

Article

Preparation of Carbon Nitride Dots with Sizes Larger than 20 nm

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Featured Application: The prepared carbon nitride dots have potential applications in fluorescent sensing, bioimaging and photocatalysis.

Abstract: Carbon nitride dots (CNDs) were obtained via carbonization of polymer formed via the reaction of 1, 2-ethylenediamine (EDA) and CCl_4 . The average diameter of CNDs is calculated to be ca. 44 nm. They possess solubility in water and polar organic solvents.

Keywords: carbon nitride dots; carbonization; ethylenediamine

1. Introduction

Carbon nitride dots (CNDs) mostly consist of carbon and nitrogen and possess similar properties to carbon dots. Due to their low cost, easy preparation, good biocompatibility, and excellent photoluminescence (PL), they have been explored for applications in fluorescent sensing [1–3], bioimaging [4–6], photocatalysis [7,8], etc. The preparation of CNDs usually relies on the carbonization of C, N-containing precursors, including various organic amines/amides in the presence of acids or other additives [1,9–12], chitosan [13], folic acid [5], ionic liquid [14], etc. Besides, CNDs can also be synthesized via etching a larger carbon nitride structure such as graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) into small nanoparticles [15]. However, work on the preparation of CNDs is still limited. Sizes for CNDs obtained by previous methods are generally smaller than 10 nm, and their PL reveals single blue color at ca. 360 nm excitation. A scalable method for preparing CNDs with sizes of several tens of nanometers is needed to exploit their applications. Here, we improve the synthesis of CNDs from 1, 2-ethylenediamine (EDA) and CCl_4 . After polymerization of EDA and CCl_4 , polymer precursor was further heated in a tube furnace under Ar protection. After the heating of the polymer, the size of the CNDs increased again. As a result, we obtain CNDs with sizes from 23 to 70 nm.

2. Experimental

2.1. Synthesis of CNDs

CNDs were prepared according to the literature with a few modifications [9,16]. Firstly, a mixture of 8 mL EDA and 10.5 mL CCl_4 (both from Beijing Chemical Reagent Co., Beijing, China) was refluxed and stirred at 90 °C for 6 h. The obtained thick paste was then dried at 120 °C for 12 h, forming a dark-brown solid. Subsequently, this was placed in a tube furnace and heated in Ar flow at 300 °C for 2 h. The yellow solid that formed at the top of the inner wall of the quartz tube was collected as the resulting CNDs. These can be stably dispersed in water.

2.2. Characterization

The optical properties of the CNDs were measured by UV-visible spectrometer (U-3010, Hitachi, Tokyo, Japan) and fluorescence spectrometer (LS 55, PerkinElmer, Waltham, MA, USA), respectively. The morphology and structure of CNDs were observed by atomic force microscope (AFM, SPM-9600, Shimadzu, Tokyo, Japan), scanning electron microscope (SEM, Sirion 200s, JEOL, Tokyo, Japan), and transmission electron microscope (TEM, H-7560B, Hitachi, Tokyo, Japan) at 80 kV, respectively.

3. Results and Discussion

As shown in Figure 1, the synthesis of CNDs was carried out by thermal treatment of carbon nitride polymer formed via the reaction of EDA and CCl_4 . After heat treatment, the polymer underwent cross-linking and ring-formation [16]. The yellow solid at the top of the inner wall of the quartz tube was collected as our CNDs. These have solubility in water and polar organic solvents. The residual solid with a black color at the bottom of the inner wall of the quartz tube was discarded. This does not dissolve in water, however can disperse in polar organic solvents such as *N,N*-dimethylformamide and ethanol.

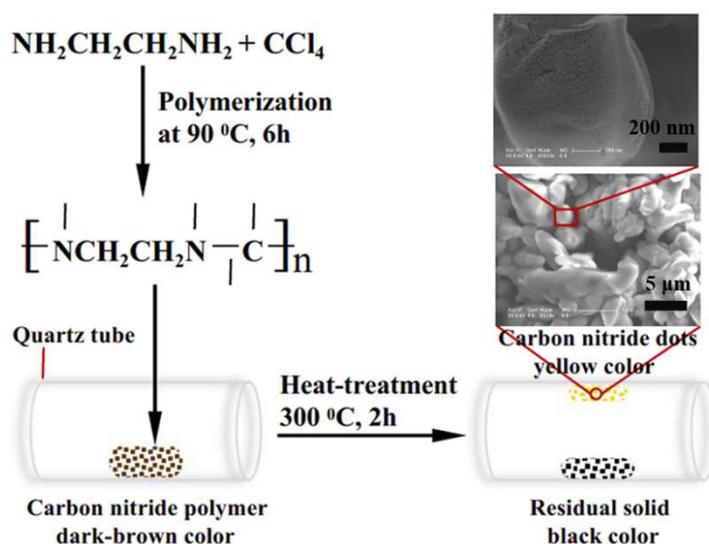


Figure 1. Schematic illustration of the procedure for preparing carbon nitride dots (CNDs).

SEM observation reveals that the yellow product is composed of micro-grade particles (Figure 1). On higher magnification, these particles are seen to be formed via high packing of smaller particles with sizes of several tens of nanometers. However, the residual black solid has structure of a similar scale (Figure 2a), which shows a glabrous surface after magnification (Figure 2b). This structure may result from excessive cross-linking and ring-formation of carbon nitride polymer.

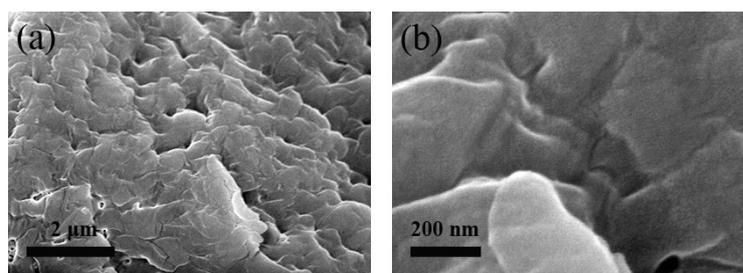


Figure 2. Scanning electron microscope (SEM) images with different magnifications of the residual black solid at the bottom of the inner wall of the quartz tube. Low magnification (a), and high magnification (b).

TEM image of CNDs and their size distribution are shown in Figure 3a,b, respectively. The size of CNDs is mostly distributed in the range 23–70 nm and the average calculated diameter is ca. 44 nm, which is consistent with SEM observation. The height of CNDs was measured by AFM, as shown in Figure 3c–f. The synthesized CNDs have heights between 0.6 and 2.5 nm, indicating that they are composed of 1–4 layers of CN.

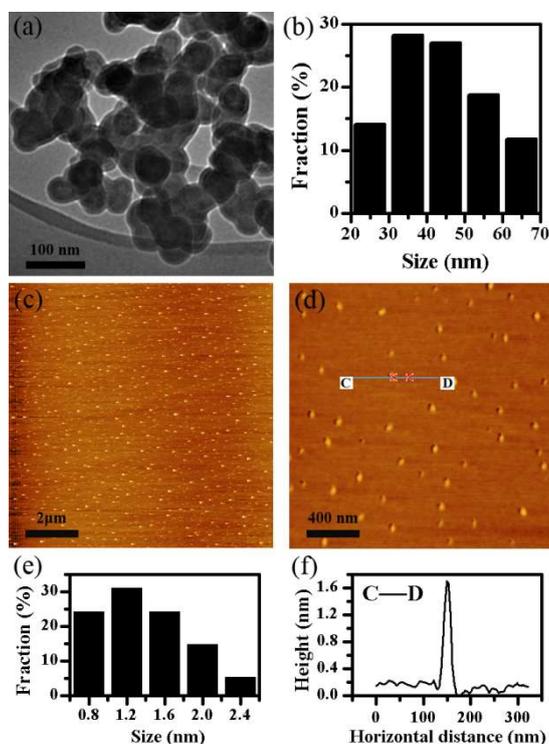


Figure 3. TEM image (a), and the corresponding size distribution (b), of CNDs; AFM images of CNDs with different magnifications (c,d), and their height distribution (e) and height profile along the line CD (f).

Figure 4 shows the optical properties of CNDs aqueous dispersion. It is seen that there are two typical absorption peaks at 275 and 325 nm, attributed to π - π^* transition of s-triazazine and n - π^* transition of defect state on the surface of the CNDs, respectively (Figure 4a) [17]. CNDs emit blue fluorescence at ca. 420 nm under the excitation of 360 nm irradiation (Figure 4b). Similar to most of carbon dots, the PL of the obtained CNDs is also excitation wavelength-dependent. The emission peak of CNDs is red-shifted from 375 to 450 nm with the excitation wavelength changing from 300 to 400 nm.

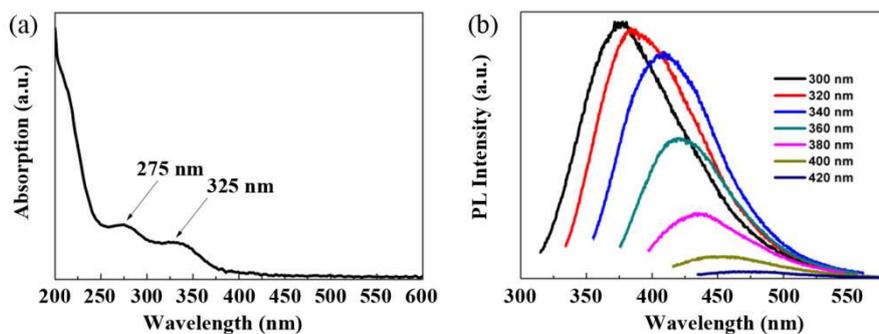


Figure 4. Optical properties of CNDs aqueous dispersion. UV-vis absorption spectrum (a), and PL emission spectra (b).

4. Conclusions

CNDs with an average diameter of ca. 44 nm were synthesized via carbonization of a polymer precursor formed via the polymerization of EDA and CCl_4 . The prepared CNDs have sizes ranging from 23 to 70 nm and emit strong blue light under 360 nm excitation. In addition to their good solubility in water and polar organic solvents, these properties benefit the CNDs for further applications in bioimaging, fluorescence sensing, and optoelectronics devices. The method reported in this work for preparing CNDs is scalable and expands the size range of synthesized CNDs.

Author Contributions: P.L. designed the experiments; P.L. performed the experiments; P.L., Y.Y., and X.G. analyzed the data; P.L. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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