Highly Efficient Green Quantum Dot Light-Emitting Diodes with Surface-treated Indium Phosphide

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ABSTRACT

The multi-shelled green InP QDs were synthesized by using the phosphorus source of $(DMA)_3P$ and the narrow FWHM of 46nm was obtained. The PLQY of 64% was achieved after the surface treatment and the maximum quantum efficiency of 2.68% and current efficiency of 7.7 cd/A were achieved for quantum dot light emitting diodes.

1 INTRODUCTION

Cadmium(Cd)–free quantum dots (QDs) have been shown great potential for real commercialization quantum dot light emitting diodes (QLEDs) due to the low-toxicity, tunable band gap through size controlling, and excellent photoelectric properties. Especially, Indium phosphide (InP)-based QDs are considered as one of promising alternative to Cd-based QDs and have been widely studied for QLEDs. For the common synthesis of InP QDs, there are two kinds of phosphorus sources which includes tris(trimethylsilyl)phosphine($(TMS)_3P$)[1, 2] and tris (di - methylamino)phosphine ($(DMA)_3P$)[3]. However, the ($(TMS)_3P$) is not only super expensive material but also dangerous to store.

In this study, we modified the synthesis method[3] and precursors[4] by using friendly phosphorus source of $(DMA)_3P$ and got the multi-shelled efficient green InP QDs which were employed for electroluminescent QLED. The raw InP QDs have many defects on the surface which can cause nonradiative recombination, oxidative degradation in the ambient environment. The surface passivation process is an effective way to enhance the stability of raw InP QDs. Therefore, the surface treatment of multi-shelled green InP QDs was applied. As a result of surface-treated strategy, the green InP@ZnSeS/ZnS QDs with a QY of 64% were obtained, achieving a maximum external quantum efficiency and the current efficiency of 2.68% and 7.7cd/A for all-solution-process electroluminescent device, respectively.

2 EXPERIMENT

2.1 Synthesis of InP@ZnSeS/ZnS green QDs

Indium chloride ($InCl_3$, 98%), zinc iodide (ZnI_2, 98%), zinc stearate (purum, 10-12%), zinc acetate ($Zn(OAc)_2$, 99.99%), sulfur (S, 99.9%), selenium (Se, 99.9%), tris(dimethylamino)phosphine((DMA_3)P), 97%) oleylamine(OAm, 70%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Sigma-Aldrich. Green InP/ZnSeS/ZnS QDs were synthesized by modifying the literature methods.[3, 4] 0.45 mmol of indium chloride, 2.2 mmol of zinc iodide and 6 ml of oleylamine were stirred in a 50 ml three-necked flask and degassed at 120 °C for 60 min, and then heated to 170 °C under N_2 flow. Subsequently, 0.35 ml of tris(dimethyl - amino)phosphine ($(DMA)_3P$) was injected to the flasks and reacted for 10min to form InP core QDs. For growing ZnSeS intermediate shell, alternative injection of anionic and cationic shell precursors was repeated and similar with the literature methods. For the ZnS outer shell, 5 ml of 1-dodecanethiol was introduced and reacted at 220 °C for 60 min, and then another Zn stock solution of Zn acetate (3 mmol) in oleic acid (3 ml), was injected and reacted at 190 °C for 2 h. After that, the final raw InP QDs were purified with hexane and excess anhydrous ethanol to remove excess ligands and precursors by centrifugation. Finally, the raw InP@ZnSeS/ZnS QDs were dispersed in toluene for surface treatment. The surface-treated solution were stirred in N_2 condition for 13h. Then, the mixture solution was precipitated with excess anhydrous ethanol by centrifugation and redissolved in octane for further use.

2.2 Device Fabrication

The conventional device of QLEDs were fabricated by the following layer structure of ITO/ PEDOT: PSS / TFB/ green InP QDs/ ZnMgO/ Al. ITO-coated glass substrates were cleaned in organic solvents of acetone and methanol for 15 min each by ultrasonication and dried in an oven at 100 °C. Then the cleaned ITO glass was treated with an ultraviolet light for 15 min by UV-ozone treatment. The HIL of PEDOT:PSS was spin coated on the ITO at 3000 rpm for 30 s, followed by annealing at 140 °C for 15 min. The TFB was spin coated as a hole transport layer (HTL) on the substrate in a nitrogen-filled glove box. Subsequently, the emission layer of green InP QDs in octane was spin coated on the surface of TFB film to form the emission region of the QLEDs. The ZnMgO nanoparticle as the ETL was spin coated on the emitting layer. Finally, the device was transferred into a

vacuum chamber of thermal evaporation and Al was thermally deposited.

2.3 Characterization

UV−vis absorption (V-630, JASCO) and PL emission spectra (G9803AA, Agilent Technologies) was performed, respectively. The fluorescent quantum yield (QE-2100, Otsuka Electronics Co., Ltd) was applied. Transmission electron microscope (TEM) (120 kV, JEM ARM 200F) was used to figure out size distribution. TRPL were measured using a fluorescence lifetime spectrometer (Quantaurus-TauC11367-12,HAMAMATSU). Luminescence (L) - current (I) – voltage (V) characteristics were handled in a source measurement unit (2400, Keithley Instruments, Inc.) and a luminance meter (CS-2000, Konica Minolta Sensing, Inc.).

3 RESULTS

The transmission electron microscopy (TEM) images of raw QD and surface-treated QD are shown in Figure 1 and 2, respectively. Two kinds of InP QDs show the similar particle size with the average of 7.0 nm and 7.2 nm for raw QD and surface-treated QD, respectively. The UV-vis and photoluminescence (PL) spectrum of raw QDs and DDAB-treated QDs were measured as shown in Figure 3. The adsorption and PL peaks of raw QDs are located at 478nm and 518nm and the FWHM is narrow as 46nm. While the PL spectrum of surface-treated QDs is red-shifted to 520nm with the quantum yield of 64%. In addition, the PL decay curves (Figure 4) shows the average lifetimes (τ_{avg}) of the raw QDs and surface-treated with 31.5 and 35.5 ns, respectively. It means the non-radiative Auger recombination is suppressed by the process of surface treatment. We were able to use the raw QDs and surface-treated QDs in green QLEDs with a conventional device structure. As we can see in Figure 5, showing the current density and luminance curves as a function of applied voltage for the QLEDs. The maximum luminance of raw QDs based device performance reached to 641 cd/m^2. After the surface treatment, the the maximum luminance of 1065 cd/m^2 was achieved. In addition, the maximum quantum efficiency (EQE) reached to 2.68% by using the surface-treated QDs.

4 DISCUSSION

This is the first time by using the phosphorus source of $(DMA)_3P$ to get the high efficiency green InP-based electroluminescent device which the maximum quantum efficiency and the current efficiency were 2.68% and 7.7 cd/A. Moreover, the maximum luminance is over 1000 cd/m^2. For the further work, we will modify the device structure and get higher device performance for green InP-based QLEDs.

5 CONCLUSIONS

The multi-shelled green InP QD with modified method was reported for this work. The raw multi-shelled InP QDs were synthesized by using the phosphorus source of $(DMA)_3P$ and the narrow FWHM of 46nm was obtained. Furthermore, the surface passivation process was applied to improve the stability of raw QDs and then enhance device performance. After the surface treatment of raw multi-shelled InP QD, the PLQY was improved to 64%. Fabricated green InP based QLED devices of all-solution-process by using surface-treated QDs as emitting layer achieved the maximum luminance of 1065 cd/m^2. In addition, the maximum quantum efficiency and current efficiency were achieved to 2.68% and 7.7 cd/A for electroluminescent device, respectively. The results suggest that the fluorescence of green InP QDs has a great potential for practical commercialization applications in QLED.

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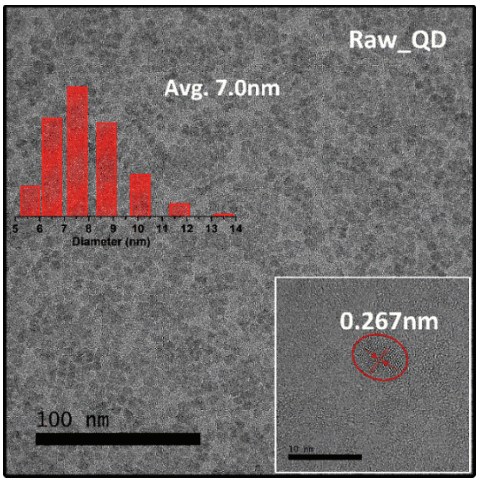

Fig. 1 High-resolution (HR) transmission electron microscopy (TEM) image of raw QD

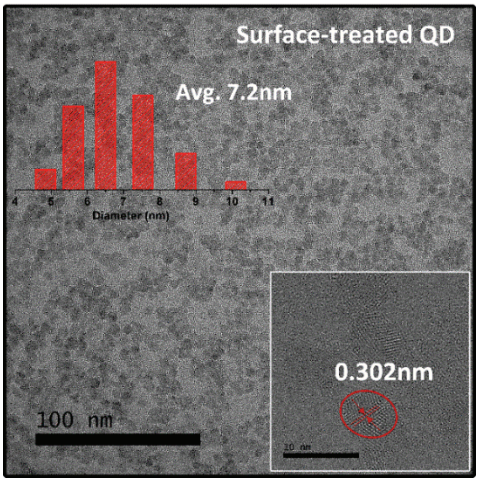

Fig. 2 High-resolution (HR) transmission electron microscopy (TEM) image of surface-treated QD

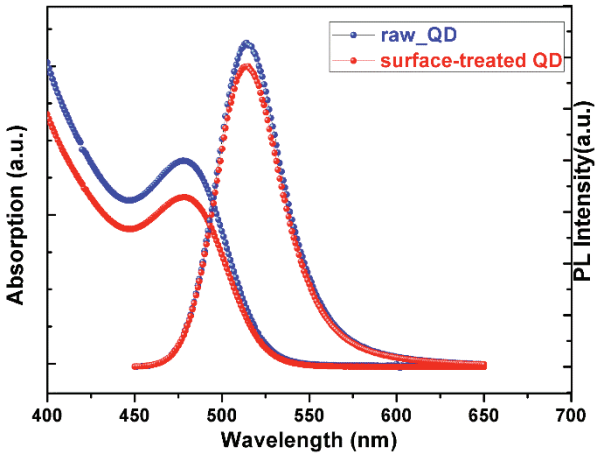

Fig. 3 The UV–vis absorption and photoluminescent (PL) spectra of of raw QD and surface-treated QD

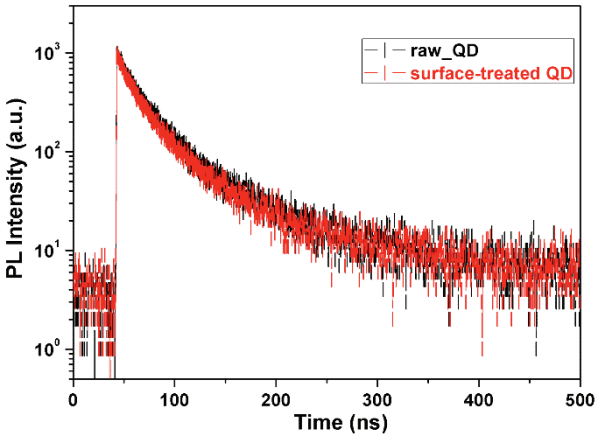

Fig. 4 Time-resolved photoluminescence (TRPL) decay curves of raw QD and surface-treated QD

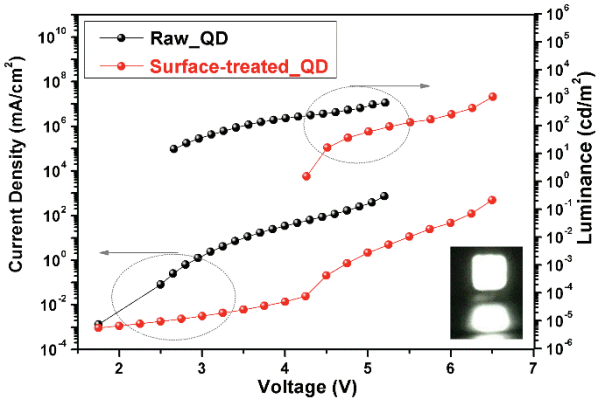

Fig. 5 The current density and luminance curves as a function of applied voltage of raw QD and surface-treated QD. (The inset is the color photograph of green emissions.)