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Rapid microwave-assisted synthesis of highly luminescent nitrogen-doped carbon dots for white light-emitting diodes

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ABSTRACT

Highly luminescent nitrogen-doped carbon dots (N-CDs) were synthesized rapidly by one-step microwave-assisted hydrothermal method using citric acid as carbon source and ethylenediamine as dopant. The influences of reaction temperature, reaction time and raw material ratio on the fluorescence performance of N-CDs were investigated. Then N-CDs with the highest quantum yield were selected as fluorescent materials for fabricating white light-emitting diodes (LEDs). Highly luminescent N-CDs with the quantum yield of 75.96% and blue-to-red spectral composition of 51.48% were obtained at the conditions of 180 °C, 8 min and the molar ratio of citric acid to ethylenediamine 2:1. As-prepared highly luminescent N-CDs have an average size of 6.06 nm, possess extensive oxygen- and nitrogen-containing functional groups on their surface, and exhibit strong absorption in ultraviolet region. White LEDs based on the highly luminescent N-CDs emit warm white light with color coordinates of (0.42, 0.40) and correlated color temperature of 3416 K.

1. Introduction

As a promising energy-saving technique for sustainable development, solid-state white light-emitting diodes (LEDs) have received widespread attention because of their high energy efficiency, low power consumption, long working life, rapid response time and environmental friendliness [1,2]. Currently, the commercial route for fabricating white LEDs is combining blue chip with yellow $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) phosphor [3]. Nevertheless, these phosphors often suffer from expensive raw materials and high reaction temperature [4]. Most recently, semiconductor quantum dots (QDs)-based white LEDs have undergone rapid development owing to their favorable optical properties such as high quantum yield (QY), tunable emission and high photostability [5,6]. However, the preparation and separation process of those QDs often involve the inherent toxicity and underlying environmental contamination, substantially limiting their large-scale application [7].

Carbon dots (CDs), with an amorphous or sp^2 carbon framework and a surface grafted with oxygen-containing groups, have been dramatically studied over the past decade owing to their admirable optical properties, robust chemical inertness and low toxicity [8,9]. To date, extensive methods have been reported for the synthesis of CDs, including arc discharge [10], laser ablation [11], electrochemical synthesis [12], ultrasonic treatment [13], pyrolysis [4], and hydrothermal synthesis [14], and so forth. Nonetheless, most of these methods are undesirable on account of time-consuming operation, harsh reaction conditions, tedious purification process and inferior yield [15]. Therefore, it remains challenging to develop a simple, rapid and efficient synthesis method. Recently, microwave-assisted synthesis has received increasing favor because of its outstanding merits, such as straightforward operation, high reaction speed, mild reaction condition, safety and no pollution [16,17]. However, at present, the QY of CDs obtained by microwave-assisted synthesis is relatively low (<40%) [15,17,18], greatly hindering their practical application in the photoelectric field.

In the last few years, various strategies, like surface passivation

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[19], surface reduction [20], metal coating [21] and internal doping [22], have been developed to improve QY of CDs. Among them, internal doping usually requires only one-step reaction. Besides, the introduction of heteroatoms and the tuning of internal/surface groups can be realized by changing the species of dopant, a preferred method adopted by researchers for improving QY of CDs. Xu et al. synthesized yellowish-green nitrogen-doped carbon dots (N-CDs) with QY of 10.1% by microwave irradiation from calcium citrate and urea [17]. Hu et al. developed a simple one-pot microwave-assisted approach for the large-scale preparation of CDs with QY of 14.3% [15]. Zhai et al. developed N-CDs with highest QY of 30.2% using citric acid (CA) as the carbon source and amines as N-doping precursors, including ethylenediamine (EDA), diethylamine, triethylamine and 1,4-butanediamine [18]. In order to preferably exert the role of CDs as a color converter and enhance the brightness and light efficiency of CDs-based LEDs in the field of lighting, the preparation of CDs with higher QY is still a major challenge at this stage.

Herein, we report a rapid and one-step microwave-assisted method to synthesize N-CDs with high QY using CA and EDA as starting materials (Fig. 1). The effects of reaction temperature, reaction time and raw materials ratio on QY of CDs were investigated by orthogonal experiment. Ultimately, warm white LEDs were fabricated by combining the highly luminescent N-CDs and UV-LED chip, thus promoting the research and application of CDs fluorescent materials in white LEDs lighting field.

2. Experimental

2.1. Materials

CA and EDA were ordered from Tianli Chemical Reagent Co., Ltd (Tianjin, China). Quinine sulfate was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All the chemicals were used as received. Deionized water was used throughout the whole experiment process. Optical sealants (OE-6250A and OE-6250B) were supplied by Dow Corning Toray Co., Ltd (Tokyo, Japan). UV-LED chip (output power = 1.0 W) centered at 365 nm was supplied by Guanghuashi Technology Co., Ltd (Shenzhen, China).

2.2. Design and analysis of orthogonal experiment

2.2.1. Design of orthogonal experiment

In the present study, the effects of reaction temperature (factor A), reaction time (factor B) and the molar ratio of CA to EDA (n_{CA}:n_{EDA}, factor C) on QY of N-CDs were explored on the basis of an orthogonal experimental design and the corresponding levels and factors are tabulated as Table 1. An orthogonal array $L_9(3^4)$ was applied to assign the considered factors and levels as indicated in Table 2. Generally, each row of orthogonal array refers to a specific set of factor levels. A column could only be assigned to a factor. Nine

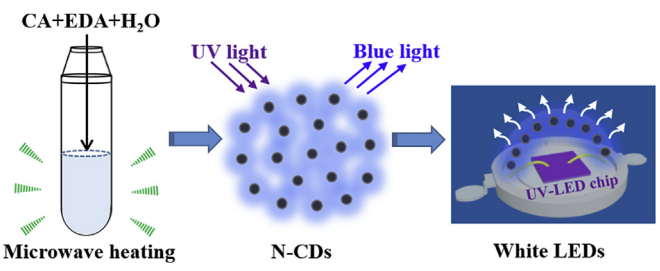

Fig. 1. Schematic representation of synthesizing N-CDs and their application in white LEDs.

Table 1
Levels and factors affecting the QY of N-CDs.

Levels	Factor		
	A (T/°C)	B (t/min)	C (n_{CA}:n_{EDA})
1	150	2	2:1
2	180	5	2:3
3	210	8	2:5

trials according to the orthogonal array $L_9(3^4)$ were carried out to accomplish the optimization process, during which the prepared samples and measured QY value are denoted as N-CDs-r and Y_r (r = 1, 2, …, 9), respectively. Note: Unless specified, the sample utilized for characterization or application in this paper referred to highly luminescent N-CDs obtained under optimal conditions. In particular, the order of the trials should be randomized to avoid any personal or subjective prejudice.

2.2.2. Analysis of orthogonal experiment

There are three critical parameters in the analysis of orthogonal experiment: K_{ji}, k_{ji} and R_j. Among them, K_{ji} refers to the sum of the evaluation indexes of all levels (i, i = 1, 2, 3) in each factor (j, j = A, B, C). The optimal level for each factor could be obtained when K_{ji} is the largest. k_{ji} (average value of K_{ji}) is usually used to determine the optimal level and the best combination of factors. R_j represents the range between the maximum and minimum value of k_{ji}, which is used to assess the significance of the factors, i.e. a larger R_j stands for a greater impact of the factor on the experimental index [23,24]. Specifically, the calculation of K_{ji}, k_{ji} and R_j are shown below:

$$\begin{array}{lll} K_{A1} = Y_1 + Y_2 + Y_3 & K_{B1} = Y_1 + Y_4 + Y_7 & K_{C1} = Y_1 + Y_6 + Y_8 \\ K_{A2} = Y_4 + Y_5 + Y_6 & K_{B2} = Y_2 + Y_5 + Y_8 & K_{C2} = Y_2 + Y_4 + Y_9 \\ K_{A3} = Y_7 + Y_8 + Y_9 & K_{B3} = Y_3 + Y_6 + Y_9 & K_{C3} = Y_3 + Y_5 + Y_7 \end{array} \quad (1)$$

$$k_{ji} = K_{ji}/3 (i = 1, 2, 3;\ j = \mathrm{A, B, C}) \quad (2)$$

$$R_j = \max(k_{ji}) - \min(k_{ji})\ (i = 1, 2, 3;\ j = \mathrm{A, B, C}) \quad (3)$$

where Y_r is the QY value of the resulting N-CDs-r (r = 1, 2, 3, …, 9).

2.3. Synthesis of N-CDs

Fluorescent N-CDs were synthesized by one-step microwave-assisted method using CA as carbon source and EDA as dopant. Specifically, CA (2.1014 g, 0.01 mol), and a certain volume of EDA and deionized water (15 mL) were added into a 30 mL reaction vial and heated at 150–210 °C using microwave irradiation for 2–8 min in MICROWAVE 300 reactor. The pressure remained at about 10 bar during the process of the reaction. After the reaction, the resulting transparent solution was filtered with 0.22 μm syringe filter to remove larger particles. The N-CDs powder was then obtained by freeze drying. In addition, the EDA-free controlled trial (N-free-CDs) was conducted only using CA under the same experiment condition as highly luminescent N-CDs (180 °C, 8 min).

2.4. Fabrication of white LEDs

The highly luminescent N-CDs powder (28 mg) with high QY was mixed with silicone (4 mL, OE-6250A:OE-6250B = 1:1) and heated at 30 °C for 30 min with constant magnetic stirring. Then the highly luminescent N-CDs/silicone mixtures (30 μL) were gently dropped onto the commercial cupped optical lens and thermally cured in a drying oven at 80 °C for 8 h. At last, the optical