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A facile hydrothermal approach towards photoluminescent carbon dots from amino acids

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ABSTRACT

A facile one-pot method to fabricate photoluminescent carbon dots (CDs) was developed by the hydrothermal treatment of amino acids at mild temperatures. Derived from three different kinds of amino acids including serine, histidine, and cystine, the resultant CDs show uniform spherical morphology with the diameters in the range of ~2.5–4.7 nm. These amino acid derived CDs also manifest excellent photoluminescence behavior with the quantum yields (QYs) of ~7.5% and high stability. More importantly, this method provides the opportunity to modify the sizes, structures, and photoluminescent behavior of CDs by the utilization of diversified amino acids with different structural characteristics.

1. Introduction

In the last few years, photoluminescent carbon dots (CDs) have attracted enormous attention due to their fascinating virtues including stable photophysical properties, good dispensability in aqueous solution, high resistance to photo-bleaching, environmental security, low cytotoxicity, excellent biocompatibility and so on, which make them appealing fluorescent materials in photocatalysis, energy conversion, optoelectronics, biological labeling, cellular imaging, and drug delivery [1–12]. According to the different starting materials, the fabrication strategies of CDs can be categorized as top-down and bottom-up approaches. Generally, the segmentation of bulky carbon-rich precursors is named as top-down methods [13–18]. Correspondingly, the bottom-up methods refer to the thermal or solvothermal conversion of small molecules or polymers to CDs [19–24]. Among various bottom-up methods, hydrothermal treatment of the precursors provides a mild, efficient and broadly applicable route to CDs [25]. Moreover, the structural and photo-physical properties of the CDs derived from hydrothermal treatment are greatly decided by the starting materials. Therefore, the delicate selection of precursors for the hydrothermal production of CDs is of great importance in the exploration of unprecedented CDs with excellent photoluminescent behavior.

As the basic building units of protein, amino acids are abundant, inexpensive and biocompatible. They possess both amino and carboxyl groups, which enable them to be easily cross-linked via amide groups. Moreover, it has been reported that the size, morphology, crystalline degrees and composition of the CDs could greatly affect their photoluminescent behavior [21,26]. The rich content of heteroatoms such as nitrogen (N) and sulfur (S) in amino acids will render the resulting CDs to contain heteroatoms in the carbon framework, which is expected to influence their photoluminescent properties accordingly. These advantages thus make amino acids the ideal precursors for the bottom-up construction of CDs.

Herein, we report a facile one-pot approach towards photoluminescent CDs by the hydrothermal treatment of different amino acids including serine (Ser), histidine (His), and cystine (Cys) at mild temperatures (Scheme 1). As the results, CDs with uniformly spherical morphology and narrow size distribution were obtained. With the diameters ranging from ~2.5–4.7 nm, the resultant CDs manifest the quantum yields (QYs) of ~7.5% and high stability, which are comparable to those of the CDs obtained at high temperatures over 900 °C [2,5,21,26].

2. Experimental section

2.1. Materials

L-Serine and L-Histidine were purchased from Shanghai Aladdin Chemical Reagent Company. L-Cystine and acetic acid were purchased from Sinopharm Chemical Reagent Company. All

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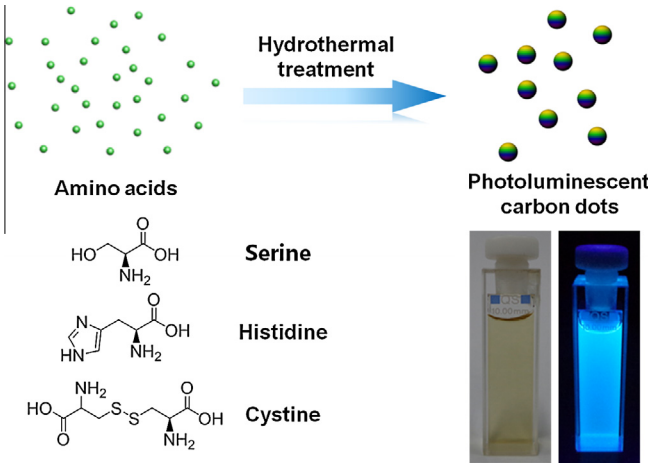
chemicals were used as received without any further purification. Ultrapure water (18.2 MΩ cm @25 °C) was used in all experiments.

2.2. Synthesis of the CDs

In a typical synthesis procedure, 0.0125 mol amino acids were first dissolved in 36 ml acetic acid (2 wt%). The mixtures were stirred at room temperature for several minutes and sealed in a 50 ml stainless steel autoclave for the following hydrothermal treatment for 12 h at 200, 220 and 250 °C, respectively. It should be noted that the amino acids only had good solubility in acidic solutions and the utilization of neutral or basic solution would lead to the precipitation of the precursors. Therefore, diluted acetic acid was used as the solvent for the hydrothermal synthesis of CDs. After the hydrothermal process, the color of the mixture solution turned from colorless into dark yellow, implying the successful conversion of amino acids to carbon nanomaterials [25]. The obtained suspension was then centrifuged at a 10,000 rpm for 10 min and the supernatants were dialyzed against Milli-Q water with a cellulose ester membrane bag (Mw = 3500) for 24 h to remove the excess precursors. After filtering through 0.2 μm Teflon filter, a clear, light yellow aqueous suspension was finally obtained. According to the carbon source and the temperatures of hydrothermal treatment, the resultant CDs are abbreviated as CDs–*X*–*T*, where *X* refers to the amino acid (Ser, His, and Cys), and *T* stands for the hydrothermal temperatures (200, 220 and 250).



Scheme 1. A schematic illustration for the preparation procedure of CDs by hydrothermal treatment of amino acids. Inset: photo image of the solutions of CDs-His-200. Left: under daylight; right: under 365 nm UV irradiation.

2.3. Characterizations

TEM measurements were performed on JEM-2010F at operating voltage of 200 kV. The sample was diluted in ultrapure water and the suspension dropped on carbon-coated copper grid by evaporation in air. UV/Vis spectra were recorded at room temperature on a Hitachi J-4100 spectrophotometer. Fluorescence spectra were recorded for progressively longer excitation wavelengths from 300 to 480 nm in 20 nm increments on a Horiba Fluoromax-4 spectrometer.

3. Results and discussion

The morphology and microstructure of the CDs were first investigated by transition electron microscopy (TEM). As indicated in Figs. 1, S1 and S2, all the CDs exhibit similar spherical structures. For the CDs from serine, the diameters of CDs-Ser-200,

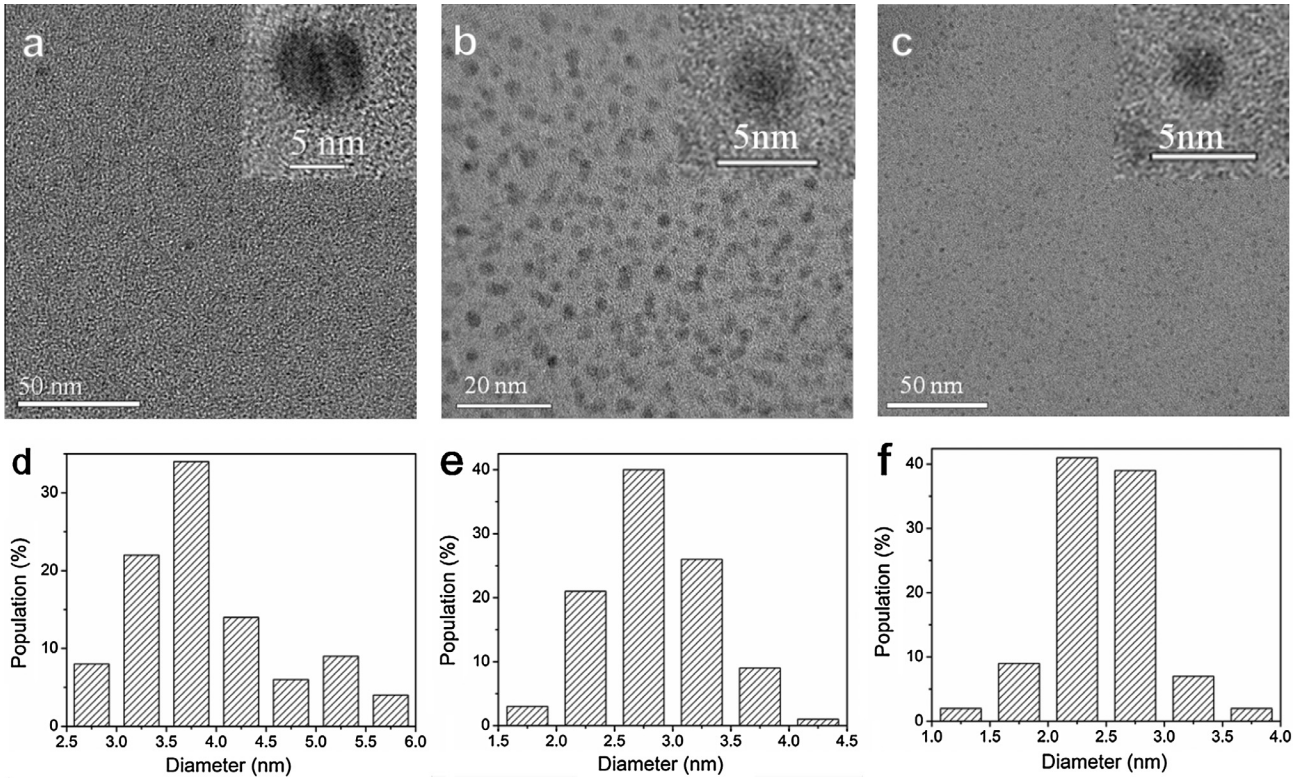


Fig. 1. TEM images of (a) CDs-Ser-200, (b) CDs-Ser-220 and (c) CDs-Ser-250. Inset: the corresponding HRTEM images of the CDs; the particles size distribution histograms of (d) CDs-Ser-200, (e) CDs-Ser-220 and (f) CDs-Ser-250 obtained from 100 particles.