

High quality CdSeS nanocrystals synthesized by facile single injection process and their electroluminescence

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Highly luminescent CdSeS nanocrystals (quantum efficiency up to 85%), showing tunable luminescence properties from red to blue region with narrow band edge (FWHM = 34 nm), were synthesized by one-step addition of Se and S source mixture into the Cd precursor solution at elevated temperature, and the resulting nanocrystals were successfully embedded in a traditional OLED structure to give spectrally clean and narrow electroluminescence emission at identical positions of the photoluminescence spectrum.

The compound semiconductor nanocrystals, widely known as quantum dots, exhibit size dependent optoelectronic properties due to quantum confinement effect. Colloidal nanocrystals, which have single crystalline structure and well-controlled size and size-distribution, can be prepared by reasonably simple crystal-growth process.¹ Since the luminescence of nanocrystals spans from infrared to UV, they have attracted much attention due to the potential promising applications such as light-emitting devices (LED).² The synthesis of II-VI group semiconductor nanocrystals emitting visible light has been intensively investigated in recent years.³ Since the nanocrystals have superior colour purity due to narrow emission spectra, there have been many efforts to develop nanocrystal OLED.⁴

Since atoms on large surface area could not be fully coordinated, dangling bonds of nanocrystal surface generated non-radiative decay energy levels to reduce quantum yield. The core/shell type nanocrystals (thin layer of inorganic material was epitaxially grown on the surface of the core) are the most recognized as robust surface passivated system with enhanced quantum efficiency up to 50%.^{5,6} However, additional coating step for inorganic passivation can cause red shift of the emission accompanied with broad size distribution.

In this report, we describe that three component semiconductor nanocrystals CdSeS can be prepared by single injection of Se and S source mixture into the Cd precursor reaction medium.[†] The resulting nanocrystals reveal very narrow PL emission at controlled wavelength mainly according to the elemental composition. The energy band gap of CdSeS can be tuned between the energy level of same sized CdSe nanocrystals and same sized CdS nanocrystals. Furthermore, the quantum efficiency of photoluminescence is improved up to 85% and stability is maintained without extra coating procedure. When these high quality CdSeS nanocrystals are embedded in traditional OLED structure, the EL emission of obtained device shows nearly identical peak position and line-width to PL spectra.

Fig. 1a shows PL spectra of colloidal CdSeS nanocrystals synthesized by injecting various compositions of Se and S mixture solutions in hot CdO/TOA/OA solution. The PL emission wavelength moved controllably from red to blue with narrow peak width (FWHM ~ 34 nm) by decreasing the ratio of Se to S. The narrow and symmetric emission spectra result in fine colour saturation (CIE 1931 diagram, Fig. 1b) that could be one of the primary benefits for true colour display. The photo of each PL spectrum in Fig. 1a was taken under 365 nm UV lamp (Fig. 1c). In addition, the colloidal nanocrystals exhibited very homogeneous shape and particle size (~5 nm) so that they

assembled to form a well-ordered close packed hexagonal array through simple drying (Fig. 1d).

The PL emission of the prepared CdSeS nanocrystals blue-shifted when the used amount of Se was fixed as 0.07 mol/mol of Cd and the used amount of S was controlled in the range of 0.5, 1.1, 2.5, 5.0 mol/mol of Cd (Fig. 2a). When the employed ratios of Se to S were changed from 1 : 7, 1 : 15, 1 : 35 and 1 : 70, real ratios of Se to S in the CdSeS nanocrystals, which were measured by ICP analysis, were changed in the range of 1 : 1.5, 1 : 3.2, 1 : 6.7 and 1 : 10. This result indicates that Cd precursor reacted with Se faster than S to form CdSe preferably and leave surplus S after the reaction. Meanwhile, the reactivity of S to Cd

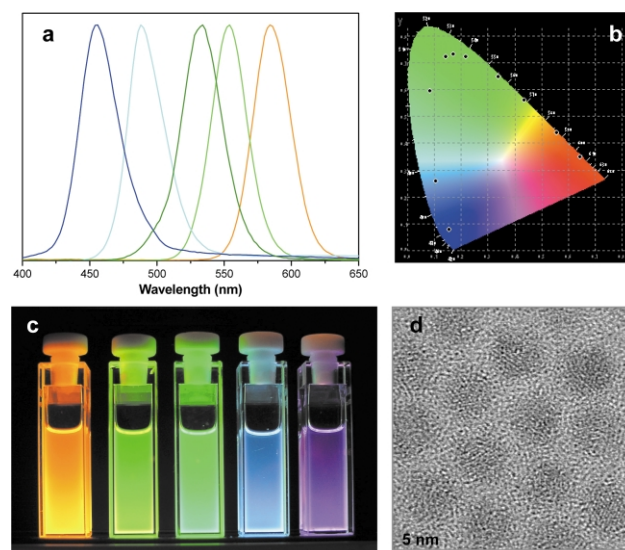


Fig. 1 a. PL spectra of colloidal CdSeS nanocrystals; b. CIE diagram of PL emission; c. the photos of PL emission of (a) samples; d. TEM image of close packed hexagonal array of 5 nm sized CdSeS nanocrystal.

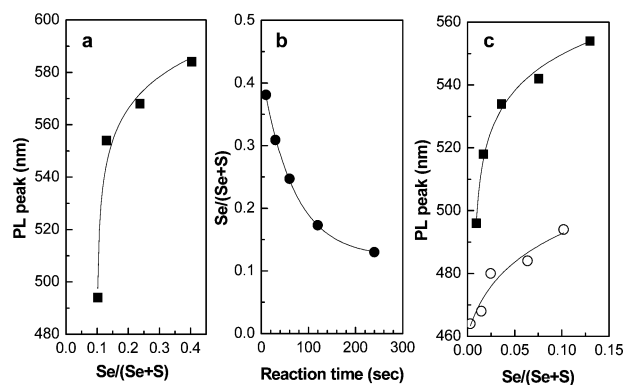


Fig. 2 a. PL emission of CdSeS nanocrystals prepared with fixed 0.07 mol Se and varied 0.5–5.0 mol S. b. Elemental composition of the CdSeS obtained at growth time. c. PL emission of CdSeS nanocrystals prepared with varied amount of Se and fixed amount of S as 2.5 times (■) and 5 times (○) to Cd mole content.

increased as the concentration of S increased so that the ratio of Se to S of the resulting nanocrystals did not increase linearly. As the Se content to S decreased from 1 : 1.5 to 1 : 6.7, PL emission shifted gradually about 30 nm into higher band gap region. However, when the ratio of Se to S was further changed to 1 : 10, PL emission suddenly dropped to blue region about 60 nm from 554 to 494 nm. Since the sizes of nanocrystals prepared with different Se/S ratios at same growth interval were quite similar according to TEM images, the blue shift of PL emission must be due to CdSeS elemental composition. This implies that the optical properties of nanocrystals could be adjusted by their elemental composition, especially Se to S ratio.

Fig. 2b shows the elemental composition of the CdSeS nanocrystals obtained at different reaction time. As growing the nanocrystals with increase of reaction time, the Se content in the crystal was decreased by the continuous growth of CdS on the crystal surface. It is hard to conclude that the resulting material forms general core/shell or gradient type structure, because CdSe and CdS have same wurzite structure of very similar lattice constants so that it is difficult to fractionate CdSe or CdS local structure in nano-sized CdSeS with TEM and EELS technique. The binding energies of CdSe and CdS are also indistinguishable in XPS analysis. However, it is evident that Se is concentrated on the centre of nanocrystal by the fast formation of CdSe at initial reaction stage from the result of Fig. 2b. Based on this assumption, the size of CdSe part in the nanocrystal centre can be compared each other qualitatively by their elemental composition. In other words, the size of CdSe interior decreases as decreasing Se fraction in the elemental composition of nanocrystals. PL emission moved to higher band gap region very rapidly when CdSe rich core was in sufficiently small size range just like energy shift increases exponentially as quantum dot size decreases to critical size regime. From these results, it could be concluded that the initially formed CdSe rich part in the crystal has more determining effect on the energy band gap of the resulting nanocrystals.

This phenomenon could be noticed more clearly for the nanocrystals prepared with various amount of Se and two level of fixed amount of S at 2.5 and 5 mol times to Cd mole content (Fig. 2c). The effect of CdSe rich interior size was examined under the conditions of the fixed amount S to produce CdS rich exterior in same rate. The PL emissions were tuned from 554 to 464 nm when the used amount of Se was varied from 0.004, 0.008, 0.017, 0.035 to 0.07 mol/mol of Cd. As the amount of Se decreased, energy band gap became larger gradually at first. When the amount of Se was extremely small, PL emission shifted to higher energy region very rapidly. This could be explained by the effect of CdSe rich core size difference. However, when the ratio of S to Cd in the synthetic mixture increased, energy shifts of nanocrystals showed the dramatic difference even though the real mole ratio of Se to S in the nanocrystals was same. It is also observed that the emission peak of the CdSeS synthesized with more S content (5 times excess) started at shorter wavelength and moved by smaller energy shift than that of the nanocrystals synthesized with less S content (2.5 times excess). It may indicate that the rate of CdS formation was accelerated to produce alloy type CdSeS nucleus instead of CdSe nucleus when the concentration of S in the synthetic mixture increased.

The structure and EL spectra of CdSeS nanocrystal OLED are shown in Figs. 3a and 3b. 2 wt% of CdSeS in chlorobenzene solution was mixed with 0.5 wt% of the hole transport polymer (poly(9,9'-dioctylfluorene-co-N-(4-butylphenyl)diphenylamine)⁸ in toluene homogeneously. The mixed solution was filtered and spin cast on patterned ITO glass substrate, followed by the deposition of 20 nm of 3-(4-biphenyl)-4-phenyl-5-tert-

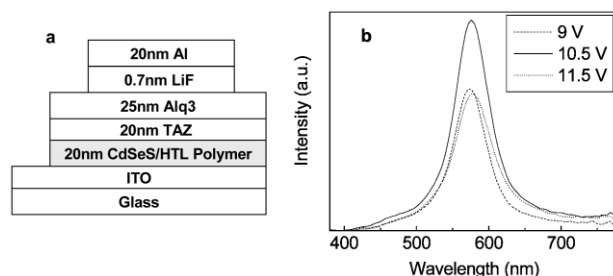


Fig. 3 a. EL device structure embedded with CdSeS nanocrystals as light emitting layer; b. EL spectra at different voltages. CIE coordination at (0.45, 0.49).

butylphenyl-1,2,4-triazole (TAZ) and 25 nm of tri(8-hydroxyquinoline)aluminium (Alq3) sequentially. 0.7 nm of LiF and 20 nm of Al cathode were deposited finally. The EL emission of CdSeS integrated device appeared at the same wavelength of original PL emission of the nanocrystal solution (570 nm) with maintained narrow FWHM (36 nm). The external quantum efficiency was about 0.005% at 189 mA cm⁻², and the brightness was 13 cd m⁻² at the same current density. The inorganic nanocrystals have quite low ionisation energy so that hole or exciton transfer from organic hole transport layer to emitting nanocrystal layer has large energy barrier. Also, the morphology of nanocrystal composite polymer film has big influence on the efficiency corresponding to the local uniformity of nanocrystals in the film.⁷ If the interlayer structure of EL device is optimised appropriately, we believe that employing these high quality CdSeS nanocrystals would enhance external quantum efficiency.

Notes and references

† A 125 ml of round-bottom flask containing 0.0496 g of CdO (0.386 mmol), 0.46 g of oleic acid (OA, 1.63 mmol) and 16 g of triethylamine (TOA) was heated to 300 °C under N₂ flow, yielding colourless solution. After the solution temperature was maintained steadily at 300 °C, 1 ml of the premixed Se and S triethylphosphine solution was rapidly injected into the CdO/OA/TOA solution with vigorous stirring and reacted for 10 sec to 4 min. The Cd : Se : S compositions of the reaction mixtures were 1 : x : y (0.004 ≤ x ≤ 0.07, 0.5 ≤ y ≤ 5). The reaction mixture was quenched with ethanol to stop further growth of the particles. The resulting precipitate was collected by centrifuging and re-dispersed in toluene.

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