

# Performance of polymer/CdS organic-inorganic hybrid LEDs

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Organic-inorganic hybrid light emitting diodes (LEDs) were fabricated by incorporating cadmium sulphide (CdS) nanoparticles in hole transporting layer and light emitting materials of a polymer LED. The CdS nanoparticles with size of 10 nm were synthesized by precipitation technique. The LEDs incorporated with the CdS nanoparticles show a reduction in turn on voltage and luminance. When the nanoparticles are incorporated in a suitable fluorene based light emitting polymer, the luminance is increased along with the decrease of turn on voltage.

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Different approaches of light emitting diodes (LEDs) are used to incorporate the organic and inorganic materials, including metal oxide nanoparticles based interfacial layers<sup>[1-4]</sup> to improve the device stability and the electron/hole injection properties, doping the interfacial buffer layer<sup>[5-9]</sup> to improve the turn on voltage, adding suitable luminophores or small molecules to organic polymers/inorganic crystals<sup>[10]</sup> to tune the emission wavelength, and blending polymers and nanoparticles<sup>[11]</sup> to enhance the luminance and quantum efficiency. Even polymers and nanomaterials are employed in the organic-inorganic hybrid light emitting diodes (HLEDs), most of them deal with the multilayer structures with organic and inorganic materials in different layers.

In this paper, it will be interesting to study the effects of incorporating nanomaterial in the hole transporting buffer layer and blending with the emissive layers on the light emitting properties of the hybrid devices. For this purpose, we use poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) and poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) as organic materials and cadmium sulphide (CdS) nanoparticles as the inorganic materials. The performances of these materials are well studied and may be taken as the references to the study of the hybrid device fabrication.

CdS nanoparticles were synthesized by precipitation technique using cadmium acetate (CdSO<sub>4</sub>) and thiourea (SC(NH<sub>2</sub>)<sub>2</sub>) in the presence of ammonium hydroxide (NH<sub>4</sub>OH). Aqueous solutions of both CdSO<sub>4</sub> and SC(NH<sub>2</sub>)<sub>2</sub> with concentration ratio of 1:1 were mixed together while the pH was maintained at 10.5 by using

NH<sub>4</sub>OH. The mixture was then heated at 75 °C for 90 min and stirred at the same time until it turned yellow and precipitated. The precipitate was then filtered, washed and dried. The chemicals used in this synthesis were obtained from Merck Ltd.

All polymers used in this investigation were obtained from Sigma-Aldrich, USA. Poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) was stirred for 2 h and filtered using syringe filter with pore size of 0.45 μm prior to spin coating. Emissive polymers of PFO and F8BT were prepared in toluene with a concentration of 15 mg/mL. The PFO:F8BT blend was made by mixing the two solutions with a volume ratio of 19:1. The polymer solutions were filtered using a suitable syringe filter with pore size of 0.2 μm before coating. For the nanomaterial-polymer blend, we added CdS nanoparticles to the polymers, namely, PEDOT:PSS, PFO and F8BT solutions, so as to maintain the CdS concentrations in the blend at 2 mg/mL, 10 mg/mL and 10 mg/mL, respectively. All the nanoparticle blends were additionally sonicated for 10 min prior to coating. Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) was prepared in methanol with a concentration of 2 mg/mL, by adding a few drops of acetic acid.

The indium tin oxide (ITO) glass plates with the sheet resistance of 8–12 Ω/□ were supplied by Delta Technologies, USA. The ITO glass substrates were cleaned with laboratory detergent and sonicated in various solvents, namely, distilled water, acetone, propanol and ethanol, for 30 min. The substrates were blown with ni-

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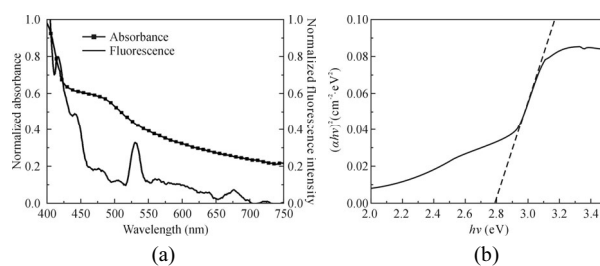
trogen gas and further treated with ultraviolet (UV) or ozone ( $O_3$ ) to remove organic contaminants. PEDOT:PSS helps to efficiently transport holes from ITO to the active layer and also smoothen the uneven ITO substrate. The hole transporting layer was coated over the pre-cleaned ITO substrate so as to get a film with thickness of 80 nm. The PFO:F8BT was coated at 8 000 r/min to give a film with thickness of 55 nm, while PFO and F8BT were coated at 4 000 r/min yielding the thickness around 100 nm. All the respective nanoparticle blends were coated with the same coating parameters as the corresponding polymers. The PFN solution was spin coated to make smooth films with thickness of 45 nm. This was followed by thermally evaporating lithium fluoride (LiF) (2 nm) and aluminum (100 nm) consecutively in a vacuum of  $5.33 \times 10^{-4}$  Pa. LiF was used as a buffer layer to modify the work function of aluminum from 4.3 eV to 3.1 eV. The cathode was coated with a shadow mask to provide an active area of  $0.09 \text{ cm}^2$ . Finally, the devices were encapsulated using a sealed cover glass before making electrical measurements.

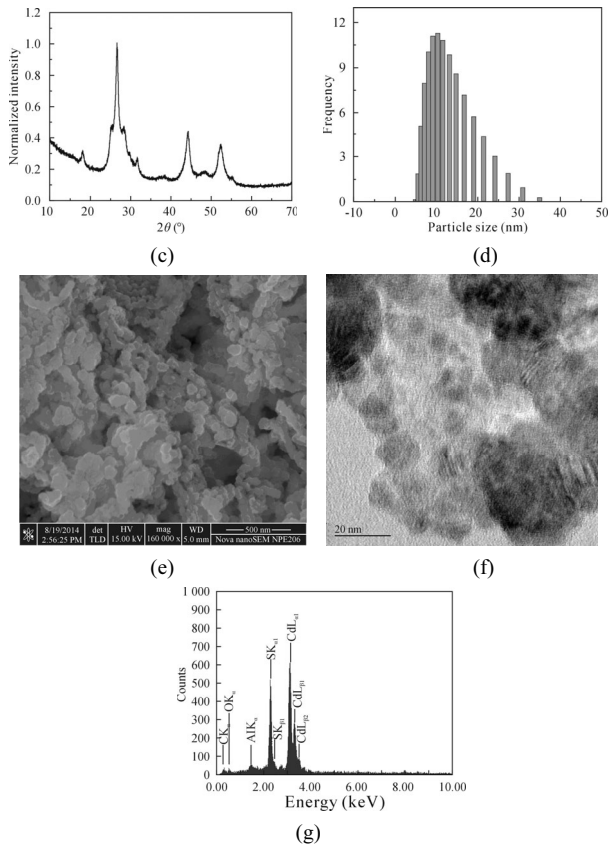
The absorbance and photoluminescence (PL) measurements were studied using Jasco V-570 spectrophotometer and Varian Cary Eclipse fluorimeter, respectively. Phase and elemental analyses were done using X-ray diffractometer (X-Pert Pro Analytical diffractometer) and energy-dispersive X-ray spectroscopy (EDS, JEOL Model JED-2300). Imaging of nanoparticles was performed by using field emission scanning electron microscope (FESEM, Nova NanoSEM NPE 206) and high-resolution transmission electron microscope (HRTEM, JEOL 3010). Size distribution of synthesized CdS nanoparticles was measured by dynamic light scattering method using SZ-100 nanoparticle, HORIBA. The luminance and current density versus voltage characteristics were simultaneously recorded using Keithley 2400 SMU and a calibrated photodiode (Thor Labs, PDA 36A-EC) connected to digital multimeter (Keithley 2000) respectively, with the help of LabVIEW program. The electroluminescence (EL) spectrum was observed using Ocean Optics (HR4000) spectrophotometer. The thickness of thin polymer films was measured by optical reflectance system using ThetaMetrisis (FR-pOrtable). All measurements were carried out in air at room temperature.

The optical, structural and morphological properties of CdS nanoparticles prepared as mentioned above were investigated in detail. Fig.1(a) shows the optical absorption and PL spectra of CdS nanoparticles dispersed in toluene. The UV-visible absorption spectrum shows a characteristic peak at 480 nm, while the bandgap energy is estimated to be 2.8 eV from the  $(ah\nu)^2$  versus  $h\nu$  plot as shown in Fig.1(b). The PL spectrum shows two prominent peaks at 416 nm and 442 nm along with a distinct peak at 531 nm when excited at 390 nm. X-ray diffraction (XRD) pattern of CdS presented in Fig.1(c) shows broad peaks at  $25.46^\circ$  with h(100),  $26.75^\circ$  with h(002) and c(111),

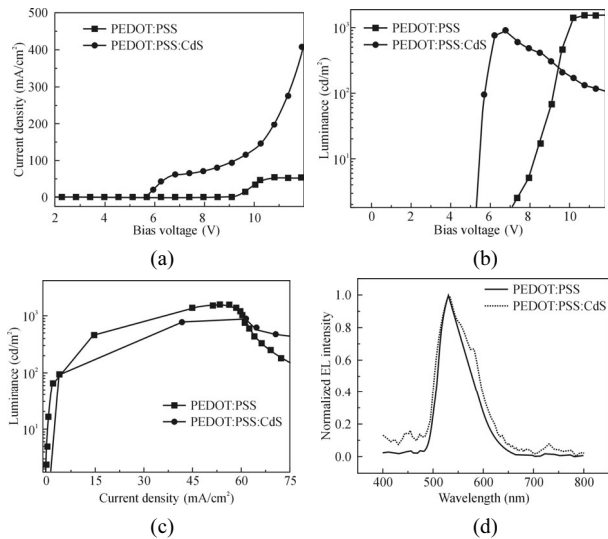
$28.40^\circ$  with h(101),  $31.72^\circ$  with c(200),  $37.85^\circ$  with h(102),  $44.28^\circ$  with h(110) and c(220),  $48.04^\circ$  with h(103), and  $52.27^\circ$  with h(112) and c(311), which are carefully compared with those of JCPDS cards with cubic *c* of 75-0581 and hexagonal *h* of 65-3414. We conclude the morphology of the synthesized nanoparticles to be hexagonal to cubic structures. The particle size of CdS nanoparticles is calculated by using Scherrer formula and found to be 12.8 nm, considering the width of the 002 plane at  $26.75^\circ$  on the  $2\theta$  scale. The elemental composition and purity of synthesized nanoparticles are verified from EDS analysis and presented in Fig.1(g). The spectrum shows some peaks of cadmium at 3.2 eV ( $L_{\alpha 1}$ ), 3.4 eV ( $L_{\beta 1}$ ) and 3.5 eV ( $L_{\beta 2}$ ) and some peaks of sulphur at 2.3 eV ( $K_{\alpha 1}$ ) and 2.4 eV ( $K_{\beta 1}$ ). The size and morphology of CdS nanoparticles are confirmed by scanning electron microscope (SEM) and HRTEM images shown in Fig.1(e) and (f), respectively, and the range of particle size is estimated from dynamic light scattering measurement as shown in Fig.1(d). We see that the particles size ranges from 5 nm to 30 nm with 40% of particles around 10 nm, which are in good agreement with the calculated results.

The device structure for the standard LED is ITO/PEDOT:PSS/PFO:F8BT/PFN/LiF/Al. The performance of hybrid hole transporting layer, obtained by incorporating CdS nanoparticles to PEDOT:PSS layer, is compared with that of the standard device. Fig.2(a) and (b) show the current density ( $J$ ) and luminance characteristics with respect to the bias voltage ( $V$ ) of devices based on PEDOT:PSS with and without CdS nanoparticles, respectively. It can be observed from Fig.2(b) that there is a reduction of turn on voltage from 7.2 V to 5.3 V by incorporating CdS nanoparticles. The decrease of turn on voltage can be speculated to the modification of barrier by CdS when CdS nanoparticles are incorporated in the hole transporting layer. The  $J$ - $V$  characteristics shown in Fig.2(a) also show two barriers in the system, most probably due to the interfacial layers. At a typical current density of  $55 \text{ mA/cm}^2$ , the maximum luminance in nanoparticle-based device is decreased to be 45% of that of the standard PEDOT:PSS device as shown in Fig.2(c). The decrease of luminance may be due to the reabsorption of emitted light by the nanoparticles. The EL spectrum for CdS embedded device shows two additional shoulder peaks at 560 nm and 580 nm apart from the dominant peak at 530 nm, as depicted in Fig.2(d). Such additional peaks have also been observed while gold nanoparticles were incorporated in PEDOT:PSS<sup>[12]</sup>.





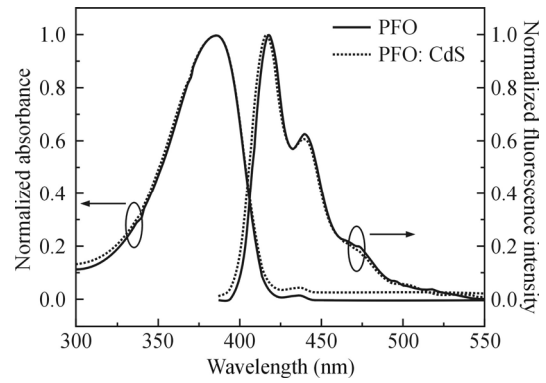
**Fig.1 (a) UV-visible absorption and PL spectra; (b)  $(ahv)^2$  versus  $hv$  plot; (c) XRD pattern; (d) Statistical particles size distribution; (e) Field-emission SEM image with scale of 500 nm; (f) HRTEM image with scale of 20 nm; (g) EDS analysis of CdS nanoparticles**



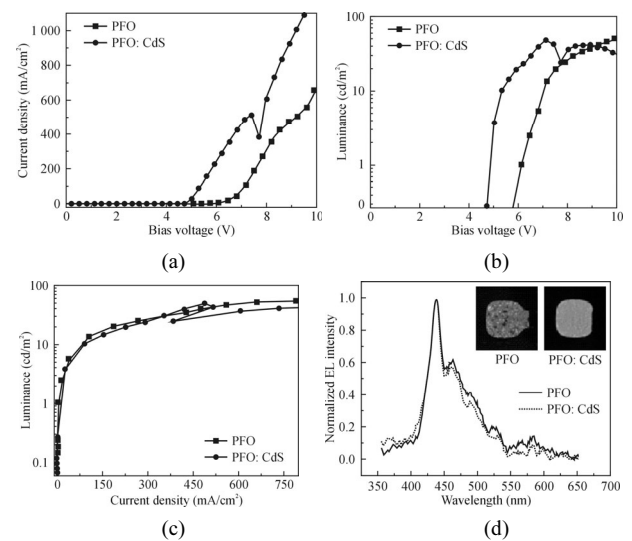
**Fig.2 (a)  $J$ - $V$  curves; Luminance performance with respect to (b) bias voltage and (c) current density; (d) EL spectra of devices based on PEDOT:PSS with and without CdS nanoparticles**

For PFO based devices, a standard device was fabricated using the following structure as ITO/PEDOT:PSS/PFO/LiF/Al. The effect of CdS on PFO was investi-

gated by incorporating PFO:CdS blend as an active layer. Fig.3 shows the absorption spectra and fluorescence spectra (excited at 390 nm) of PFO and PFO:CdS blend with weight ratio of 1.5:1 in toluene. We can perceive that the full-width half-maximum ( $FWHM$ ) of the emission spectrum from PFO is reduced by 6 nm after the addition of the nanoparticles. By the incorporation of nanoparticles, as shown in Fig.4(a), the turn on voltage is reduced by 1 V. As shown in Fig.4(b), the maximum luminance of  $50 \text{ cd/m}^2$  is achieved at 7.1 V in PFO:CdS device and at 10 V in standard PFO device, which may be due to the enhancement of injection of the charge carriers by the nanoparticles into the active layer at a reduced voltage. However, there is no improvement in luminance performance and almost no change in EL spectrum as seen in Fig.4(c) and (d). The inset in Fig.4(d) shows the photographs of blue emission from PFO based devices with and without CdS nanoparticles.

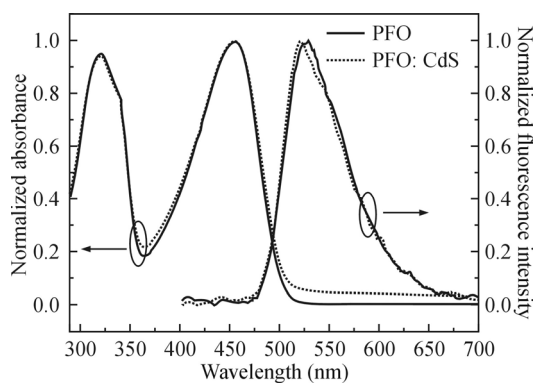


**Fig.3 Absorption spectra and fluorescence spectra of PFO and PFO:CdS blend**



**Fig.4 (a)  $J$ - $V$  curves; Luminance performance with respect to (b) bias voltage and (c) current density; (d) EL spectra of devices based on PFO with and without CdS nanoparticles (Inset in (d) shows the actual photographs of devices with PFO and PFO:CdS blend as active layers, respectively.)**

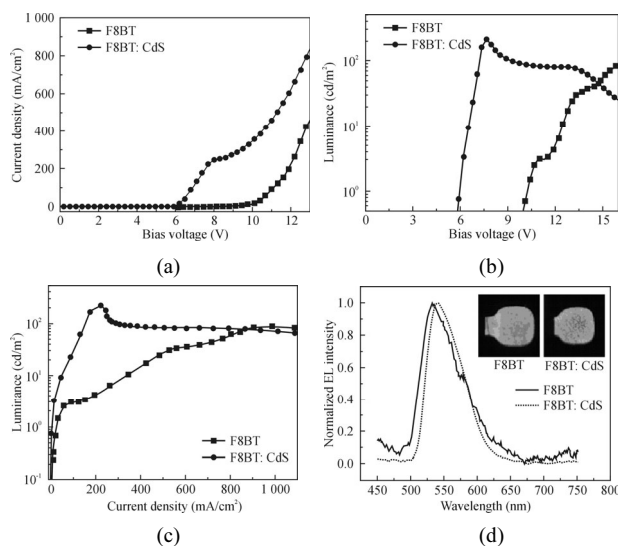
Fig.5 reveals the fluorescence spectra (excited at 390 nm) of F8BT and F8BT:CdS blend with weight ratio of 1.5:1 in toluene. We find the PL peak of F8BT at 529 nm is blue shifted by 9 nm after the addition of CdS nanoparticles along with a slight narrowing of the spectrum by 2 nm. The standard device is similar to the PFO based device, except for the active layer as F8BT. Compared with the effect of nanoparticle on PFO, CdS based F8BT device exhibits better performance than the standard F8BT device. As can be seen from Fig.6(a), the turn on voltage in F8BT:CdS device is drastically reduced to 5.9 V from 10 V in the standard device. Fig.6(b) and (c) show the improved luminance performance of F8BT:CdS device ( $217 \text{ cd/m}^2$ ) compared with the standard device ( $5 \text{ cd/m}^2$ ). This increased luminance is ascribed to the combined EL from the nanoparticles and the polymer. As shown in Fig.6(d), the EL spectrum of hybrid is red shifted by 9 nm from the peak of device only with polymer at 532 nm. The enhancement in color purity is observed by the reduction of *FWHM* of the EL spectra, which is reduced by 11 nm for F8BT:CdS device in comparison with that of the standard device. This change also confirms that F8BT is not the only emissive material in the hybrid device. The red shift observed in EL spectrum (541 nm) of the hybrid device with respect to PL spectrum (520 nm) is attributed to Förster resonance energy transfer and/or Stark effect<sup>[13]</sup>. The photographs of the actual green emission from the devices with F8BT and F8BT:CdS blend as active layers are shown in the inset of Fig.6(d). Fig.7 shows the Commission Internationale de L'Eclairage (CIE) 1931 color chromaticity coordinates of all the devices, which are obtained from the EL spectra.



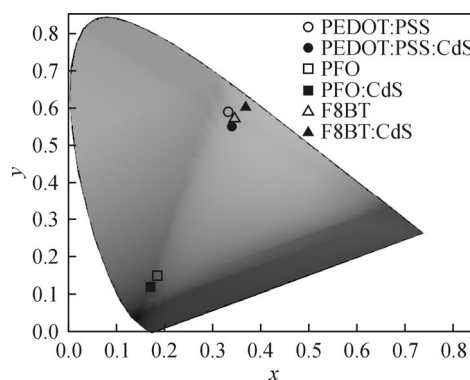
**Fig.5 Absorption spectra and fluorescence spectra of F8BT and F8BT:CdS blend**

In all CdS-based devices, we observe an improvement in turn on voltage. The turn on voltage is reduced by 1 V when the nanoparticles were blended with PEDOT:PSS, by 1.6 V when the nanoparticles were blended with PFO, and by 4.1 V when the nanoparticles were blended with F8BT. Comparing the luminance performances of the devices, we can also perceive that the maximum luminance of CdS doped devices is achieved at lower volt-

ages in comparison with the undoped devices. We see the increased luminance performance in green emitting polymer rather than blue emitting polymer, due to the emission of CdS in the green region. There is no improvement in the luminance of blue emitting PFO devices, while the luminance from CdS doped F8BT devices is increased from  $5 \text{ cd/m}^2$  to  $217 \text{ cd/m}^2$ .



**Fig.6 (a) J-V curves; Luminance performance with respect to (b) bias voltage and (c) current density; (d) EL spectra of devices based on F8BT with and without CdS nanoparticles (Inset in (d) shows the actual photographs of devices with F8BT and F8BT:CdS blend as active layers, respectively.)**



**Fig.7 CIE 1931 color coordinates of devices with PEDOT:PSS, PEDOT:PSS:CdS, PFO, PFO:CdS, F8BT and F8BT:CdS as active layers, respectively**

In summary, we synthesized CdS nanoparticles by precipitation technique, and the CdS nanoparticles were characterized to observe the structural, morphological and optical properties. We further fabricated polymer LEDs and incorporated CdS nanoparticles in their hole transporting layer and emissive layer separately. We observe an improvement of turn on voltage in all nanoparticle-based devices. In addition, the CdS nanoparticles improve the luminance performance of F8BT-based de-

vices compared with that of PFO-based LEDs. However, the luminance is decreased when CdS nanoparticles are blended with PEDOT:PSS. The luminance performance is attributed to the modification of interfacial morphology and the resonant energy transfer between the polymer and the nanoparticles.

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