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Carbon dots originated from carnation for fluorescent and colorimetric pH sensing

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ABSTRACT

Herein, fluorescent carbon dots (CDs) originated from carnation were creatively synthesized with well-distributed size. By detailed characterization, the prepared CDs were mainly composed of C and O as well as limited amount of N, and there existing O–H, N–H, C–H, C=N, C=O, C=C and C–O groups on their surfaces. Significantly, these CDs showed a distinct pH-sensitive feature. To be specific, the fluorescence intensity of CDs exhibited a linear fashion over the pH range from 11.7 to 3.2. Simultaneously, the color of the CDs solution varied from yellow to yellow–orange, and the corresponding hue parameter decreased linearly with the pH value range from 10.6 to 5. All these evidence illustrated that this CDs have potential as colorimetric and fluorescent sensors for pH sensing. Additionally, The CDs were applied for cellular imaging and painting.

1. Introduction

Emerging as the newcomers to the carbon nanomaterials, carbon dots have remarkable properties consisting of stable photoluminescence, small size, low toxicity, favorable biocompatibility [1] and satisfactory fluorescent performance [2]. Hence, this kind of material has attracted tremendous attention in the fields of biological labeling, photocatalysis [3], sensing [4] and biomedicine [5]. Inspired by these advantages and the vast potential applications, great efforts have been exerted on the better synthetic routes and more detailed fundamental studies about the properties of CDs [6]. Nevertheless, these proposed methods usually involved severe reaction conditions, complex post-treatment, time consuming, and expensive raw materials. Thus, developing simple and rapid methods for synthesizing CDs are still meaningful.

As an important parameter, pH values usually adjust the function of many organelles and may give rise to various diseases including cancers and neurological disorders [7] even Alzheimer's disease [8]. Thus, accurately measuring intracellular pH value is meaningful. To date, several materials have developed for pH sensing, such as quantum dots [9], encoded red fluorescent protein sensor [10], Ag@SiO2 core–shell nanoparticle [8], semiconducting polymer dots [11] and quantum dot fluorescent protein FRET probes [12]. However, these materials were limited by large size, high toxicity or biocompatibility. CDs owing to a number of advantages have been demonstrated as a suitable candidate for pH sensing [13].

Hereby, synthesizing CDs has been innovatively built up by using carnation as carbon source (Fig. 1), and these CDs showed blue fluorescence with a quantum yield of 11.36%. Importantly, we further applied it for pH sensing on the basis of the variations of the color and fluorescence of CDs upon different pH values.

2. Results and discussion

2.1. Characterizations of CDs

To investigate the synthesized CDs, the maximum excitation and emission spectra were recorded as 320 nm and 435 nm respectively, and the UV–vis absorption spectrum showed a peak at 348 nm, owing to n–π* transition of C=O (Fig. 2A). Besides, the emission peak shifted from 425 nm to 460 nm and its corresponding fluorescence intensity decreased (Fig. S2A), this size-dependent emission may be caused by the bandgap opening of quantum confinement. Remarkably, the as prepared CDs exhibited upconversion fluorescence property (Fig. S2B) was attributed to multi-photon active process, likely due to anti-Stokes photoluminescence. Moreover, HR-TEM revealed these CDs were spherical and well-dispersed and their diameters were in the range of 6–9 nm confirmed by DLS histogram (Fig. 2B). Furthermore, the FTIR spectrum described there were O–H, C–H, C≡C, C=O and C–O groups on the surface of CDs (Fig. 2C). To gain insight into the components of CDs, ^{13}C NMR and XPS survey spectra were

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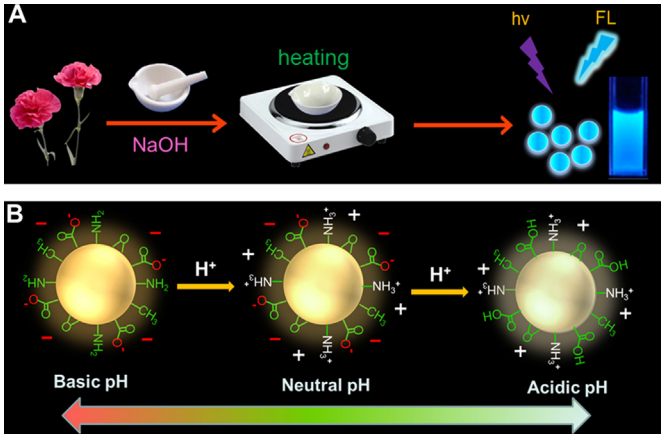

Fig. 1. Schematic illustration of synthesizing CDs (A); mechanism for sensing pH (B).

provided. Specifically, the ^{13}C NMR spectrum exhibited three kinds of carbon peaks around three ranges: 20–100 ppm (sp^3 carbon atoms, C–O), 100–150 ppm (sp^2 carbon atoms, C=C) and 150–185 ppm (sp^2 carbon atoms, C=O), respectively (Fig. S3). Meanwhile, two prominent features of C1s and O1s accompanied with a small peak of N1s were observed in the survey spectrum (Fig. 2D). Furthermore, the deconvolution of the C1s spectrum (Fig. S4A) indicated the presence of four types of carbon bonds: C–C (283.37 eV), C=C (284.79 eV), C–O (286.74 eV) and O=C–O (288.26 eV). The N1s spectrum (Fig. S4B) showed the nitrogen signals of C–N–C at 396.45 eV and N–H at 398.42 eV. The O1s spectrum (Fig. S4C) showed the oxygen signals of C=O at 529.87 eV, C–O at 531.5 eV and O=C–O at 534.5 eV.

2.2. Stability of CDs

For evaluating the stability of CDs, further experiments were performed. In detail, the fluorescent intensities of CDs scarcely exhibited variation along with different concentrations of NaCl and various time (Fig. S5A and B), describing their satisfactory stability. Furthermore, there existing an obvious quenching for the fluorescence intensity of CDs while Cu^{2+} and Fe^{3+} were introduced (Fig. S5C), suggesting their potential of CDs for sensing these ions. However, the CDs exhibited different fluorescence intensity while existing in different organic solvents (Fig. S5D). On the whole, the CDs synthesized here implied promising fluorescence, stability and environmental-friendliness.

2.3. Fluorescent and colorimetric sensing pH

Interestingly, we observed that the fluorescence intensity of CDs varied along with pH while estimating the stability of CDs towards different pH values. Based on this phenomenon, we addressed whether the proposed CDs could be ideal candidates for pH sensing. Specifically, the fluorescence intensity of CDs decreased linearly along with pH value altering from 11.70 to 3.20 with a linear correlation coefficient of 0.991 (Fig. 3A and B). To further explore the reversibility of CDs, the pH value changed from 11.20 to 3.60 and again to 11.20, and their related fluorescence was recorded upon each pH. Specifically, there was scarce fatigue for

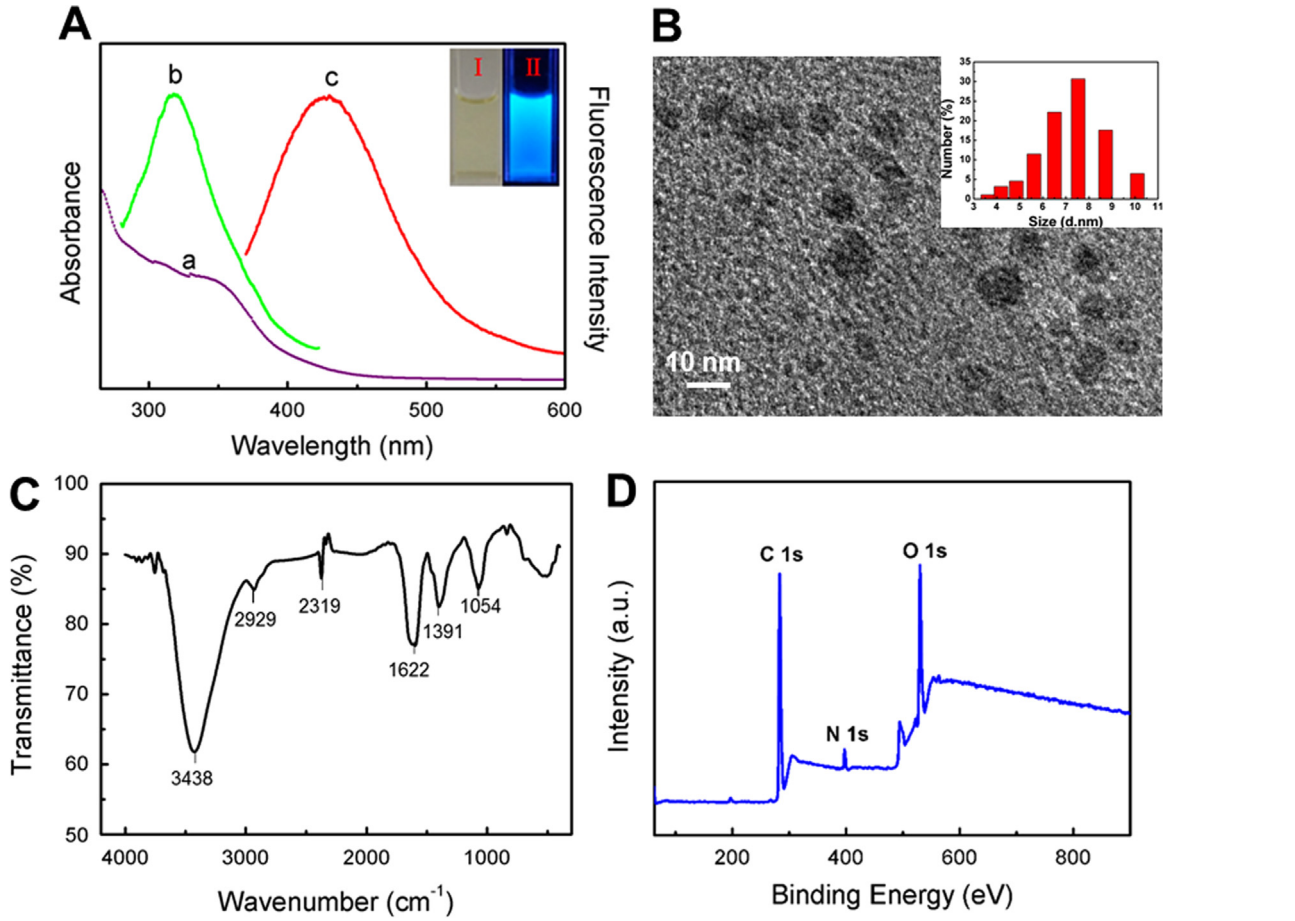

Fig. 2. (A) Fluorescence excitation (b) and emission (c) spectra of CDs; (B) HR-TEM image of CDs, Inset: DLS histogram of CDs. (C) FTIR spectrum of CDs; (D) Survey XPS data of CDs.