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Yellow emissive carbon dots with quantum yield up to 68.6% from the solvent and manganese ions

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ABSTRACT

The development of high quantum yield (QY) carbon dots (CDs) is a key requirement for applications. However, how to engineer well-defined absorption band in visible region is a critical challenge to obtaining highly efficient long wavelength emissive CDs. In this work, the strategies of solvent-tuning absorption band and manganese ions-enhancing optical performance are introduced to prepare yellow emissive CDs. The utilization of toluene as solvent is a basis for achieving absorption band at 435 nm and realizing yellow emissive CDs with QY of 46%. Addition of manganese ions increase the degree of conjugated sp^2-domians and surface states, further enhancing QY up to 68.6%. Using the yellow emissive CDs, a UV-pumped light-emitting diode (LED) was fabricated based on a 395 nm LED chip. The LED shows warm light with correlated color temperature (CCT) of 1596 K and color purity of 99%. This work provides a new insight for the development of high-quality CDs with versatile properties in pursuit of promising applications.

1. Introduction

Carbon dots (CDs), one of the most important carbon-based fluorescent nanomaterials, have received extensive attention due to their advantages such as tunable emission, photostability, environment friendliness and low-cost [1–3]. Owing to these merits, CDs can be used in many promising applications, such as fluorescent probes [4,5], bio-medicine [6,7] and optoelectronic devices [8,9]. Quantum yield (QY) is one of pivotal criterions to evaluate optical performance of CDs. High QY is the key requirement for implementing CDs in nearly all applications [10–12]. As a result of great studies have been devoted to improve the properties of CDs, high QYs of blue and green emissive CDs have been obtained [13,14]. In contrast, achievement of highly efficient long wavelength emissive CDs in yellow or red light region is rather challenging due to the lack of effective synthetic methods for fabricating high-quality CDs with well-defined visible absorption band. These drawbacks must greatly hamper their wide spread utilization and studies, because many applications are particularly in favorable of long wavelength emissive CDs. The yellow or red emission light is an indispensable component for generating white light in lighting devices [15,16], and efficient long wavelength emissive CDs have promising prospect for biological applications [17–20]. One of useful approaches to overcome this problem is developing a simple method for preparation of highly efficient yellow emissive carbon dots with visible excitonic absorption band.

So far, few reports have been reported for synthesizing yellow emissive carbon dots. The as-prepared CDs, one component of multicolor CDs, were synthesized from hydrothermal method or heating treatment with acid or reductant to control surface states, and subsequent separation techniques, such as silica column chromatography or molecular weight ultrafiltration, require sophisticated operations. However, the highest QY of the as-prepared CDs is 27.57% [21,22]. Although the fluorescence mechanism of the CDs is still blur, it is found that high efficient emission is directly determined by well-defined absorption peak, and emission color is determined by the absorption peak wavelength [23,24]. Similar to optical properties of the CDs with QY up to 50% [25,26], yellow emissive CDs synthesized from different organic solvents by Lin and Chen groups displayed characteristic absorption peak and an excitation-independent emission peak in the spectra, with respectable QYs of 32.2% and 46%, respectively [27,28]. However, various ingredients can hardly provide a clear guidance on how to engineer absorption band for achieving efficient yellow emissive CDs.

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In this work, we demonstrate solvent-tuning absorption band strategy. We have obtained high-quality yellow emissive CDs with QY up to 46% based on toluene solvent from solvothermal treatment of citric acid and urea. Further addition of manganese ions promoted increased conjugated sp^2-domains and surface states. Finally, QY of the yellow emissive CDs were further enhanced to 68.6%. Using yellow emissive CDs as a single conversion layer, we have fabricated a UV-pumped light-emitting diode (LED). The LED displayed a correlated color temperature (CCT) of 1596 K, commission internationale d'Éclairage (CIE) coordinate (0.5860, 0.4129) and color purity of 99%, which provides a potential healthy lighting for retinal protection because it staves off strong blue spike of light [29].

2. Experimental section

2.1. Materials

All chemical reagents were analytical grade without further purification. Citric acid monohydrate, *N,N*-dimethylformamide (DMF), ethanol and toluene were purchased from Beijing Chemical Work. Urea and dimethylsulfoxide (DMSO) were purchased from Xilong Chemical Reagent Co., Ltd. Manganese acetate tetrahydrate, zinc acetate dihydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. Copper acetate tetrahydrate and poly (methyl methacrylate) were purchased from Aladdin Chemical Reagent Co., Ltd.

2.2. Synthesis of the yellow emissive carbon dots (CDs:Mn)

Firstly, 1 mmol citric acid, 2 mmol urea and 1 mmol manganese acetate were dispersed in 12.5 mL toluene. Then, the mixture was transferred into a Teflon-lined autoclave and heated at 180 °C for 12 h. After the reactor was cooled to room temperature, the raw samples were purified by centrifugation at 10000 r/min for 25 min, then the collected solution was further filtered using 0.22 μM filter member.

2.3. Fabrication of light-emitting diodes (LEDs)

Yellow emissive CDs:Mn in toluene solution were mixed with poly (methyl methacrylate) (PMMA) by vigorously stirring until the PMMA was totally soluble to form homogeneous solution. The solvent was vaporized under ambient conditions to form sticky CDs/PMMA composites. Then, the composites were deposited on a UV-chip with 395 nm excitation light to fabricate LED devices.

2.4. Characterization

Transmission electron microscopy (TEM) images were record using FEI Tecnai G^{2}F20 TEM. Dynamic light scattering (DLS) measurements were performed on malvern nano-ZS90. X-ray diffraction pattern (XRD) measurements were carried out using D8 FOCUS power X-ray diffractometer. Atomic force microscopy (AFM) measurements were performed on a Bruker MultiMode 8 instrument. Fourier transform infrared (FT-IR) spectra were measured on a Bruker Vertex 70 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) were recorded using a Thermo ESCALAB 250Xi instrument. UV–Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were measured using a Hitachi F-4500 fluorescence spectrometer. Fluorescence lifetimes were measured using FLSP-920 steady state and time resolved fluorescence spectrometer. Molecular weight (MW) was measured by gel permeation chromatography (GPC) method using tetrahydrofuran (THF) as solvent on a Waters 1525 instrument. Absolute quantum yields of the samples were measured in a calibrated integrating sphere on a C-9920-02 instrument. The LED parameters were measured on a SSP6612 photometric colormetric electric tester.

3. Results and discussions

The as-prepared CDs from solvothermal treatment of citric acid, urea and manganese acetate is denoted as CDs:Mn (Fig. 1a). Subsequently, the morphologies of the CDs:Mn were analyzed. The transmission electron microscopy (TEM) image of the CDs:Mn reveals they are uniform and narrowly distributed particles with an average diameter of about 2.95 nm (Fig. 1b and c), which is also confirmed by dynamic light scatting (DLS) analysis (Fig. S1 in Supporting Information). As shown in Fig. 1d, the atomic force microscopy (AFM) image of the CDs:Mn reveals their topographic heights in the range about 1.0–2.0 nm, corresponding to three to six layers of graphenen-like sheets in the CDs:Mn [30].

To better understand the effect of manganese (Mn^{2+}) ions on optical property of the CDs:Mn, CDs without Mn^{2+} ions were prepared by the same approach. As shown in Fig. S2, the pure CDs are well-dispersed with average particle size of 2.68 nm which is smaller than that of CDs:Mn of 2.95 nm. As shown in fluorescence spectra (Fig. 2a and b), both CDs:Mn and CDs exhibit excitation-wavelength-independent emission while shifting excitation wavelengths from 350 to 450 nm, indicating the fluorescence behaviors originate from homogeneous emissive states [31]. The maximum emission peak of the CDs was centered at 550 nm, whereas addition of Mn^{2+} ions caused the as-prepared CDs:Mn show red-shifted emission peak centered at 555 nm. The CDs:Mn exhibit deeper and more bright yellow fluorescence than that of the CDs in dilute toluene solution under 395 nm hand-held UV lamp illumination (insets of Fig. 2a and b), which ties in well with the emissive features of the both samples. As shown in Fig. 2a and b, it is interesting to find that fluorescence spectra of the both samples show relatively weak emission peak centered at 450 nm, which is excited in wide wavelengths from 350 to 400 nm. This result is further confirmed by a relatively weak absorption peak at 318 nm in fluorescence excitation spectra (FLE) of the both samples (Fig. S3). The origin fluorescence features of the both samples will be discussed in detail below. The UV–via absorption spectra of the both samples, as presented in Fig. 2c, show broad absorption bands covering UV and visible light regions. Absorption bands centered at 435 and 450 nm correspond to CDs and CDs:Mn, respectively, which can be ascribed to n→π* transitions from highly conjugated domains containing C=O/C-O groups [32,33]. In comparison with CDs, CDs:Mn show broader absorption band and red-shifted emission peak, suggesting that Mn^{2+} ions could enlarge conjugated sp^2-domains, thus lowering the band gap of the as-prepared CDs:Mn (Fig. 2c) [34]. In order to elucidate effects of interactions between Mn^{2+} ions and pure CDs, the pure CDs solution mixed with Mn^{2+} ions was denoted as CDs (Mn^{2+}). As shown in Fig. 2c, absorption band and fluorescence emission peak of CDs (Mn^{2+}) almost overlap with that of CDs, indicating optical behaviors of CDs:Mn should be not mainly from the interactions between pure CDs and Mn^{2+} ions. As shown in Fig. S4, the absolute QY of CDs without Mn^{2+} ions is 46%, on the other hand, QY of CDs:Mn can be further enhanced up to 68.6% due to synergistic effect of increased conjugated sp^2-domain and minimal increase nitrogen and oxygen content as discussed below [32,35]. The photoluminescence (PL) decay curves of both samples are fitted to two-exponential (Fig. 2d). The fast (τ_1) and low (τ_2) components for both samples are on a nanosecond time scale, indicating both samples possess fluorescent properties (Table S1) [36]. As shown in Table S1, the percentages of the low component (τ_2) are 73.71% and 89.66% for CDs and CDs:Mn,