

White-light emission from organics-capped ZnSe quantum dots and application in white-light-emitting diodes

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Organics-capped ZnSe quantum dots were synthesized by a colloidal chemical approach using ZnO and Se powder as precursors. The photoluminescence of the specimens showed strong white emission (~ 200 nm full width at half maximum) in the visible range under ambient conditions. The white emission was attributed to the mixing of blue emission of ZnSe nanocrystals exhibiting quantum confinement effect with green-red emission of radiative deep levels from ZnSe surface strained lattice. Based on organic-capped ZnSe quantum dots, the white-light-emitting diodes were fabricated using a near-UV InGaN chip as the excitation source. The diodes emitted white light with CIE chromaticity coordinates of (0.38 and 0.41) and show great potential for use in lighting applications. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886894]

White-light-emitting diodes (WLEDs) have the potential to replace conventional fluorescent or tungsten lamps as lighting sources. Three structures of WLEDs have been reported: phosphor-converted InGaN WLEDs (blue InGaN chip+yellow YAG phosphor),¹ ZnSe-based WLEDs (blue-green ZnSe epilayer+orange doped ZnSe substrate),² and multichip WLEDs (red+green+blue chips). The phosphor-converted WLEDs are highly promising because they consist of a single InGaN chip and possess high luminescence efficiency. These WLEDs produce white light by mixing the yellow light emitted by a phosphor with the blue light emitted by a LED chip. Various phosphors have been reported for the development of the phosphor-converted WLEDs, including yttrium aluminum garnet (YAG, yellow emission),³ Sr₂SiO₄: Eu (yellow emission),⁴ conjugate polymer (PPV, yellow or orange emission),⁵ and dyes with low molecular mass (PtF₂₀TPP+Al_{q3}, red emission+green emission).⁶

On the other hand, colloidal II–VI quantum dots (QDs) have attracted interest because they have high luminescence efficiency (quantum yield > 50%) and size-tunable band-gap characteristics.^{7–11} The QDs could be functionalized using various surfactants to make them soluble in polar or nonpolar solvents, and could be well dispersed in resins. Based on these unique characteristics, the CdS QDs have been justified as a new yellow-emitting phosphor for use in WLEDs.¹²

This work reveals that organics-capped ZnSe QDs, which were synthesized using ZnO and Se powder as precursors, can directly emit white light in the visible range. The WLED was assembled by coupling a near-UV InGaN chip with organics-capped ZnSe QDs.

ZnSe QDs were prepared by using ZnO and Se powder as precursors: 4 mmol ZnO, 40 mmol SA (stearic acid), and 3.8 mmol TOPO (trioctylphosphine oxide) were heated to 300 °C to form a complex. At about 300 °C, TOPSe stock solution (4 mmol Se powder dissolved in 9 mmol trio-

cetylphosphine) was injected into the hot ZnO/SA/TOPO complex. The stearic acid and TOPO served as solvents as well as surfactants that stabilize the surfaces of the nanocrystals. QD were grown as the surfactants underwent absorption-desorption on the initially produced ZnSe surface. The growth temperature was sufficiently high (~ 300 °C) to enable good-quality nanocrystals to be formed.¹³ After around 10 min, the clear liquid became a yellowish mixture. The product was then cooled to room temperature, washed with methanol for three times, and preserved in toluene.

The x-ray diffraction (XRD) pattern in Fig. 1 indicates that the specimen included wurtzite ZnSe nanocrystals. The extra peaks were contributed by SA and TOPO. The Zn atom is an acceptor and forms a coordinated complex with donor ligands such as oxygen or sulfur, so bonding is feasible between ZnSe and stearic acids or TOPO. The thermogravimetric analysis (TGA) revealed that the proportion of remaining

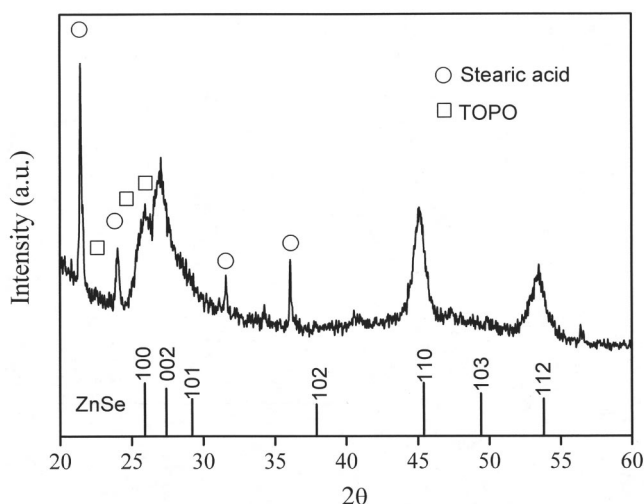


FIG. 1. XRD OF SA/TOPO-capped ZnSe QDs.

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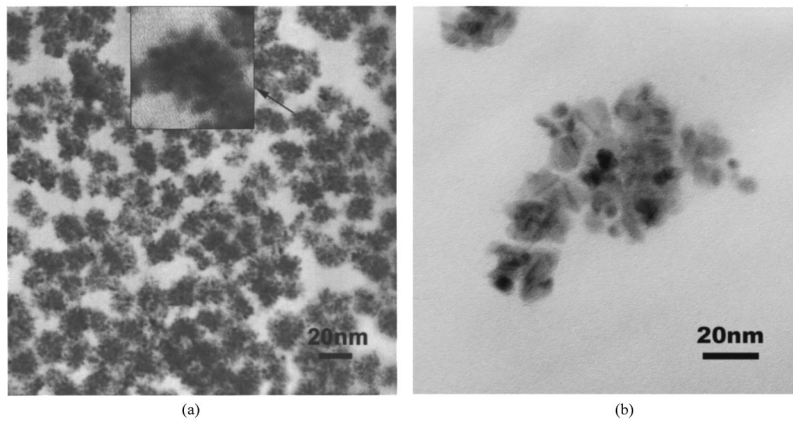


FIG. 2. (a) TEM image of SA/TOPO-capped ZnSe QDs; (b) SA/TOPO was removed from ZnSe QDs.

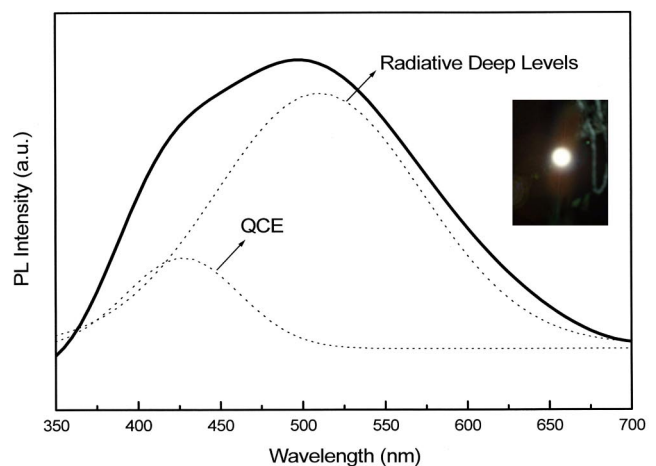
inorganic materials was ~ 68 wt % at 800°C (not shown). Restated, the specimen contained ~ 32 wt % organic SA/TOPO molecules.

The transmission electron microscope (TEM) image of the specimens shows that the ZnSe QDs were encapsulated in a low crystalline matter so that the image is unclear, as shown in Fig. 2(a). The energy dispersive spectrometer (EDS) spectrum indicates the presence of Zn, Se, O, and P in the clusters (not shown). These results, along with the XRD and TGA data reveal that the ZnSe QDs were capped by SA and TOPO molecules. Additionally, QDs aggregated because the SA/TOPO molecules coalesced following the elimination of the solvent in the TEM vacuum chamber. To examine the morphology of the QDs the SA/TOPO was removed from the ZnSe by washing them three additional times with hot methanol. Figure 2(b) shows that some of the ZnSe QDs were polyhedral and their longest dimension ranged from 4 to 15 nm. The estimated average diameter is 7.5 nm for a sample of over 100 particles.

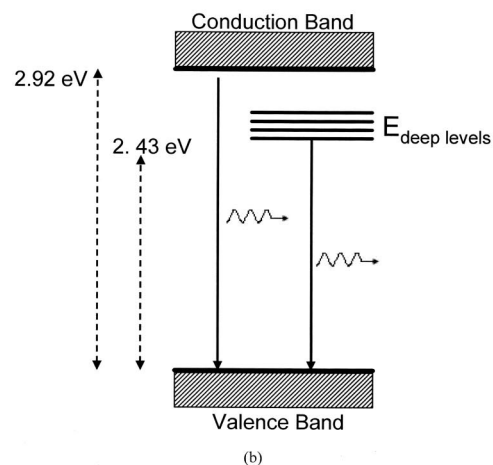
The PL spectrum of the SA/TOPO-capped ZnSe QDs was measured after the sample was dispersed onto a piece of Si wafer, as shown in Fig. 3(a). It shows the SA/TOPO-capped ZnSe QDs had an ultrabroad white-emission band in the visible region with a full width at half maximum (FWHM) of ~ 200 nm. The white-emission band is proposed to be composed of a blue emission band (~ 425 nm) and a green-red emission band (~ 510 nm). The energy of the blue band exceeds the band-gap energy (E_g) of bulk wurtzite ZnSe (~ 2.8 eV, $\lambda_{em} = 443$ nm). From the TEM image, the dimension of ZnSe nanocrystals was comparable to the bulk exciton diameter so the carriers were confined in the ZnSe crystallites, increasing the band-gap energy.¹⁴ Therefore, blue emission is attributed to the nanocrystalline ZnSe with the quantum confinement effect (QCE).

Recently, Xiang *et al.* observed a green PL band ($\lambda_{em} = 505$ nm) from ZnSe nanowires and ascribed the PL origin to the medium deep acceptor of Au.¹⁵ They grew nanowires by vapor deposition using Au as the catalyst, so that the Au diffused easily into the as-grown ZnSe structures. However, in the present case, the green-red band was ascribed to the radiative deep levels generated by extremely strained near-surface lattice of the polyhedral ZnSe nanocrystals. Damage to a lattice structure of semiconductor typically results in the appearance of a broad PL band. Figure 2(b) shows that the ZnSe nanocrystals were polyhedral so the near-surface lattice was expected to be strongly extended and twisted. In a perfect single crystal, a symmetric, the periodic lattice generates

a bulk electronic energy band structure, but structural defects destroy the symmetry of the lattice and perturb the energy band structure. In this situation, a local energy potential appears in the lattice and traps the carriers. This local perturbation effect could be described by a series of energy levels which lie within the band gap. Consequently, the sub-band-



(a)



(b)

FIG. 3. (a) Room-temperature PL spectrum of organics-capped ZnSe nanocrystals. The dotted lines were obtained by fitting a Gaussian curve. It indicates that the broad emission band consists of a blue emission band (~ 425 nm) and a green-red emission band (~ 510 nm). The inset shows the organics-capped ZnSe QDs that produced white light when irradiated with a 325-nm-He-Cd laser; (b) band diagram of SA/TOPO-capped ZnSe QDs.

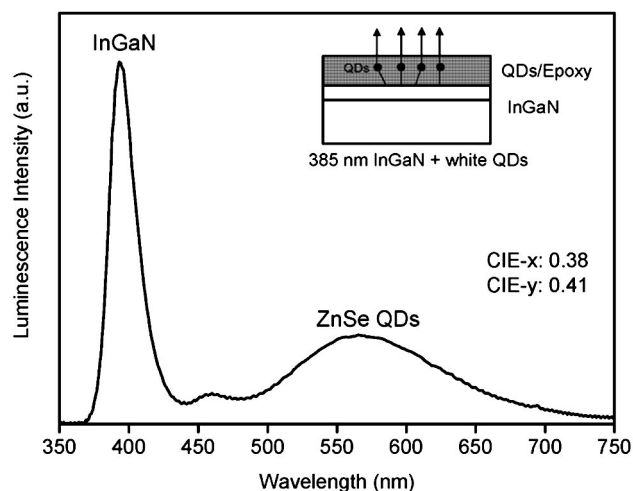


FIG. 4. Luminescence spectrum of a near-UV InGaN/white-emitting QDs WLED. The InGaN chip was operated at 20 mA. The SA/TOPO-capped ZnSe QDs emitted white light when irradiated from InGaN irradiation. The CIE chromaticity is (0.38 and 0.41), which is in the white color region.

gap broad PL was observed. A broad PL band was not observed for spherical ZnSe QDs. They merely showed a sharp PL peak.^{13,16} Figure 3(b) shows the PL mechanism of the organics-capped ZnSe QDs.

The surface dangling bond states that lie within the band-gap typically quench the PL intensity. Surface passivation usually reduces the number of the surface dangling bonds. In this study, the organic capping layer was used not only as a passivation medium, but also to promote dispersivity of nanocrystals in organic solvents or resins.

The SA/TOPO-capped ZnSe QDs showed a white-emitting characteristic so it was used as the phosphor of the phosphor-converted WLED. A near-UV InGaN chip (385 nm, Toyoda Gosei) was used as an excitation source. The SA/TOPO-capped ZnSe QDs were mixed with epoxy resin and coated onto the InGaN chip. The device exhibited white emission with a CIE (Commission Internationale de L'Eclairage) of (0.38 and 0.41), as shown in Fig. 4. Given a 10 wt % (~6.5 wt % of ZnSe nanocrystals in the resin) concentration of SA/TOPO-capped ZnSe QDs the device emission efficiency was ~30% relative to RGB phosphors (R:Y₂O₂S:Eu, G:ZnS:Cu, B:BAM:Eu, 10 wt % in resin). The maximum load of the SA/TOPO-capped ZnSe QDs was limited to 10 wt % in the resin. If the concentration exceeds

10 wt %, then particles aggregate, eventually reducing the efficiency of the device.

Although the efficiency remained low, the SA/TOPO-capped ZnSe QDs prepared by this simple process demonstrated potential for application in WLEDs. Further study is needed to enhance efficiency of the device by eliminating nonradiative defects and increasing loading of the SA/TOPO-capped ZnSe QDs without aggregation.

In summary, this work addresses the synthesis of organics-capped ZnSe QDs. The PL from these QDs was a white-emission band (400–700 nm) and visible to the naked eye. A WLED using a near-UV InGaN chip as the excitation source and white-emitting organics-capped ZnSe QDs was demonstrated. The device exhibited white light with CIE chromaticity coordinates of (0.38 and 0.41).

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