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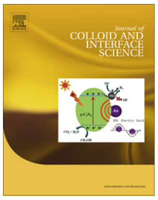

Regular Article

Bright alloy type-II quantum dots and their application to light-emitting diodes

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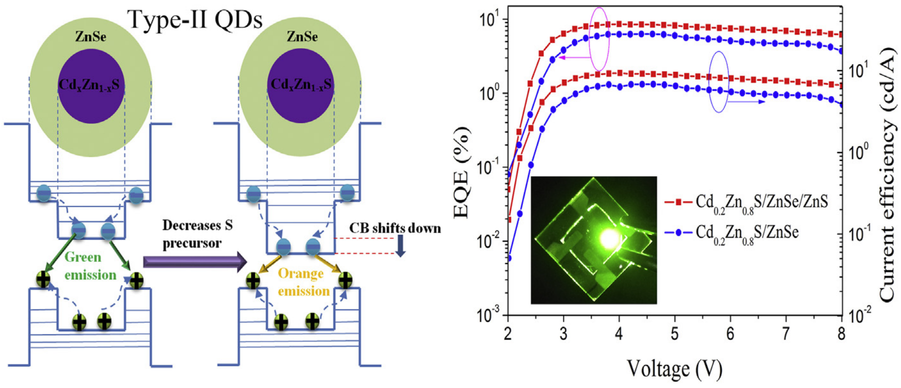
GRAPHICAL ABSTRACT



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ABSTRACT

Type-II quantum dots (QDs) are emerging as a promising candidate for full color light sources owing to their advantages in achieving full color light by tuning the heterostructures. Despite the recent developments in type-II QDs, the choices of proper materials are limited for the composition of a high-quality QD and it still remains a big challenge to enhance the photoluminescence (PL) quantum yields (QYs) of type-II QDs for light-emitting diode (LED) applications. Here, we develop $Cd_xZn_{1-x}S$/ZnSe/ZnS type-II QDs with a maximum quantum yield as high as 88.5%. Time-resolved PL results show that the ZnS shell suppresses non-radiative pathways by passivating the surface of $Cd_xZn_{1-x}S$/ZnSe, thus leading to a high QY. Moreover, our results demonstrate that the outer ZnS also benefits the charge injection and radiative recombinations of the $Cd_xZn_{1-x}S$/ZnSe. The LED based on green $Cd_{0.2}Zn_{0.8}S$/ZnSe/ZnS QDs achieves a current efficiency (CE) of 9.17 cd A^{-1}, an external quantum efficiency (EQE) of 8.78% and a low turn-on voltage of ~2.3 V.

1. Introduction

Colloidal quantum dots (CQDs) have attracted much attention during the past decades [1–8], owing to their excellent optical and electrical properties [9], such as good optical stability, large

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absorption cross-section, tunable emission ranges [9] and high emission efficiency [10]. Among these, core/shell systems, especially type-I quantum dots (QDs) are of great interest, because they have demonstrated high light emission efficiencies. Usually the shell materials can act as a passivating layer to reduce redundant dangling bonds at the surface. Despite the rapid development of the type-I QDs, prolific and closely spaced hole bound states stands still near the valence band (VB) for type-I QDs, which facilitates the non-radiative recombination, thus leading to a voltage degradation of solar cells or emission decrease of quantum dot light emitting diodes (LEDs). However, type-II QDs may provide a new material of choice to overcome this obstacle [11–14]. Type-II QD is a core-shell hetero-nanocrystal that combines two semiconductor materials with staggered band alignment between the core and the shell [15]. In this architecture, the electrons and holes are spatially separated, i.e., the electrons are confined in the core and the holes are confined in the shell or vice versa. In principle, the hole bound states can be greatly inhibited in type-II QD, owing to its intrinsic staggered energy alignment.

The band energies of type-II QDs depend on energy level offsets between the core and the shell [16]. Therefore, it allows one to access to band gaps that would otherwise not be available with a single material, by which researchers have well interpreted the infrared radiation of CdSe/ZnTe QDs far beyond the band gap energies of the two constituents CdSe and ZnTe. The extended absorptions with tunable fluorescent wavelengths of type-II QDs provide new potential to the LEDs. Furthermore, their extremely long excited carrier lifetimes are also important to the biological imaging and solar cell applications [17]. However, a critical issue faced by current type-II QDs is that their photoluminescence (PL) QYs are still quite low, thus restricting their further applications in optoelectronics. Currently, most of the type-II QD systems are Cd(Zn)-chalcogenide based binary type-II systems and their emission efficiencies are fairly low [12–14,18]. Although recent progress reveals that a ZnS passivating shell is capable of enhancing the PLQY (~61%) of ZnSe/CdS type-II QD, it remains a challenging task to increase PLQY further as compared to those well-developed type-I QDs [18]. Unlike type-I QDs whose band gaps are solely determined by the core, the band gaps of type-II QDs are determined by the energy level difference between the core and the shell. Therefore, the intrinsic core-shell component, especially the interface between the core and shell is of great importance in designing robust type-II structures. In fact, defect states may be formed when a shell is coated onto a core, possibly owing to the lattice strain. These defect states provide more channels for non-radiative relaxation that quenches the fluorescence. According to some publications on type-I systems, an alloy hetero-structured interface between the core and the shell may prevent defect formation, because the lattice strain is relaxed in the continuous composition gradient [19–21].

In this work, we employ an alloy interface $Cd_xZn_{1-x}S/ZnSe$ to construct a type-II system for the first time. With the continuous composition gradient at the interface of $Cd_xZn_{1-x}S$ and ZnSe, defect states originated from lattice mismatch of the two constituents are expected to be diminished, thus providing potential for a high luminescent efficiency. Besides, theoretical and experimental results reveal that $Cd_xZn_{1-x}S$ ($x < 0.3$) has a band gap of ~3.0 eV which is higher than that of ZnSe 2.8 eV. The conduction band edge of $Cd_xZn_{1-x}S$ core and ZnSe shell are about −3.6 eV and −2.8 eV, while their valence band are −6.6 eV and −5.7 eV, respectively [22,23]. When $Cd_xZn_{1-x}S$ and ZnSe are combined together, their energy levels are staggered to each other, and therefore one can expect the type-II behaviors of $Cd_xZn_{1-x}S/ZnSe$.

Herein, we report one-pot synthesis route for the bright $Cd_{1-x}Zn_xS/ZnSe$ based on a recent study by Lee et al. [21], but with substantial improvements. Cadmium stearate ($CdSt_2$) and Zinc stearate ($ZnSt_2$) were synthesized to reduce surface defects. Furthermore, a ZnS shelling process is introduced to passivate $Cd_{1-x}Zn_xS/ZnSe$. The resultant green-emitting, chemical composition gradient-shell $Cd_{0.2}Zn_{0.8}S/ZnSe/ZnS$ QDs show a remarkable PLQY (over 88.5%) which is the highest reported value in type-II QDs to our best knowledge. Electroluminescent devices are fabricated based on the $Cd_{0.2}Zn_{0.8}S/ZnSe$ and $Cd_{0.2}Zn_{0.8}S/ZnSe/ZnS$ QDs. Highly color-saturated green $Cd_{0.2}Zn_{0.8}S/ZnSe/ZnS$ LED displays a low turn-on voltage of ~2.3 V together with a maximum EQE of 8.78%, indicating the great potentials of this type-II QDs. This one-pot synthesis procedure simply produces high quality and scalable CQDs in a short time, which is of great importance for commercialisation.

2. Experimental

2.1. Materials

Stearate acid (HSt, 97%), tetramethylammonium hydroxide (TMAH, 97%), sulfur powder (S, 99.5%), cadmium acetate dihydrate ($CdAc_2 \cdot 2H_2O$, 99%), 1-octadecene (ODE, 90%), selenium (Se, 99%), zinc acetate ($ZnAc_2$, 99%), tributylphosphine(TBP, 98%), poly-(ethy lenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, 1.3 wt% dispersion in H_2O), 1-Dodecanethiol (DDT, >98%) and dimethyl sulfoxide (DMSO, 98%) were purchased from Sigma-Aldrich. Poly(N, N′-bis(4-butylphenyl)-N, N′-bis(phenyl)benzidine) (poly-TPD) was purchased from Xi 'an Polymer Light Technology Corp. Toluene (98%), ethanol (99.7%), and hexane (95%) were purchased from Sinopharm Reagents.

2.2. Synthesis of cadmium stearate ($CdSt_2$) and zinc stearate ($ZnSt_2$)

$CdSt_2$ powers were synthesized according to the previously reported method [24]. In details, HSt (20 mmol) was neutralized with TMAH (20 mmol) in methanol (200 mL) by stirring. $CdAc_2 \cdot 2H_2O$ (10 mmol) dissolved in methanol (50 mL) was added dropwise to this solution under vigorous stirring. The mixture was then stirred for 20 min after finishing the dropping process to ensure complete reaction. The formation of a white precipitate indicated the formation of $CdSt_2$. Subsequently, the precipitate was collected by filtration, washed twice with methanol, and then dried under vacuum at room temperature overnight before use. The synthesis of $ZnSt_2$ was similar to the synthesis of $CdSt_2$, where the $CdAc_2 \cdot t2H_2O$ was replaced by $ZnAc_2$.

2.3. One-pot synthesis $CdxZn_{1-x}S/ZnSe/ZnS$

0.5 mmol of $CdSt_2$, 5 mmol of $ZnSt_2$ and 8 ml of 1-ODE were placed in a 100 ml round flask. The mixture was heated to 150 °C, degassed under 100 mtorr pressures for 60 minunder Ar_2 gas, then rapidly heated to 300 °C to form an optically clear mixture solution. At this temperature, 0.5 M (1 ml) of S powder dissolved in 1-ODE were quickly injected into the reaction flask. After the first injection of S precursors, the temperature of the reaction flask was elevated to 310 °C for further growth of $Cd_xZn_{1-x}S$ cores. After 5 min of reaction, 1 mmol of Se powder dissolved in 1 ml of Tributylphosphine (Se-TBP) and diluted by 2 ml 1-ODE. The Se precursors were dropwised at a rate of 3 mL/hr into the reactor to overcoat the existing $Cd_xZn_{1-x}S$ cores with ZnSe shells without any purification steps. After 20 min of ZnSe shell formation reaction at the elevated temperature, 1.2 M DDT were dropwised at a rate of 1 mL/hr into the reactor to form the ZnS shell on $Cd_xZn_{1-x}S/ZnSe$. The reaction was preceded for 30 min to form the ZnS shell, and then cooled down to room temperature to complete the reaction.