) and the

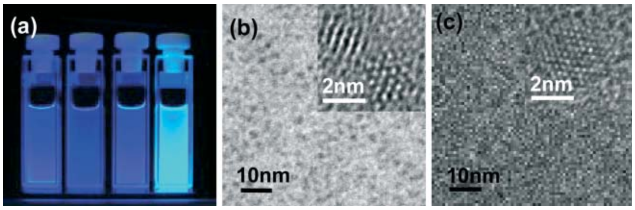

Fig. 1 (a) (From left) 9,10-diphenylanthracene, CdSe//ZnS-1 h, CdSe//ZnS-40 min, and CdSe//ZnS-20 min. All the optical densities of the solutions are 0.1; (b) TEM image of the CdSe core; (c) TEM image of the CdSe//ZnS-1 h. Each inset represents HR image of the nanocrystals.

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† Electronic supplementary information (ESI) available: Fig. S1 XRD pattern of the CdSe//ZnS interfused nanocrystal and the CdSe core, Fig. S2 PL spectra of the interfused nanocrystals and their respective cores. See http://dx.doi.org/10.1039/b509196a

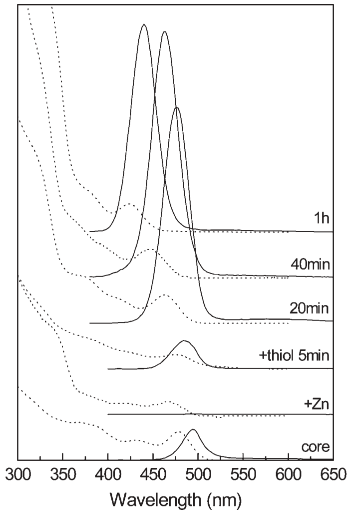

Fig. 2 Normalized UV-Vis spectra (···) and PL spectra (—) at the same optical density (excited at 365 nm) according to the reaction procedures.

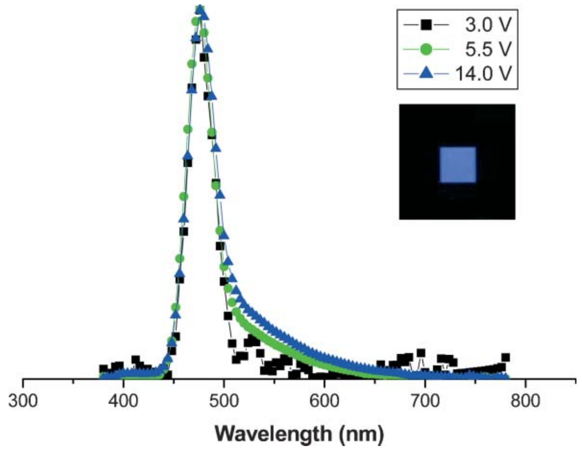

Fig. 3 EL spectra of CdSe//ZnS nanocrystals embedded in LED at different operating voltages and photo taken at 5.5 V. 1.5 cd A^{-1}, at 1.0 mA cm^{-2} (at 5.5 V), 0.4 cd A^{-1} at 142 mA cm^{-2} (at 14 V).

PL peak wavelength (484 nm) were slightly blue-shifted from those of the core, but slightly red-shifted from those of nanocrystals in Zn solution. During the reaction, the energy band gap of the nanocrystals continuously increased after thiol injection. The collected samples after 20 min, 40 min and 1 h showed strong emissions at 470 nm, 464 nm and 440 nm respectively as shown in Fig. 1. After 1 h, the change in absorption/emission wavelength reached a steady state. The ICP-AES analysis showed that the ratio of Zn to Cd reached a steady value ($\sim$11) for both samples collected after 40 min and 1 h. This indicated that ZnS growth was completed in 40 min and that the ZnS layer diffused into the CdSe core for the rest of the reaction time. Therefore, it was expected that the energy band gap increased as the ZnS diffused to form an alloy with CdSe after 40 min. Generally metallic Zn was regarded as more mobile than S, however, the blue shift of the emission wavelength was more dependent on the concentration of S in our experiments. When we increased the concentration of S precursor, the PL maximum of the CdSe//ZnS shifted faster. Based on this, we concluded that ZnS diffused into the CdSe crystal lattice rather than metallic Zn diffused to make the CdZnSe alloy phase. At this moment, it is not clearly understood that the CdSe//ZnS nanocrystals have an homogeneous alloy structure or gradient core/shell structure. The energy band gap of the alloy crystals showed clear dependency on the elemental ratio of Zn to Cd.[4b,7,8] Because the CdSe//ZnS nanocrystals give different PL emission at the same ratio of ZnS to CdSe, their structures might be closer to gradient structures. In addition, the interfused types of nanocrystals can be prepared with various materials according to the same procedure (ESI Fig. S2†).

We integrated CdSe//ZnS nanocrystals (470 nm) in a conventional OLED structure as an active light-emitting layer. The fabrication procedure and the materials used were introduced in a previous report.†[2b] The EL spectra at different operating voltages and the photo of the operating device taken at 5.5 V are shown in Fig. 3. The pure EL emission from the CdSe//ZnS appeared at the same wavelength as the original PL emission with narrow spectrum width (32 nm). The EL from CdSe//ZnS nanocrystals were quite stable at high operating voltages maintaining original PL maximum. The external QE of the device was 1.5 cd A^{-1} at 1.0 mA cm^{-2} and 1.1 cd A^{-1} at 12 mA cm^{-2} (Brightness $\sim$125 cd m^{-2}). This is the 10 times improvement upon the efficiency disclosed in the previous report[4a] in which the pure EL spectrum from the nanocrystal hardly appeared even at low current density. In our LED system, we cannot use energy transfer from the electron transport layer (Alq3) to QD because CdSe//ZnS had larger energy band gap than Alq3. For blue light-emitting nanocrystals, it would be more effective to adopt a larger band gap organic transport layer such as 4,4′-bis(carbazol-9-yl)biphenyl and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and these are now under optimization. The design of the nanocrystal structures and the functional layers in the EL device is in process to achieve better efficiency and stability in the blue light-emitting QD-LED.

In conclusion, a new synthetic method was developed to prepare highly luminescent nanocrystals in the pure blue region. The interfused type nanocrystals were produced by the diffusion of the shell components into the core at high temperatures. An LED incorporating the interfused CdSe//ZnS nanocrystals showed a pure EL spectrum from the nanocrystals at 470 nm with high efficiency (max = 1.5 cd A^{-1}). We believe that this synthetic method can be applied to the design of various kinds of nanocrystals with high efficiency and stability for multiple applications in the future.

Notes and references

‡ 0.4 mmol of CdO (Aldrich, 99.99+%) and 0.8 mmol of ODPA (Alfa) were mixed in 16 g of TOA (Aldrich 95%). The solution was degassed and heated to 150 °C with rapid stirring and then the temperature was further increased to 300 °C under N_2 flow. The selenium precursor solution was made with Se (Alfa, −200 mesh 99.999%) and trioctylphosphine (Aldrich, -tech 90%) as a 2.0 M solution. The CdSe core was prepared by the quick injection of 1 ml of Se precursor solution into the Cd-containing reaction mixture at 300 °C. After 2 min, the heating mantle was removed and the reaction mixture was cooled to 50$\sim$60 °C. Sludge was first precipitated from the CdSe dispersed solution by single centrifugal separation. Ethanol (Fisher, HPLC grade) was added to the CdSe solution until the opaque flocculation appeared. The CdSe cores were separated by another centrifugal step, and the precipitates were dispersed in toluene (Sigma Aldrich, anhydrous 99.8%). The optical density of the 100× diluted CdSe core solution was adjusted as 0.1 at first absorption maximum. 0.4 mmol of

zinc acetate (Aldrich, 99.99%) and 0.8 mmol of oleic acid (Aldrich, -tech 90%) were mixed in 16 g of TOA. It was heated and degassed to 150 °C, and further heated to 300 °C under N_2 flow. 1 ml of the CdSe core solution was injected into the Zn containing solution at the rate of 30 ml h^{-1}. Right after the core injection, 1.6 mmol of *n*-octanethiol in 2 ml of TOA was added at the rate of 60 ml h^{-1}. The blue shift of the energy band gap of the interfused nanocrystals can be controlled by reaction time, temperature, and the concentration of precursors. All chemicals were stored in air and used as purchased without additional treatment. The absorption was measured with Shimadzu UV-3150 and PL spectrum was obtained with ISS PC1 photon counting spectrofluorometer. TEM was performed on a UT F30 Tecnai electron microscope operated at 300 keV. For the fabrication of the nanocrystal LED, 1 wt% of CdSe//ZnS in chloroform was mixed with 2 wt% of *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (HWSands, Sublimed) in chloroform, and the solution was spin-cast on a patterned ITO. After the film was dried at 50 °C for 10 min, 20 nm of 3-(4-biphenylyl)-4-phenyl-5-*t*-butylphenyl-1,2,4-triazole (HWSands, Sublimed) and 25 nm of tri-(8-hydroxyquinoline)aluminium (HWSands, Sublimed) were vacuum-evaporated on the nanocrystal film sequentially. Then, 0.7 nm of LiF and 20 nm of aluminium were deposited as a cathode and finally the unit operating cell was encapsulated in the glove box. The IVL data were obtained with a high current source measure unit (SMU238 of Keithley) and PR650 SpectraScan.

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