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Highly efficient orange–red electroluminescence from a single layer MEH-PPV-POSS:$CdS_{0.75}Se_{0.25}$ hybrid PLED

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ABSTRACT

In this study, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] end capped with polyhedral oligomeric silsesquioxanes (MEH-PPV-POSS): cadmium sulfide selenide quantum dots ($CdS_{0.75}Se_{0.25}$ QDs) nanocomposites based OLEDs were fabricated. By the addition of $CdS_{0.75}Se_{0.25}$ QDs into the polymer active layer, a considerable enhancement was observed in terms of hole and electron injection in devices. Additionally, the presence of QDs reduced the interchain interaction of polymer that resulted in narrower electroluminescence (EL) spectrum. The device structure of ITO/PEDOT: PSS/MEH-PPV-POSS: 25 wt% $CdS_{0.75}Se_{0.25}$/Ca (40 nm)/Al demonstrated the best performance with a brightness of 8672 cd/m^2 at 10 V, current efficiency of 2.5 cd/A at 8 V, and an EQE of 0.55% at 150 mA/cm^2.

1. Introduction

Organic light emitting diodes (OLEDs) represent one of the optoelectronic devices that have a great potential on replacement of current technologies in both display and lighting application fields. The use of conjugated polymers as active organic materials in these devices provide many advantages such as simple processing, color variety, low turn-on voltage, light weight, large area, flexibility and low cost [1–5]. However, they still have some fundamental limitations such as, imbalance of hole and electron fluxes due to high electron injection barrier and low electron mobility and formation of aggregates and/or excimers due to the interchain interaction in most of organics. Among the strategies used to overcome these limitations, the addition of quantum dots (QDs) into the polymer matrix would be an attractive approach since the polymer/QD composites have presented highly enhanced optical and electrical properties.

Several groups have reported successful combinations of II–IV semiconductor nanoparticles, such as cadmium selenide (CdSe), cadmium sulfide (CdS) core QDs or cadmium selenide/zinc sulfide (CdSe/ZnS) core/shell QDs with polymers, such as a polymer derivative of 9,9-dioctylfluorene and 2,1,3-benzothiadiazole (PFBT8) or poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV). The improved results by incorporation of conventional binary QDs are summarized in Table 1 [6–11]. In such hybrid system, where electroluminescence originates only from the polymer, QDs enhance a particular property of polymer (not overall optical behavior) by their superior charge carrier mobility and stability. It is also reported that QDs neutralize the defects in the polymer matrix resulting in an enhanced structural stability of polymer [8]. They may act as hole trapping centers that serve to a better balance of charge carriers and cause a decrease in the interchain interaction of the polymer [10].

In general, optical properties of binary QDs can be tuned by controlling their size and composition. In case of the alloyed QDs (i.e. CdSSe) optical properties are tailored not only by size dependent quantum confinement effect but also by controlling composition of the components of alloyed materials [12]. In this study, the precursor of sulfur and selenium along with cadmium are used to obtain colloidal alloy of cadmium sulfide selenide ($CdS_{0.75}Se_{0.25}$) capped with trioctylphosphine oxide (TOPO) as an organic ligand and used as a dopant in a MEH-PPV-POSS based OLED. The advantage of the ternary alloyed QDs are to produce improved optical and electrical properties as well as enhanced device performances due to fine tuning of composition of QDs at a constant size [13]. Nonetheless, to the best of our knowledge, no study to date in literature has reported the incorporation of $CdS_{0.75}Se_{0.25}$ and highly efficient hybrid OLED

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Table 1
The reported efficiencies in the literature for MEH-PPV: QD composite based PLEDs in which the electroluminescence has been obtained from polymer.

Ref. #	Device structure	Brightness [cd/m^2] (V_{appl})	Current efficiency [cd/A] (V_{appl})	EQE [%]	Power efficiency [lm/W]	Operating voltage [V]	FWHM [nm]	$\lambda_{EL\,max}$ [nm]	Active area (mm^2)
[6]	ITO/MEHPPV/Al	6 (9 V)	–	–	–	6	–	590	–
	ITO/MEHPPV: aggregated 10 wt% CdSe/Al	60 (8 V)	–	–	–	5	–	590	–
[7]	ITO/PEDOT: PSS/PFBT8/LiF/Al	–	–	1	–	10	–	~530	–
	ITO/PEDOT: PSS/PFBT8: 5 wt% CdSe/LiF/Al	–	–	>1	–	4	–	~530	–
[8]	ITO/PEDOT: PSS/MEHPPV/Al	~25 (12 V)	<0.005			8		590	4
	ITO/PEDOT: PSS/MEHPPV: 0.4 wt% CdSe (ZnS)/Al	~100 (12 V)	~0.02			7	–	590	4
[9]	ITO/PEDOT: PSS/FP-PPV-co-MEH-PPV/Ca/Al	3949 (10 V)	0.27 (10 V)	–	–	4	–	560	4
	ITO/PEDOT: PSS/FP-PPV-co-MEH-PPV: CdSe (ZnS)/Ca/Al	8192 (7 V)	1.27 (7 V)	–	–	4	–	560	4
[10]	ITO/PEDOT: PSS/MEH-PPV-POSS/Ca/Al	1083 (10 V)	0.63 (8 V)	–	0.14	2.2	87	588	12
	ITO/PEDOT: PSS/MEH-PPV-POSS: 0.3 wt% $CuInS_2$/Ca/Al	2701 (10 V)	0.89 (8 V)	–	0.20	2.1	73	588	12
[11]	ITO/PEDOT: PSS/MEH-PPV/Al	12 (75 mA/cm^2)	–	–	–	13	–	590	–
	ITO/PEDOT: PSS/MEH-PPV: 20 wt% CdSe (ZnS)/Al	290 (75 mA/cm^2)	–	–	–	21	–	> 590	–

devices based on MEH-PPV-POSS: $CdS_{0.75}Se_{0.25}$ nanocomposites (Table 2).

2. Experimental

2.1. Preparation of Se precursor (NaHSe)

Sodium borohydrate ($NaBH_4$, Riedel de Haen) and selenium powder (Aldrich) were mixed in a flask at room temperature and kept under nitrogen atmosphere for a few minutes. And 6 ml of ultra pure water was added into the flask and the solution was refluxed for 1 h to obtain transparent NaHSe solution [14]. According to the reaction presented below, $NaBH_4$ leads to the reduction of selenium.

$$4NaBH_{4(aq)} + 2Se_{(s)} \rightarrow 2NaHSe_{(aq)} + Na_2B_4O_{7(s)} + 14H_{2(g)}$$

Fresh NaHSe solution was used without any purification for each experiment since it can be oxidized easily when exposed to air.

2.2. Synthesis and characterization of ternary alloyed quantum dots

Ternary-alloyed colloidal nanocrystals were synthesized in one step and one-pot based on the two – phase method introduced by Pan et al. for core/shell QDs [15]. In their synthetic pathway, the colloidal CdSe nanocrystals was first prepared and purified, and then in the second-step, thiourea and cadmium myristate were added to the purified CdSe solution to form core–shell CdSe/CdS nanocrystal [15]. We modified the method to synthesize alloyed QDs. The modification applied is the mixing of aqueous solution of NaHSe and thiourea with non-aqueous solution of cadmium myristate and TOPO in one-pot and one-step, forming the ternary-alloyed nanocrystals. The synthesis was briefly described here and the details will be published elsewhere. Cadmium oxide (Alfa Aesar) and myristic acid (Sigma Aldrich) were reacted at 250 °C for 2 h to form cadmium myristate. Cadmium myristate (0.4 g) and 2 g of TOPO were dissolved in toluene (80 ml), and kept at 80 °C. NaHSe (3 mg) and thiourea (60 mg) were dissolved in nitrogen-saturated water (80 ml) and heated to 100 °C for 30 min. Cadmium myristate and surfactant dissolved in toluene at 80 °C was transferred to aqueous solution of NaHSe and thiourea while stirring it. The

Table 2
Performances of hybrid PLEDs with the device structure of ITO/PEDOT: PSS/MEH-PPV-POSS: *x* wt% $CdS_{0.75}Se_{0.25}$/Ca/Al at 1000 cd/m^2.

Dopant amount [*x* wt%]	Voltage [V]	Current density [mA/cm^2]	Current efficiency [cd/A]	EQE [%]	Power efficiency [lm/W]	$\lambda_{EL\,max}$ [nm] at 6 V	FWHM [nm]
0	6.7	96	1.00	0.23	0.43	588	87
5	6.7	92	1.06	0.23	0.49	588	87
10	6.0	85	1.21	0.27	0.63	588	84
15	5.4	72	1.28	0.28	0.75	588	82
25	4.7	67	1.42	0.43	0.92	588	81
50	4.9	204	0.47	0.11	0.30	588	75