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# Electroluminescent properties of a device based on terbium-doped ZnS nanocrystals

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## Abstract

Rare earth terbium (Tb)-doped zinc sulfide (ZnS) nanocrystals (NCs) sized between 3 and 4 nm were synthesized via a co-precipitation reaction of precursors, zinc acetate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ), terbium chloride ( $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ ), lithium fluoride (LiF) and thiocarbamide in a methacrylic acid/citric acid/methanol mixing solution. The NCs were characterized by means of x-ray powder diffraction, a transmission electron microscope and a fluorescence spectrophotometer. Electroluminescent (EL) properties of the device having a hybrid organic/inorganic multilayer structure with ITO/(poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT-PSS)(70 nm)/poly(vinylcobarzale)(PVK)(100 nm)/ZnS:Tb NCs(120 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)(30 nm)/LiF(1 nm)/Al(100 nm) were studied. Injecting electrons and holes were recombined to form excitons which were confined within the ZnS:Tb NC host and then the exciton energy was transferred to the  $\text{Tb}^{3+}$  centre, and finally the green emission of the  $\text{Tb}^{3+}$  ion was observed. The four emissions which peaked at 430, 491, 546 and 577 nm were attributed to the electronic transitions of the ZnS host and the  $^5\text{D}_4-^7\text{F}_6$ ,  $^5\text{D}_4-^7\text{F}_5$  and  $^5\text{D}_4-^7\text{F}_4$  of the  $\text{Tb}^{3+}$  centre, respectively, when the EL device was driven at 10 V. The maximum luminance of the ZnS:Tb NCs-based device is about  $15 \text{ cd m}^{-2}$  at 25 V driving voltage.

## 1. Introduction

Nanometre-sized semiconductor clusters have attracted growing interest during the last decade [1, 2]; therefore, they have become an important class of luminescent materials because of the flexibility in controlling optical and electronic properties by changing only the size of the materials. Generally, they exhibit strong size-dependent optical properties, i.e. observed increased energy gap, which leads to a blueshift in the absorption band with the decreasing particle sizes. This effect occurs when the size of the

nanocrystal is smaller than the bulk Bohr exciton radius, as a result of the quantum confinement effect due to the localization of charge carriers [3].

Zinc sulfide (ZnS) is a wide-gap ( $\sim 3.6 \text{ eV}$ ) II–VI compound semiconductor material and is commercially used as a phosphor and also in thin film electroluminescent (EL) devices. Since Bhargava *et al* first reported on the remarkable optical properties of Mn-doped ZnS nanocrystals (NCs) that were prepared by chemical process at room temperature in 1994 [4, 5], a large number of the investigations on semiconductor NCs have been focused on the photoluminescent (PL) properties of Mn-doped ZnS NCs

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[2,6–12], Cu-doped ZnS NCs [7, 13], Sm-doped ZnS NCs [1, 14], Tb-doped ZnS NCs [1, 15, 16] and Eu-doped ZnS NCs [3,17–20] prepared by different techniques. In these papers, the broad emission and excitation of the ZnS:Sm<sup>3+</sup> and ZnS:Eu<sup>2+</sup>, respectively, were observed. A few papers have also reported on the EL properties of nano-semiconductors doped with the transition elements Mn [21–24] and Cu [25]. Emissions from both poly-vinylcarbazole (PVK) from the recombination of holes and electrons and the ZnS:Mn NC-layer from the impact excitation of Mn luminescent centres were observed in the organic–inorganic hybrid device fabricated by mixing PVK and ZnS:Mn NCs. The EL properties of rare earth (RE) ions doped ZnS NCs have, however, never been studied.

In this work, ZnS:Tb NCs sized between 3 and 4 nm were synthesized by the co-precipitation method, and the EL properties of ZnS:Tb semiconductor nanocrystals were studied with the hybrid EL device structure of ITO// (poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate (PEDOT-PSS)(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP)(30 nm)/LiF(1 nm)/Al(100 nm).

## 2. Experiments

ZnS:Tb NCs were prepared in the following manner. A three-neck flask was charged with a solution containing 4.5 g of citric acid, 2.0 mL of methacrylic acid, and 100 mL of methanol. A second aqueous solution containing 0.228 g of 0.003 mol thiocarbamide and 50 mL of methanol, and a third aqueous solution containing 0.275 g of Zn(CH<sub>3</sub>COO)<sub>2</sub> (0.0015 mol), 0.0295 g of TbCl<sub>3</sub>·6H<sub>2</sub>O ( $7.89 \times 10^{-5}$  mol, Tb<sup>3+</sup>/Zn<sup>2+</sup> molar ratio 5:95), 0.002 g of LiF ( $7.89 \times 10^{-5}$  mol) and 50 mL of methanol were prepared and then dropped slowly into the first solution simultaneously via two different necks. The solutions were stirred constantly at 70 °C for 5 h and a white fluid of ZnS:Tb was obtained. The resulting solution was then transferred into a 100 mL stainless Teflon-lined autoclave and heated at 160 °C for 12 h. The resultant powders were collected and washed several times with methanol and distilled water, respectively. Finally, the ZnS:Tb NCs were obtained after the samples were centrifuged and dried in a vacuum at room temperature. The hybrid EL device with a structure of ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) was constructed in the following manner. The 70 nm thick PEDOT-PSS layer was spin-cast onto the cleaned ITO-coated glass substrate and the 100 nm thick PVK layer was spin-coated on the PEDOT-PSS layer, followed by casting methanol-dispersed ZnS:Tb NCs. The ZnS:Tb NC layer was dried in a vacuum oven at 80 °C and resulted in a ZnS:Tb NC layer 120 nm thick. The BCP layer, 30 nm in thickness, was vacuum-evaporated onto the NC layer, followed by the 1.0 nm thick LiF and the 100 nm thick Al cathode, without breaking the vacuum. Nanocrystal size and morphology were measured using a JEM-2010 transmission electron microscope (TEM) operated at 200 kV for imaging and direct determination of the crystal size. The structure of the NC was characterized by x-ray powder diffraction (XRD) using a Japan Rigaku D/max-II B diffractometer with CuK $\alpha_1$  radiation ( $\lambda = 0.1541$  nm).

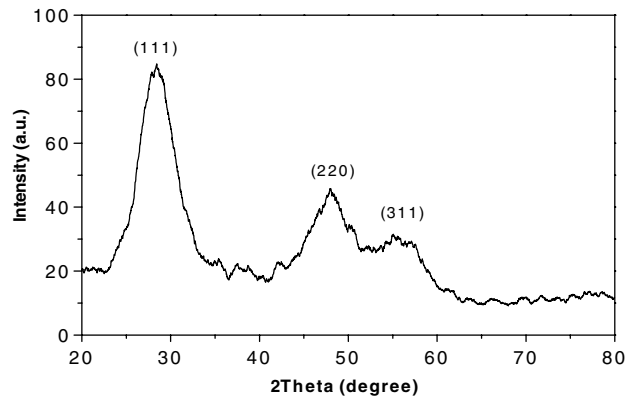


Figure 1. XRD pattern of ZnS:Tb nanocrystals.

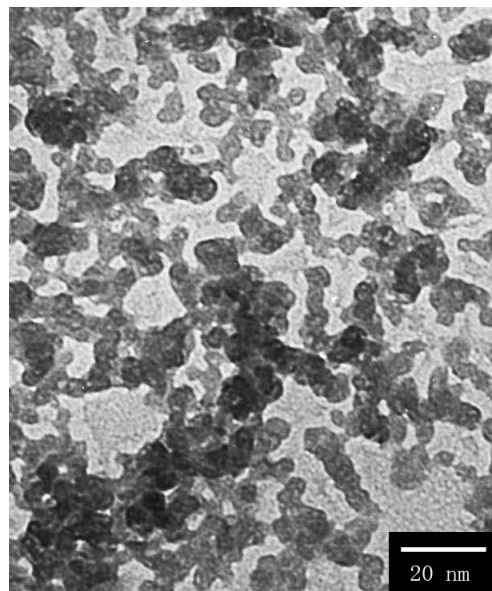


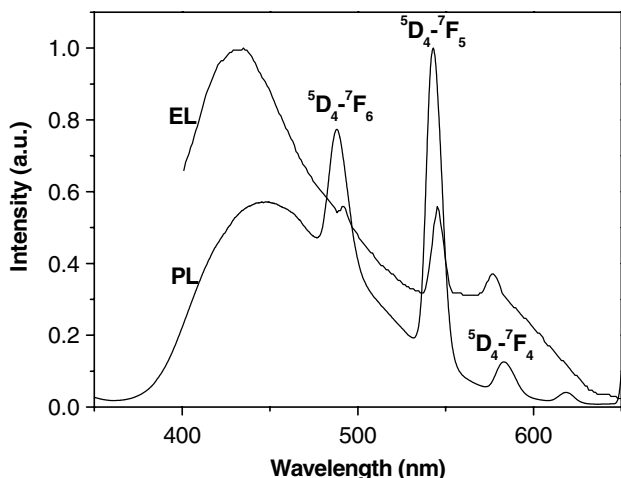
Figure 2. TEM micrograph showing ZnS:Tb nanocrystals with sizes between 3 and 4 nm.

PL spectra were measured using a Hitachi F-4500 fluorescence spectrometer. EL emission spectra were collected using a fibre optic spectrometer and dispersed onto a CCD Si-detector.

## 3. Results and discussions

The XRD pattern of ZnS:Tb NCs is shown in figure 1. It is revealed that the crystals exhibit a zinc-blend crystal structure. The three diffraction peaks correspond to the (111), (220), and (311) planes, respectively, of the cubic crystalline ZnS. Due to the size effect, the XRD peaks broaden and their widths become larger as the crystals become smaller. From the XRD analysis, no characteristic peaks of impurity phases were observed. The average sizes of the ZnS:Tb NCs were calculated from the Debye–Scherrer equation to be around 3 nm. A typical TEM image is shown in figure 2; it is noticed that the average size of the ZnS:Tb NCs is between 3 and 4 nm which is in agreement with the estimation by XRD analysis.

Figure 3 shows the typical PL spectra of the ZnS:Tb NC film and the EL spectra of the device with ZnS:Tb

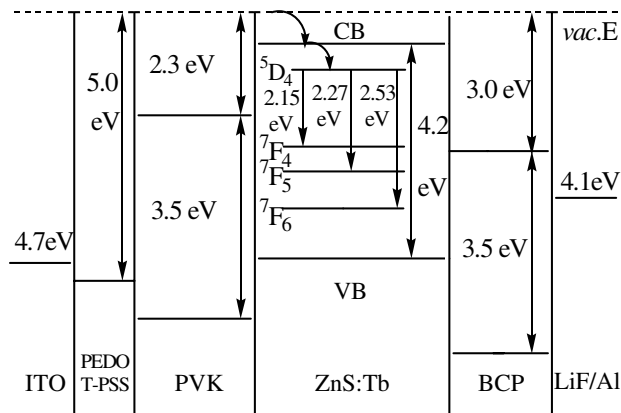


**Figure 3.** PL spectrum ( $\lambda_{\text{exc}} = 379$  nm) of the ZnS:Tb NCs and EL spectrum from an ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) device.

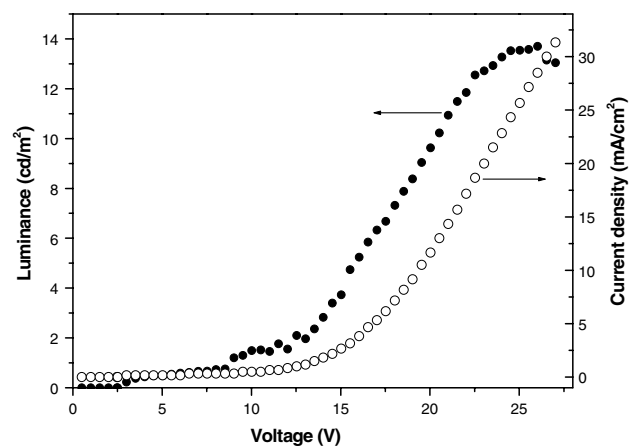
NCs. We can see that the PL spectra of ZnS:Tb excited by 379 nm are composed of five peaks located at 430, 488, 543, 583 and 618 nm, respectively, and the broad band at 430 nm resulted from the ZnS host [1] and the other four sharp bands which peaked at 488, 543, 583 and 618 nm are due to the  $^5D_4-^7F_6$ ,  $^5D_4-^7F_5$ ,  $^5D_4-^7F_4$  and  $^5D_4-^7F_3$  electron transitions respectively, of the  $Tb^{3+}$  ions [15]. When the EL device with ZnS:Tb NCs was driven by a voltage of 10 V, four peaks located at 430 nm from the ZnS host, 491 nm ( $^5D_4-^7F_6$ ), 546 nm ( $^5D_4-^7F_5$ ) and 577 nm ( $^5D_4-^7F_4$ ) were observed. The EL emission intensity increased slightly with increasing applied voltage, but the emission wavelength did not change. No noticeable EL emission was observed in the absence of the PEDOT-PSS layer, indicating that the PEDOT-PSS layer plays an important role in lowering the energy barrier for the injection of holes from the ITO anode to the PVK layer. Most NCs-based EL devices using a conjugated polymer as hole transporting material show emissions from both the NCs and polymer layers which are because of the electrons holes recombining in both the components [22, 24]. In this work EL emission from the PVK polymer is, however, not observed in the EL device of ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm), showing that only the ZnS:Tb NC layer contributes to EL emissions and the carrier recombination was confined within the ZnS:Tb NC layer because of the hole blocking role of the BCP layer.

On the other hand, EL and PL spectra were recorded on different spectrometers, which resulted in a small difference between the EL and PL peaks in figure 3. PL emissions from NCs were readily measured on a Hitachi F-4500 fluorescence spectrometer. However, the EL spectrum obtained in the same system is not reliable, because observable device degradation occurs when sweeping the wavelength from 400 to 700 nm (usually 200 s). The CCD Si-detector (designed for EL device measurement) which can take in a light signal at a glance is, therefore, used for measurement of the EL spectrum.

The energy-level diagram of the EL device with ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) is shown in figure 4 [24, 25]. The band gap energy of the ZnS NCs of 3 nm is



**Figure 4.** Energy-level diagram and the EL processes of ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm).



**Figure 5.** Current density-voltage-luminance characteristics of the ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) device.

about 4.2 eV, which is much larger than that of nanocrystalline ZnS (3.6 eV) due to the quantum size effect. The energy barrier of 0.8 eV for the holes injection at the PEDOT-PSS/PVK interface would lead to a high turn-on voltage and a low flowing current. The holes and electrons were injected into the ZnS:Tb NCs layer through the PVK and BCP layer, respectively, so the carriers were recombined to form the excitons on the ZnS host, and the exciton energy was then transferred to the resonant levels of the  $Tb^{3+}$  ions to achieve the characteristic emissions of the  $Tb^{3+}$ . The EL emission wavelength which peaked at 491 and 546 nm was shifted to a lower energy compared with its PL spectrum, indicating the local heat effect from the large current and poor thermal conductivity of the emitting layer [25].

The current density-voltage-luminance characteristics of the ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) device are shown in figure 5. It can be seen that the threshold voltage of the device is not too low (about 10 V), suggesting that the greater parts of the voltage were dropped at the ZnS:Tb NC layer. The result further confirms that the ZnS:Tb NC layer can control the current density-voltage properties of the EL device. The maximum luminance of the ZnS:Tb NCs-based device is about  $15 \text{ cd m}^{-2}$  at 25 V driving voltage.

#### 4. Conclusions

In summary, ZnS:Tb NCs sized between 3 and 4 nm were synthesized by the co-precipitating reaction route. The EL device with a structure of ITO/PEDOT-PSS(70 nm)/PVK(100 nm)/ZnS:Tb NCs(120 nm)/BCP(30 nm)/LiF(1 nm)/Al(100 nm) was fabricated. The four peaks located at 430 nm (ZnS host lattice excitation), 491 nm ( $^5D_4-^7F_6$ ), 546 nm ( $^5D_4-^7F_5$ ) and 577 nm ( $^5D_4-^7F_4$ ) were observed when the hybrid device was driven at a voltage of 10 V, and it further confirms that the EL emission is from the ZnS:Tb NCs layer. The hybrid EL emission of the device resulted from the f-f electrons transition of  $Tb^{3+}$  ions, which is from the energy of excitons by recombining the holes and electrons on the NC ZnS host; the excitons energy was then transferred to the  $Tb^{3+}$  centre, and the characteristic emissions of the  $Tb^{3+}$  were achieved. The EL device based on the RE ion-doped nanocrystalline ZnS obviously shows EL emission under a driving bias of 10 V, although its turn-on voltage is also relatively high and the stability of the EL device will further be improved. The EL mechanism and physical process on nanocrystalline-based devices need to be understood. In order to improve the performance of the NC-based devices, a new material system and a new structure device will be designed. It is believed that many kinds of RE ion-doped NCs semiconductors/polymer hydride organic devices will be constructed.

#### Acknowledgment

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