Electroluminescence of Metal Free Quantum Dots

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ABSTRACT
Here we report some of our first studies on the synthesis and characterisation of metal free luminescent nanomaterials, their optical properties and incorporation into functional electroluminescent devices.

1 Introduction

In modern electronics light-emitting diodes (LEDs) are widely used. They have brought a revolution in the fields of lighting and displays due to their improved contrast, higher current-to-light efficiency, and larger color space than conventional liquid-crystal displays. In the last two decades quantum dots and perovskite nanocrystal-based LEDs have aroused extensive attention worldwide. Great accomplishments on this kind of high-performance device have been achieved.[1-4] Heavy-metal (such as Cd^{2+} and Pb^{2+}) based devices could be viewed unfavorably due to toxicity of these metals, they can have low-stability, and high-cost problems. These problems have seriously hindered their further developments and practical uses in consumer markets. Therefore, development of non-toxic luminescent materials that can be employed in LED devices with greater safety for the environment and human health and good stability is urgently needed.

In recent years fluorescent carbon dots (CDs) have emerged as new luminescent materials with significant potential on account of their photoluminescence properties, high stability, and low toxicity. The application of organic based material in electroluminescent light-emitting diodes (LEDs) have provoked interest in recent years.[5]

Generally, CDs are constituted of abundant organic elements like carbon, hydrogen, nitrogen, and oxygen and are free from heavy metals. Due to size, surface and edge effect CDs own unique color-tunable photoluminescence (PL) emission property. The accidental discovery of CDs during the purification of single-walled carbon nanotubes can be traced back to 2004, by Xu et al.[6] They were named as CDs in 2006, by Sun et al.[7] when they achieved luminescent carbon nanoparticles via laser ablation.

With the development of methods for rapid and high-quality CDs in recent years, studies on CD-based LEDs have drawn the attention of researchers. CD-based LEDs can be prepared by two general strategies: CDs as phosphors and CDs as active emitters.

The optimal device performance of phosphor-based LEDs has already reached the standard of practical application.

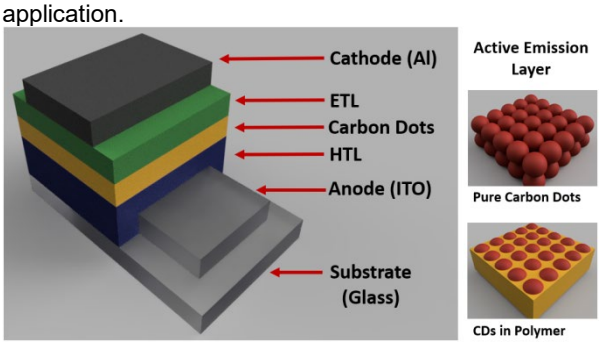

Figure 1. A typical device structure of CD-based electroluminescent LEDs.[8]

However, this approach is dependent on the intrinsic quality of the LED chips. Besides, this kind of LED merely utilises the PL properties of the CDs. Actually, by employing CDs as an emissive layer in electroluminescent LEDs is the most promising application for flat-panel displays. In our current work we are exploring the emissive property of CD's for OLED applications.

2 Experimental

2.1 Synthesis of Carbon Dots

CDs were synthesized following the methods according to the published procedures.[9]

2.2 Electroluminescent Device Fabrication

First, ITO-coated substrates were scrubbed by a cleanser, and sonicated with deionized water, acetone twice and isoproanol for 20 min, separately. Then, to decompose the residual organic solvents on the ITO surface and improve the work function of ITO, the ITO was oxidized using a UV lamp with ozone for 10 min. Second, a PEDOT:PSS film (50 nm) was spin-coated on the ITO surface and dried at 150 °C for 15 min in air. After cooling to room temperature, the ITO-coated substrates were transferred into a nitrogen glovebox ($O_2 \leq 1$ ppm, $H_2O \leq 1$ ppm). Subsequently, the emitting layer of PVK:CDs was spin-coated on the top of the hole injection layer and baked at 80 °C for 40 min. Finally, the ITO-coated substrates were loaded into a thermal evaporator for the deposition of the electron transport layer TPBi or

TmPyPB, the electron injection layer LiF, and the cathode Al layer in a vacuum of less than 5×10^{-4} Pa. The effective area of the luminous layer is 3 mm × 3 mm. All the measurements were performed at room temperature in a dark room, without packaging the devices.

2.3 Optical Measurements

The Quantum yield (QY) was measured on a Horiba Jobin Yvon Fluorolog-3. The photoluminescence (PL) spectra were measured using a Jeti 1201 spectroradiometer under 366 nm excitation.

3 Result and Discussion

3.1 Optical properties of CDs

To explore the optical properties of the CDs, photoluminescence emission (PL) were investigated. The PL spectra of the CDs show the emission peak at 526 and 584 nm (Fig. 2). The CDs exhibit excitation-dependent PL, which is probably related to the various energy level structures caused by the nonuniform surface states of the CDs. PL centers correspond to the surface states of CDs.[7] Thus, the CDs with multiple PL centers could be excited by different excitation energies to give different PL.[8, 10]

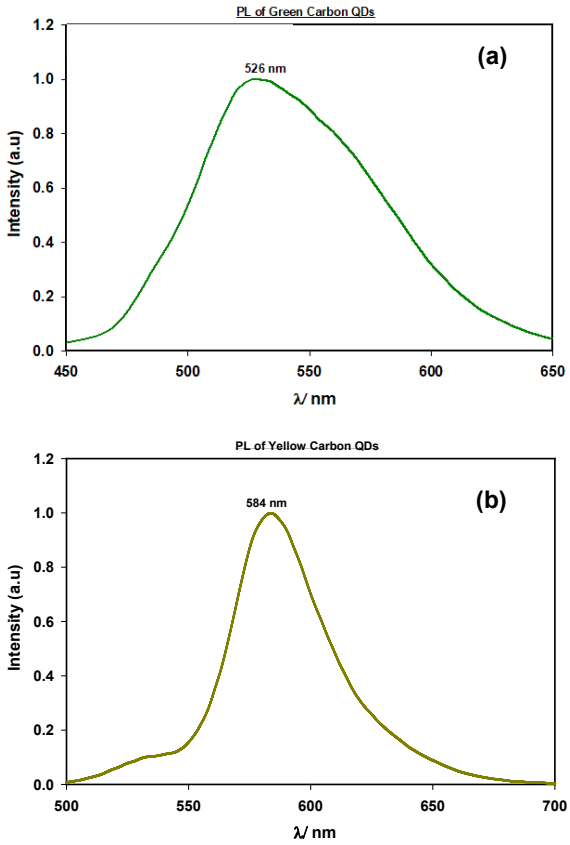

Figure 2. (a) PL spectrum of green CD's (b) PL spectrum of yellow CD's

3.2 Quantum Yields of CD's:

The QY of the CD toluene solution was measured using internal reference (0.1 mol L^{-1} in dilute H_2SO_4) as the standard. A series of standard and CD solutions with different absorption intensity values were prepared. To reduce the reabsorption effect, the absorption value of the solution should be less than 0.1, the PL spectra were then recorded. The integrated PL intensity is the area under the PL spectra curve from 380 to 700 nm. The linear fitting lines of the integrated emission intensity against the absorbance were plotted. Finally, the QY was calculated using equation (1)

$$Q = Q_{st} \times \frac{K}{K_{st}} \times \left(\frac{n}{n_{st}}\right)^2 \quad (1)$$

where Q is the QY, K refers to the slope of the linear fitting lines of the integrated emission intensity against the absorbance, n is the refractive index of the solvent, and the subscript "st" means the standard sample.[11] The QY results are presented in Table 1.

Table 1. The quantum yields of the CD samples

Sample	Quantum yield (%)
Green	6.70 ± 0.17
Yellow	3.73 ± 0.22

3.3. CD-LED Device Performance

Shown in Figure 3 and 4 are the OLED/CD devices in operation. In Table 2 are the results of the device performance.

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Table 2. CD-LED device performance results.

CQD	CIE (x,y)	V/V	Max. Current Efficiency /CdA	Max. Power Efficiency lm/W
Green	(0.278, 0.184)	9.1	0.002	0.001
Yellow	(0.299, 0.363)	8.4	0.8	0.3

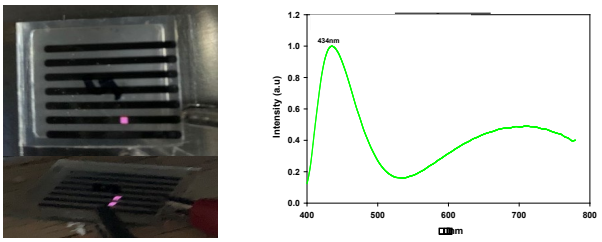

Figure 3. Green Carbon QD Device (a) Illuminated device and (b) Electro-luminescence spectrum

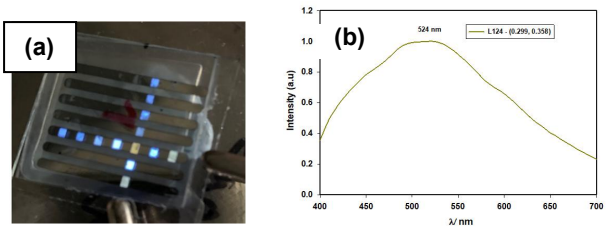

Figure 4. Yellow Carbon QD Device (a) Illuminated device and (b) Electro-luminescence spectrum.

4. Conclusion

CD-LED devices were prepared in a process combining pre-fabricated ITO coated substrate, solution processing (spin coating) of PEDOT:PSS and PVK:CDs, and vacuum thermal evaporation of TPBi or TmPyPB, LiF and Al. Measurements of CD-LED optical performance were made establishing maximum current efficiencies of 0.002 cd/A for Green and 0.9 cd/A for Yellow. It is anticipated that optimizing CD properties and layer thickness will increase both device efficiency and colour gamut.

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