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Excellent luminescence films of excitation-independent carbon quantum dots toward non-rare-earth phosphor-based white light-emitting diodes

Haobo Gao [a], Daqin Chen [a, b, *], Gaoliang Fang [a], Shuo Yuan [a], Xiao Chen [a], Jiasong Zhong [a]

[a] College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, PR China
[b] College of Physics and Energy, Fujian Normal University, Fuzhou, Fujian, 350117, PR China

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ABSTRACT

Currently, fluorescent carbon quantum dots have been extensively studied for their promising application in solid-state lighting. However, most of the reported carbon quantum dots exhibit short-wavelength blue-green emissions and the obtained carbon solid powders usually show weak luminescence due to aggregation-induced emissive quenching. In this work, carbon quantum dots with excitation wavelength independent yellow emission were synthesized by a facile and green hydrothermal route using water as solvent and o-phenylenediamine as carbon source. Structural and spectroscopic characterizations evidenced that N-related defect state was responsible for yellow luminescence. Importantly, the carbon quantum dots embedded solid films were successfully prepared, which exhibited strong blue light absorption and retained intense yellow emission. As a proof-of-concept experiment, carbon polymer monolith was demonstrated to be an alternative to traditional Ce: $Y_3Al_5O_{12}$ phosphors as color converter for constructing white light-emitting diode device with improved color rendering index and correlated color temperature.

1. Introduction

Benefited from low electric consumption, high brightness and long lifetime, the application of white light-emitting diodes (wLEDs) has led to significant advances in lighting technology [1–4]. Currently, commercial wLEDs are mainly made of blue-emitting InGaN chip with a yellow phosphor Ce^{3+}: $Y_3Al_5O_{12}$ (Ce: YAG) [3]. However, this strategy suffers from the shortage of red spectral component of Ce: YAG phosphor and the abundant usage of scarce rare-earth resources [5]. Therefore, developing the alternative phosphor converters that are inexpensive and simple to prepare is highly desirable.

Fluorescent carbon quantum dots (CDs) represent a new class of nanomaterials showing great merits in terms of facile synthesis, non-toxicity, low-cost and superior optical performance [6–10]. So far, many kinds of CDs have been reported, but most of them exhibit dominant emissions at the blue-green region [11], which limits their practical applications. Therefore, it is a huge challenge to fabricate CDs with intense long-wavelength emission [12–16]. Additionally, compared to the CDs dispersed in solution, carbon solid-state powders exhibit low photoluminescence quantum yield (PLQY) owing to the effect of aggregation-induced emission quenching [17–21]. As a consequence, there are few reports on CDs-based wLEDs so far, where only pure CD powders or films are used as color converters [22,23]. In the present work, we have successfully prepared long-wavelength emitting yellow CDs (Y-CDs) through a facile hydrothermal route using water as solvent and o-phenylenediamine (oPD) as carbon source. The obtained CDs show an excitation-independent luminescence and can be easily converted into CD films as color converters to apply in solid-state lighting.

2. Experimental section

Synthesis of Y-CDs. 250 mg oPD was first dissolved in 10 mL ultrapure water and stirred to form a transparent solution. Then the solution was transferred into a 25 mL Teflon-lined stainless-steel autoclave. After heating at 180 °C in an oven for 2 h and cooling to room temperate naturally, yellow suspensions were achieved.

* Corresponding author. College of Materials & Environmental Engineering, Hangzhou Dianzi University, Hangzhou, 310018, PR China.
E-mail address: dqchen@hdu.edu.cn (D. Chen).

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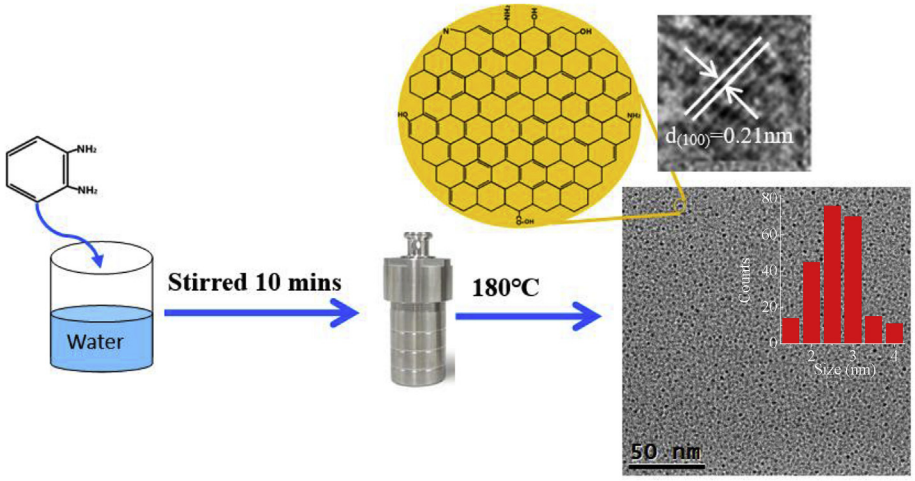

Fig. 1. Schematic illustration of the synthesizing procedure for the Y-CD sample, the proposed structural model and the corresponding TEM, HRTEM images and histogram of size distribution of the as-prepared CDs.

Finally, the solution was purified by the 0.45 μm dialysis membrane and transferred into a vacuum freeze drier for drying 2 days to obtain carbon solid powders.

Preparation of CD Films. A slightly modified procedure reported by Yu et al. was adopted to prepare the Y-CD film [24]. Firstly, a selected Polyvinyl alcohol (PVA) of 2.0 g was mixed with 10 mL of water solution (Y-CD contents: 0.1–0.4 mg/mL) and stirred for 30 min. Then the resulting mixture was transferred into a clean glass substrate and naturally dried for 3 days under room temperature to get a solid composite film monolith.

Construction of Y-CD-Based wLEDs. wLED devices were constructed by directly coupling the as-fabricated Y-CD films with different thicknesses on the InGaN blue chip. Opaque silica gels were filled around the edges of the devices in order to avoid the leakage of blue light.

Characterization. Microstructure observation was performed on a JEOL JEM-2010 transmission electron microscope (TEM) at 200 kV accelerating voltage. Topographic image of the as-prepared CDs was obtained using an atomic force microscope (AFM, Agilent 5500). The actual compositions of CD samples were determined by X-ray photoelectron spectroscopy (XPS) using a VG Scientific ESCA Lab Mark II spectrometer equipped with two ultra-high-vacuum 6 chambers. All the binding energies were referenced to the C1s peak of the surface adventitious carbon at 284.6 eV. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 FTIR spectrometer in the range 400–4000 cm^{-1} using the KBr pellet technique. Raman spectra were recorded on a microscopic confocal Raman spectrometer (Renishaw Trade Co., Ltd., England) under the excitation of a 633 nm laser. Absorption and emission spectra were recorded on an Edinburgh Instruments (EI) FS5 spectrofluorometer equipped with continuous (150 W) and pulsed xenon lamps. Excitation-emission mappings of Y-CDs were recorded by continuously changing the excitation wavelength with a fixed step of 1 nm, and the offset between excitation wavelength and emission was set at 30 nm to reduce scattering light. Absolute photoluminescence quantum yield (PLQY), defined as the ratio of emitted photons to absorbed ones, was determined by a spectrofluorometer (FS5) equipped with an integrating sphere. Time-resolved spectra of Y-CDs were performed on a fluorescent lifetime spectrometer (LifeSpec-II, EI) based on a time-correlated single-photon-counting technique under the excitation of 375 nm picoseconds laser. Electroluminescence spectra, Commission Internationale de L'Eclairage

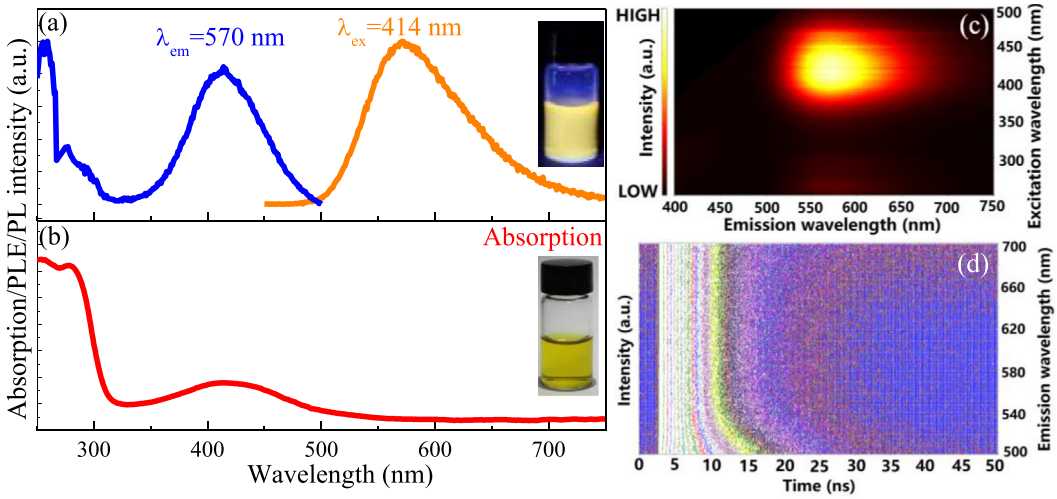

Fig. 2. (a) PLE/PL spectra and (b) absorption spectrum of Y-CDs dispersed in aqueous solution. Insets are the corresponding solution and luminescent photographs under UV lamp excitation. (c) Two-dimensional excitation-emission mapping and (d) contour plot of time-resolved data for the corresponding sample.