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论文题目：Facile Synthesis of Carbon Quantum Dots with Green Fluorescent for Photocatalytic and Bioimaging Applications

Facile Synthesis of Carbon Quantum Dots with Green Fluorescent for Photocatalytic and Bioimaging Applications

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Abstract:

Due to the molecular and atomic dynamic, concentrate Sulphuric acid can carbonize organic molecule. Carbon Quantum Dots(CQDs) can be synthesized by this process. CQDs have many applications, they can enhance the photocatalytic activity of TiO2, and modified CQDs have high expressive with breast cancer cell.

Keyword:

CQDs, bioimaging, photocatalytic, fluorescence

1. INTRODUCTION

1.1 Background

Carbon nanomaterials, including graphene, carbo nanotube, carbon nanofiber, and fullerene, have attracted widespread interest due to their various applications ranging from catalysis, energy storage, electronics, drug delivery, bioimaging, and so forth. In particular, carbon quantum dots (CQDs) have been an emerging nanomaterial with photoluminescence and photochemical properties distinct from bulk material.

CQDs with typical dimensions of 2 – 10 nm are much smaller than the wavelength of visible light, exhibiting quantum confinement effects that enable a stable, tunable, and size-dependent photoluminescence[1]. CQDs also have good capability in up-conversion UV fluorescence emissions from visible light excitation, and can achieve enhanced photocatalytic efficiency under natural light when doping with conventional photocatalytic materials (such as TiO_2) that can be predominately exited by UV light[2].

Moreover, CQDs have low cytotoxicity, robust chemical inertness, and high aqueous solubility as compared to traditional semiconductor quantum dots. CQDs thus have great potential in a wide spectral of biochemical applications, including bioimaging, biosensors, tumor theranostics, and detection and degradation of hazardous substance in environments.

1.2 Current approach

CQDs are generally synthesized by two routes, namely the top-down route[3] and the bottom-up route[4]. The former involves breaking down larger carbon structures by methods like electrochemical oxidation and laser ablation. On the other hand, bottom-up approaches fabricate CQDs from molecular precursors through combustion/thermal treatments. However, these methods may involve costly precursors, special instruments, or dangerous heating procedure (100 – 900 °C) and the resultant CQDs generally have low emission efficiencies at wave lengths > 500 nm (green)[1]. Facile synthesis of green fluorescent CQDs can significantly broaden their practical applications.

1.3 Objective

To address the aforementioned issue, the project intends to develop a facile method for synthesis of carbon quantum dots with green fluorescence. Taking advantages of dehydration of concentrated sulfuric acid, CQDs can be fabricated from sucrose in a rapid, low cost, controllable, and passivation-free manner. The resultant CQDs exhibit good optical properties, good stability, and low toxicity, showing great potential for photocatalytic and bioimaging applications.

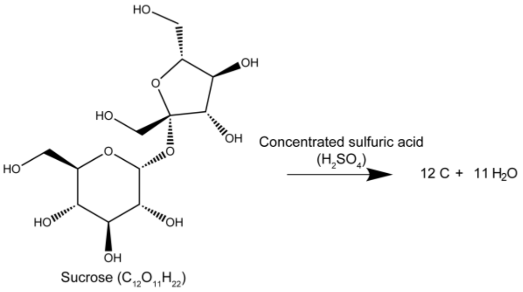

Figure 1. Formula of the bottom-up CQD synthesis mediated by dehydration of sucrose.

2. METHODOLOGY

2.1 Overview

Concentrated sulfuric acid (H_2SO_4) has a strong dehydration effect, can carbonize many organic compounds. When mixed with concentrated sulfuric acid, sucrose will change from white to black and foamed as carbon is formed. Finally, a black, porous carbon obtained. By exploiting the dehydration of sucrose at room temperature, a simple and rapid method was developed to produce green fluorescent CQDs (Figure 1).

2.2 Effect of phase state of sucrose

The effect of phase state sucrose for carbonization was first investigated, in the consideration that the phase state can affect the reaction rate and morphology of carbon. The dehydration of solid sucrose and aqueous solution of sucrose was performed by using a 98 wt % sulfuric acid. If solid sucrose was added into concentrated sulfuric acid, we got black porous carbon materials. If we directly added sucrose solution into concentrated sulfuric acid, a dark red carbon solution was obtained. The sucrose solution was eventually selected for the synthesis of CQDs because the sucrose molecule in sucrose solution can mix with sulfuric acid more effectively than solid sucrose, which is preferable for achieving uniform and small CQDs.

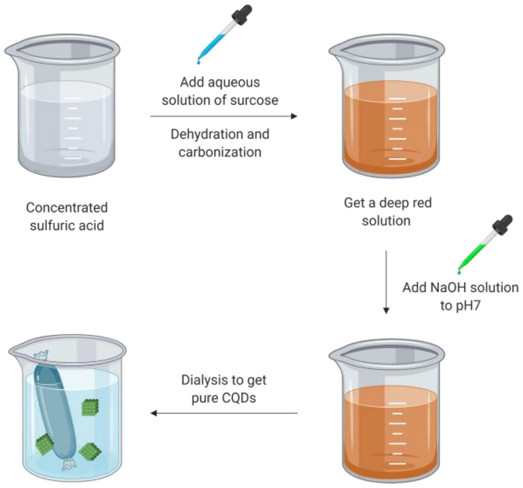

Figure 2. Schematic of the work flow for the synthesis of CQDs from sucrose based on sulfuric acid-mediated dehydration.

2.3 Established protocol

The specific operation as follows: 3 g of sucrose was dissolved into 3 mL of distilled water, then dropping slowly into the sucrose solution below the liquid surface of 20 mL of concentrated sulfuric acid (98 wt%) under stirring the liquid. The solution was kept stirring for 10 min. Then, adjusted the pH of the solution to 7 by NaOH solution. And then, the CQDs solution was separated with a dialysis bag (8000 Da) to remove the Na$^+$ (sodium ion), SO$_4$ (sulphate ion) ions and unreacted sucrose. Finally, we got the reddish solution containing the green fluorescent CQDs. No other passivation agents and steps were used in this synthesis method (Figure 2).

3. RESULTS AND DISCUSSION

3.1 Excitation dependent fluorescence spectra of two CQDs samples

By adjusting the proportion of sulfuric acid and sucrose solution, we obtained a series of CQD solution. CQDs solutions are as shown in Figure 3A-D. The color of CQDs obtained by this method was yellow or dark red depending on the concentration of CQDs. The A bright green fluorescence was emitted when excited the CQDs solution using UV light with a wavelength of 254 nm, as shown in Figure 3E-H.

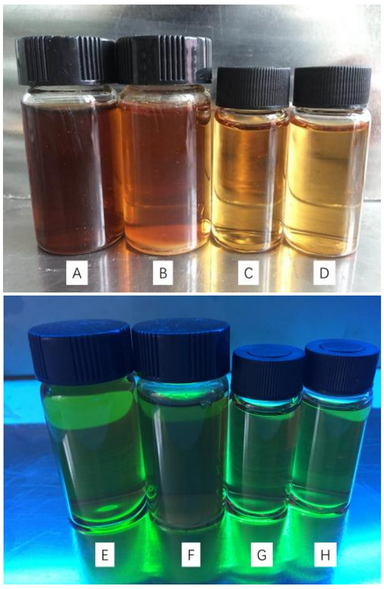

Figure 3. Resultant CQDs fabricated by carbonization of sucrose solution.

We further characterized the fluorescence spectra of the synthesized CQDs (Figure 4). We can obtain that the synthesized CQDs have excitation dependent fluorescent spectra. For one sample, when the excitation wavelength was 440 nm, the maximum emission spectrum was at550 nm. We observed a red shift of photoluminescence spectra from 520 to 575 nm and 475 to 575 nm, respectively. The PL spectra shifting of CQDs could be related to the extent of oxidation and oxygen containing groups presented on the surface of the CQDs. To determine the stability, the resultant CQDs were stored at room temperature for up to 3 months. No precipitation was observed after the long-time storage and the stored CQDs remained strong green fluorescent, showing a good stability of the CQDs.

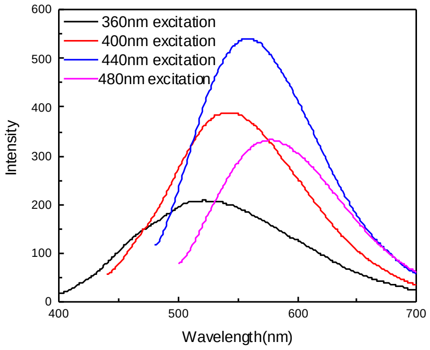

Figure 4. Emission spectra of the CQDs excited by different wavelengths characterized by spectrometry.

3.2 Size and morphology characterization by TEM

The fast Fourier transform (FFT) image of the CQDs obtained by high-resolution TEM (HRTEM) showed lattice spacing with interplanar distance of 0.21 nm, which is consistent with the (100) diffraction planes of graphitic carbon (Figure 5A). The morphology and size of CQDs were also investigated by TEM (Figure 5B-C). The CQDs exhibited small size of less than 10 nm (Figure B). Under larger magnifications up to 8,560,000×, lattice structure with a periodic distance of ~ 0.2 nm was clearly observed, in consistency with the FFT results (Figure 5C-D).

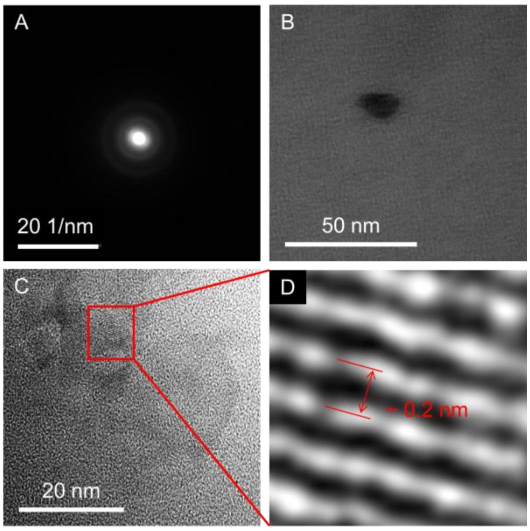

Figure 5. Characterization of dimension and morphology of the CQDs by high-resolution TEM (HRTEM). (A) Interplanar distance 0.21 nm in consistent with that of (100) diffraction planes of graphitic carbon. (B) Overall morphology of the CQDs at low magnification (150,000×). (C,D) Detailed morphology showing lattice structure at high magnifications (300,000× in C and 8,560,000× in D).

4. APPLICATION

4.1 Enhanced photocatalytic effect of TiO_2-doping CQDs

It has been reported that CQDs can improve the photocatalytic activity of TiO_2 when being doped with TiO_2[5]. We prepared CQDs/P25 nano-composite by modifying the commercial TiO2 product P25 (Degussa). First, the CQD solution and P25 were mixed together. After hydrothermal treatment at 150 °C for 4 h, the CQDs/P25 nano-composite was obtained. The photocatalytic activity of the CQDs modified P25 was evaluated by degradation of methylene blue under Xenon lamp. The CQDs/P25 nano-composite showed higher photocatalytic activity to degrade methylene blue as compared with P25 alone, showing a great potential in water treatment.

Figure 6. Photographs showing the enhanced degradation of methylene blue after treatment of CQDs/P25 (left) as compared with P25 (right).

4.2 Targeted imaging of breast cancer cells using folic acid-conjugated CQDs

The CQDs were also used for fluorescence imaging of tumor cells to show the potential of biomedical applications (Figure 7). The CQDs were functionalized with folic acid to exhibit their ability in targeting tumor cells. In vitro fluorescence imaging of a breast cancer cell line, MCF-7, was performed using laser confocal scanning microscopy (CLSM) after incubating the MCF-7 cells with folic acid-conjugated CQDs or bare CQDs for 2 h. The MCF-7 cells treated with folic-conjugated CQDs showed strong green fluorescence, indicating targeted accumulation of CQDs at the cells. In contrast, vanishing fluorescence was observed for MCF-7 cells treated with bare CQDs, showing the absence of unspecific binding of CQDs. These results collectively showed the great potential of CQDs in bioimaging in tumor biology.

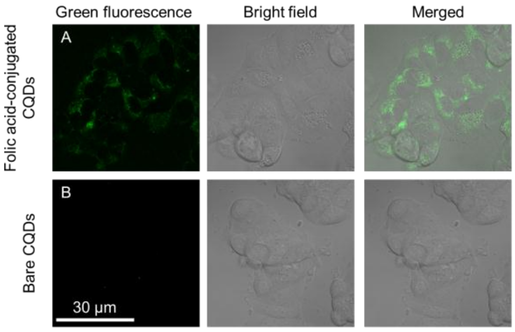

Figure 7. Targeted imaging of breast cancer cell line, MCF-7 by folic acid-conjugated CQDs.

5. CONCLUSION

In this work, we developed a rapid, low cost, and passivation-free approach for fabricating green fluorescent CQDs at room temperature, based on dehydration and carbonization of sucrose using 98 wt % sulfuric acid. The resultant CQDs showed strong green fluorescence, which was tunable depending on the excitation wavelength. The CQDs also showed good stability in size and illuminance. CQDs/P25 nano-composite exhibited enhanced photocatalytic activity. CQDs functionalized with folic acid had good performance in targeted imaging of breast cancer cells. The facile synthesis of green fluorescent CQDs holds great promise to facilitate the practical applications of CQDs.

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说明：

这个论文来源一次好奇的实验，我把浓硫酸和蔗糖放在一起，无意中发现了浓硫酸可以把有机分子碳化为碳纳米，后来经过多次实验和反复摸索，制备出了带有绿色荧光的碳量子点，然后在指导老师们的引导和帮助下，进行了进一步的检测确认，并在应用方面进行了尝试，取得成功。老师们的帮助都是无偿的。

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