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One-step synthesis of high quantum-yield and excitation-independent emission carbon dots for cell imaging

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ABSTRACT

Here a facile and economical one-step approach for synthesizing high quantum-yield (about 80.3%) and water-soluble carbon dots has been well established, while citric acid (CA) and glutathione (GSH) serve as precursors. Specifically the synthesized C_{CA+GSH} dots described here existed in tunable diameters of 2.5–3 nm, and exhibited bright blue fluorescence together with excitation-independent emission behavior. Significantly, this proposed carbon dots with low toxicity may provide potential to broaden avenues for various applications in bioimaging and beyond.

1. Introduction

Carbon nanomaterials, mainly including carbon nanotubes, fullerenes and graphene, have generated extensive attention for a wide variety of promising applications in fields of nanotechnology, biosensing and drug delivery [1,2]. Recently carbon dots (CDs), emerging as a new class of fluorescence materials, attracted considerable interest. Based on the carbon skeleton structure, carbon dots usually exist in the size of less 10 nm showing excellent properties such as satisfactory fluorescent performance, low cytotoxicity and biocompatibility owing to their specific nanometer dimension [3–6]. Thus, CDs have been considered as a satisfactory candidate for biosensing [7], catalysis [8] and imaging [9–11]. Due to these advantages, many works have been carried out on the facile synthesis methods and intensive studies of the photoluminescence properties.

Since carbon dots were originated from carbon nanotubes during the process of electrophoresis in 2004, two major synthesis methods have been reported [12]. One way was known as top down, consisting of electrochemical oxidation [13,14], acidic oxidation [15], arc discharge [12] and laser ablation [16]. Hydrothermal [17], microwave [18], and ultrasonic [19], serving as another way defined as bottom up, have been normally applied to synthesize CDs. Nevertheless, the generality of CDs showed a relatively low fluorescence quantum-yield (QY) compared with conventional semiconductor QDs. Recently, doped CDs were obtained with high fluorescence [20]. But their corresponding synthesis procedures are usually complicated and the poor chemical inertness of doped CDs limits applications of the CDs [21]. Thus, there is a great need to develop a facile, low-cost, and high-yield method for the preparation of CDs with strong fluorescence emission.

In this study, we employed citric acid and glutathione to produce C_{CA+GSH} dots based on a one-step strategy (Fig. 1). In particular, CA played the role as carbon source due to its low carbonization temperature ($<200\ ^{\circ}C$) and GSH provided nitrogen and sulfur simultaneously.

2. Results and discussion

Characterization of CDs: To characterize this synthesized C_{CA+GSH} dots, the maximum excitation and emission spectra peaks of synthesized C_{CA+GSH} dots were initially recorded at 368 nm and 450 nm respectively. The C_{CA+GSH} dots aqueous solution at very low concentration ($10\ \mu g\ mL^{-1}$) emitted obvious blue fluorescence (photograph II) under UV light (365 nm) while appearing as completely colorless transparent under daylight (photograph I) in Fig. 2A. Again the UV–vis absorption spectrum showed a peak at 345 nm, owing to n–π* transition of C=O and C=N (Fig. 2A). The synthesis of C_{CA+GSH} dots showed excitation-independent emission character, the emission peak did not shift and the fluorescence intensity decreased with the excitation wavelengths varying from 310 nm to 410 nm (Fig. 2B). Such excitation-independent fluorescence behavior makes the C_{CA+GSH} dots appropriate candidates for extensive applications, like bioimaging and biolabeling. Meanwhile the UV absorption and fluorescence emission spectra of C_{CA} dots and C_{GSH} dots were also studied, and

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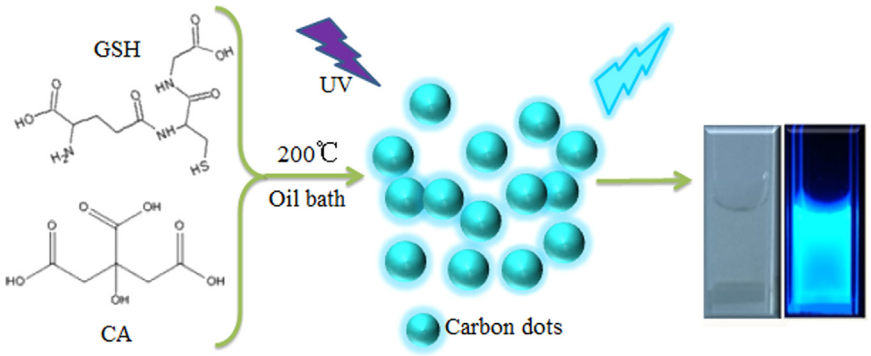

Fig. 1. Schematic illustration of synthesizing CDs.

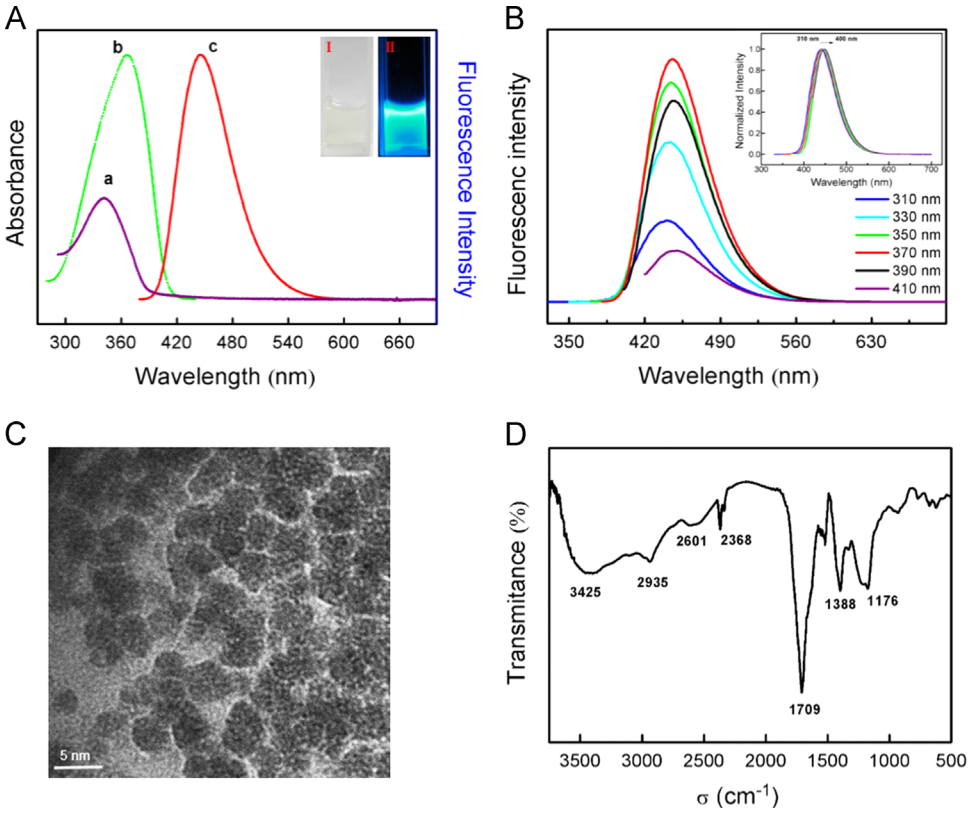

Fig. 2. (A) Fluorescence and UV–vis absorption spectra of C_{CA+GSH} dots, (B) Emission spectra of C_{CA+GSH} dots for varying excitation wavelengths, (C) HR-TEM images of C_{CA+GSH} dots, (D) FTIR of C_{CA+GSH} dots.

found to be slightly different from those of C_{CA+GSH} dots. The fluorescence spectra in Fig. S1A and C showed optimal emission peaks at 453 and 482 nm when excited at 367 nm. This is due to the fact that the fluorescence behavior also depends on the synthesis process, such as the carbon source. We also calculated the QY of C_{CA} and C_{GSH} dots as 2.5% and 1.3% respectively. In addition, the two C-dots (C_{CA} dots and C_{GSH} dots) exhibited excitation-dependent fluorescence behavior (Fig. S1B and D). To further investigate the nanostructures of CDs, HR-TEM was employed to directly observe the morphology and particle size distributions. As shown in Fig. 2C C_{CA+GSH} dots obtained here existed as a majority population at the size of 3 nm and no aggregation emerged, depicting their satisfactory disparity. Next, Fourier Transform Infrared Spectroscopy (FTIR) was applied to explore the surface groups and structure of this synthesized C_{CA+GSH} dots in detail. As revealed in Fig. 2D, O–H, N–H, C–H, S–H, C═O, C═N, C–O, C–S, and C–N groups exist on the surface of C_{CA+GSH} dots. Specifically, the absorption bands of O–H and N–H stretching vibrations appeared at 3425 cm^{-1} with C–H and S–H stretching vibrations at 2935 cm^{-1} and 2601 cm^{-1} respectively. Similarly, C═O and C═N stretching vibrations were at 1709 cm^{-1}. Simultaneously, the peak at 1388 cm^{-1} was associated with C–H, N–H, C–S, C–N, bending vibrations and the peak at 1176 cm^{-1} with C–O bending vibrations.

Optimization of synthesis conditions: Subsequently, to identify the optimized conditions for synthesizing C_{CA+GSH} dots, various experiments were performed. As revealed (Fig. S2A–C) the fluorescent intensities of C_{CA+GSH} dots exhibited variations along with varying reaction time, temperature and molar ratio of GSH and CA, demonstrating that synthesis of C_{CA+GSH} dots is dependent on these selected conditions; thus 10 min, 200 °C and 1:1 of GSH and CA served as the optimal conditions towards the following experiments.