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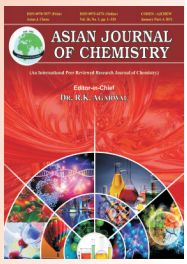

A Simple and Practical Synthetic Method of Carbon Quantum Dots

LIANG GUO[1], YONG ZHANG[1,*] and RUO-XI ZHANG[2]

[1]College of Materials and Chemistry and Chemical Engineering, Chengdu University of Technology, Chengdu 610059, P.R. China
[2]College of Earth Science, Chengdu University of Technology, Chengdu 610059, P.R. China

*Corresponding author: Tel: +86 13350869109; E-mail: yongzh@cdut.edu.cn

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Compared with the traditional quantum dots, carbon quantum dots have excellent optical properties, low cell toxicity, good biocompatibility, easy functionalization and low cost, *etc*. Recently the synthesis of water-soluble carbon quantum dots have attracted more and more attention of researchers. This experiment used nitric acid and hydrogen peroxide as mixed oxidants to activate commercial carbon to synthesize water-soluble fluorescent carbon dots. We investigated the effect of different factors on the fluorescence intensity of carbon dots. Under the optimal conditions, the particle size of carbon dots is about 5 nm, the fluorescence intensity is high and soluble in water, the fluorescence of carbon dots of surface modification is stronger and more stable. We also found that hydrogen peroxide contributed the synthesis of carbon dots. The synthesis method is very simple, low cost, without expensive and large equipment and owns high practicability.

Keywords: Carbon quantum dots, Hydrothermal method, Mixed oxidants, Charcoal activated.

INTRODUCTION

Fluorescent carbon dots, also known as fluorescent carbon nanoparticles, are a kind of new fluorescence nanomaterials following the quantum dots. Fluorescent carbon dots not only have the structural characteristics of carbon nanomaterials and the advantages of traditional quantum dots, but also have more advantages than the traditional quantum dots. The average particle size of this new type of fluorescent carbon nano-particles is less than 10 nm, the luminescent properties are very stable and have a long fluorescence lifetime[1]. Carbon quantum dots have caused the people's extensive concern and become a new research focus in the field of fluorescent nanomaterials[2-4]. There are a lot of carbon dots preparation methods[5-16], but the synthesis conditions of most methods are complex, the fluorescence quantum yields of carbon dots is low and the high cost.

In this paper, we used commercial charcoal activated as carbon source and nitric acid and hydrogen peroxide mixed oxidant oxidation reaction to synthetic water-soluble fluorescent carbon dots and organic reagent passivate the surface of carbon dots, fluorescent of carbon dots is stronger and more stable, the carbon dots can be stored for a long time. We investigated the effect of different factors on the fluorescence intensity of carbon dots and finally found the optimal synthesis conditions, measuring 150 mL nitric acid of 5 mol/L and 30 % hydrogen peroxide 30 mL as mixed oxidants, heating reflux 13 h with magnetic stirring. Under the optimization conditions the particle size of carbon dots is about 5 nm, soluble in water, insoluble in organic solvents.

EXPERIMENTAL

Synthesis of carbon quantum dots: Weighing about 50 mg activated charcoal, measuring 150 mL nitric acid of 5 mol/L and 30 % hydrogen peroxide 30 mL in the three bottle neck, heating to boiling (about 110 °C), refluxing for 13 h with magnetic stirring. After the reaction, cooling to room temperature, in the 3000 rpm TGL-16 desktop high-speed centrifuge (The jin tan city branch analysis instrument co., LTD) centrifuge 10 min to separate unreacted activated charcoal, shallow brown yellow supernatant fluid was collected. Then the supernatant fluid was steamed slowly to nearly dry, the precipitation was dissolved in a small amount of water, adding proper amount of chloroform in 12000 rpm high speed centrifuge centrifuge 10 min. to remove the particles of large particle, The liquid contains fluorescent carbon quantum dots. Ultrasonic oscillations disperse as the standby.

Surface modification of carbon quantum dots: There are many methods of synthesizing carbon quantum dots, but usually the carbon dots prepared are no fluorescent carbon nanoparticles or fluorescence properties of carbon dots are worse. In order to further improve the fluorescence properties of the carbon dots, in addition to select more suitable carbon sources and more efficient preparation method, we can also

use chemical methods to modify surface of carbon dots. The surface modification methods commonly used are: passivation agent modification, metal clad method and doping method. Measuring prepared carbon dots 50 mL (containing about 50 mg carbon dots) in three neck flask of 250 mL, adding 100 mg polyethylene glycol 1500 N, refluxing 36 h with stirring at 110 °C in nitrogen atmosphere. After the reaction, the reaction mixture was cooled to room temperature and then slowly steamed to nearly dry, the product dissolved in water obtain modified carbon dots.

Determination of fluorescence spectra of carbon quantum dots: Through the F-4600 fluorescence spectrometer (Hitachi company) spectral scan carbon quantum dots prepared, we can explore its fluorescence properties. The emission spectra of carbon quantum dots are symmetrical. Using different excitation wavelength spectral scanning on carbon quantum dots, the fluorescence spectra of carbon dots are shown in Fig. 1. The fluorescence emission peak of carbon dots in aqueous solution has a tendency to red shift and the fluorescence intensity decreased with the increase of excitation wavelength. The reason for this phenomenon may be that the surface of carbon dots has different emission sites or particle diameter is not uniform.

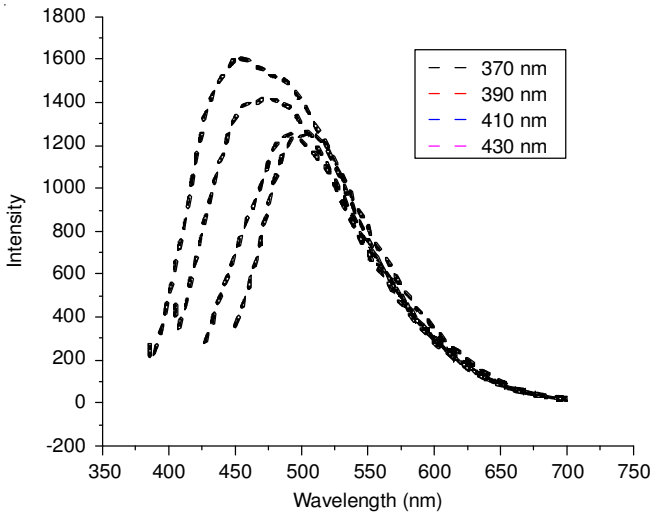

Fig. 1. Fluorescence spectra of carbon dots

RESULTS AND DISCUSSION

Optimization of preparation process: In the optimization of preparation technology, the fluorescence intensity of carbon dots is determined by F-4600 fluorescence spectrometer at room temperature, measuring fluorescence intensity of carbon dots prepared under different conditions in the same instrument conditions to explore the best experimental conditions.

Optimization of reaction time: Measuring fluorescence intensity of carbon dots solution of reacting for 9, 11, 13 and 15 h in the experiment, the results are shown in Fig. 2. Fig. 2 shows that the fluorescence intensity measured also increase with the increase of the reaction time. However, when the reaction time is 15 h, the fluorescence intensity decreases, which maybe the long time reaction leads to carbon dots

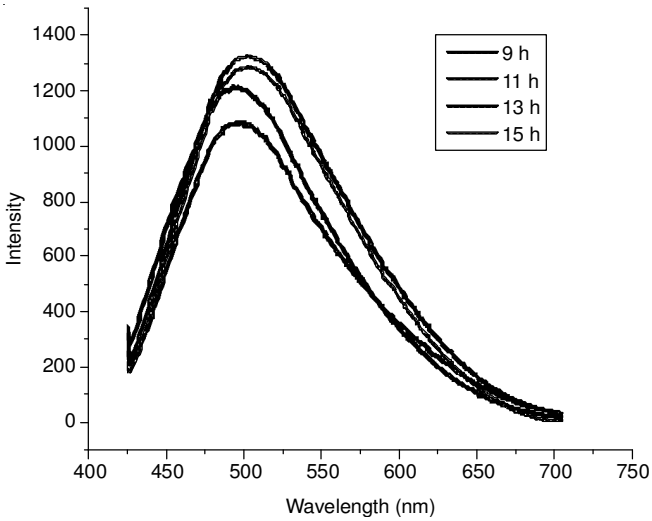

Fig. 2. Selection of response time

corrosion, so that the fluorescence intensity of carbon dots decreased. Therefore, 13 h is the best reaction time.

Optimization of the amount of nitrate: The experiment discussed the influence of nitric acid dosage on synthesis of carbon quantum dots. When nitric acid volume number of mL and mg ratio of charcoal activated is 2:1, 2.5:1, 3:1 and 3.5:1 in the experiment, the measured fluorescence intensity are shown in Fig. 3. Within a certain range, with the increasing of the amount of nitrate, the fluorescence intensity of carbon dots solution also increased. When nitric acid volume mL number and mg ratio of charcoal activated is 3:1, the increasing trend of the fluorescence intensity slow down. Comprehensive consideration, we determine nitric acid volume mL number and mg ratio of charcoal activated is 3:1 as the best dosage of nitric acid.

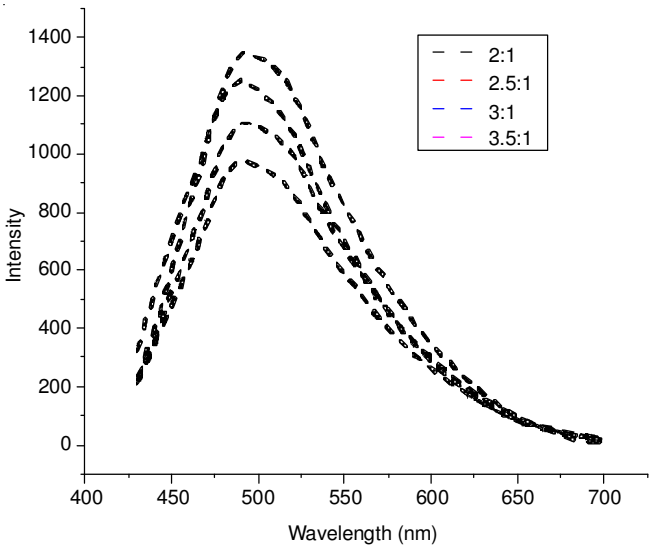

Fig. 3. Optimization of volume of nitric acid

Optimization of the dosage of hydrogen peroxide: Nitrate is the main oxidant, hydrogen peroxide is used as auxiliary oxidant, the dosage of hydrogen peroxide can affect the synthesis of carbon dots. The amount of nitric acid (150 mL) and concentration unchanged, the fluorescence intensity

of carbon dots of adding 10, 15, 20, 25 or 30 mL hydrogen peroxide participate in the reaction were measured, respectively, schematic diagram of the fluorescence intensity change is shown in Fig. 4.

We can see from Fig. 4, compared with the pure nitric acid, after adding hydrogen peroxide, the fluorescence intensity of carbon quantum dots decreased. When volume of hydrogen peroxide was added is larger than 25 mL, the fluorescence intensity of prepared carbon dots has increased significantly, thus a small amount of hydrogen peroxide has quenching effect on carbon dots. When volume of hydrogen peroxide is larger than 25 mL, the hydrogen peroxide contributes to the synthesis of carbon quantum dots. We also found that gradually adding hydrogen peroxide is better than the effect of one-time addition.

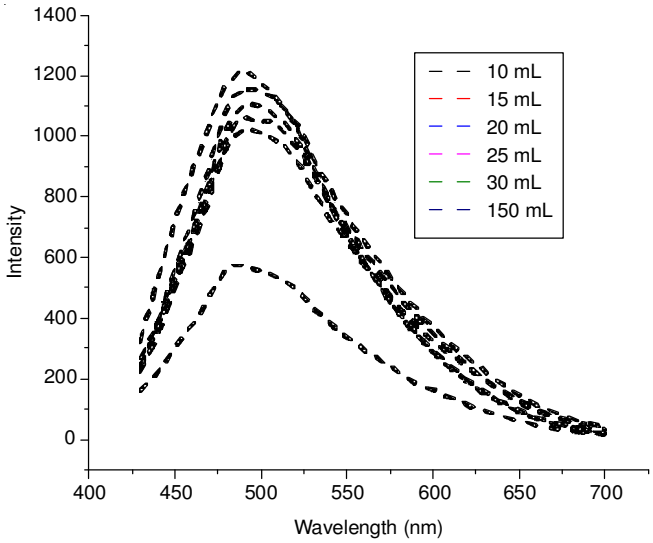

Fig. 4. Optimization of hydrogen peroxide dosage

Characterization of carbon quantum dots: The degree of dispersion of carbon dots and its particle size can be measured by field emission electron microscope. The X ray powder diffraction can be used to characterize the crystallinity of carbon dots and it can roughly determine the particle size. The surface properties of carbon dots can be detected through the Fu Li Ye transform infrared spectrometer.

TEM image of carbon quantum dots: Characterizations of unpassivated carbon quantum dots and passivated carbon quantum dots are detected by TecnaiG2F20 field emission type transmission electron microscope (Holland Philip), TEM images of carbon quantum dots are shown in Fig. 5 (a) and (b).

By the TEM micrographs of the carbon dots shown in Fig. 5, we can see the distribution of unpassivated carbon quantum dots in aqueous solution is uniform, the average particle size is about 5 nm. The particle size of polyethylene glycol passivate carbon dots compared with particle size of unpassivated carbon quantum dots, the particle size of the former should be larger, but the increasing trend is not obvious, which maybe because molecular weight of polyethylene glycol is very small. Most of the particles are perfect sphere, there are also a few irregular particles. This maybe because the chemical bond rupture randomly in the process of chemical oxidation, TEM images of carbon quantum dots look fuzzy, the cause of this phenomenon is mainly that carbon dots are

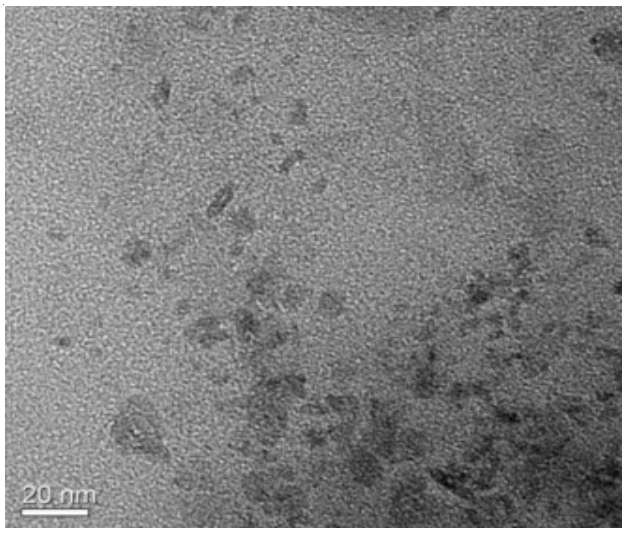

Fig. 5 (a) TEM image of unpassivated carbon dots

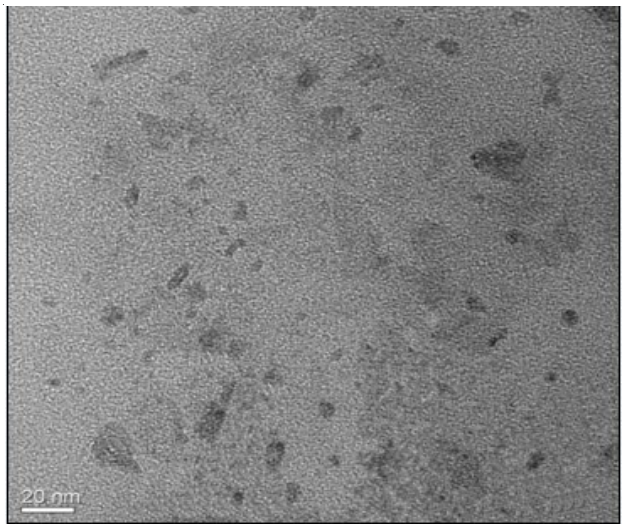

Fig. 5 (b) TEM image of passivated carbon dots

dripped on the carbon film in scanning, target of detection and background are carbon material, so that the detection result is not ideal, at the same time, the concentration of carbon quantum dots is too low, which will also lead to there are not significant scanning traces.

XRD spectra of carbon quantum dots: XRD spectra of carbon quantum dots are measured by DX-2700X ray powder diffraction (Dan dong Fang yuan Instrument Co., Ltd.), the XRD spectrum is shown in Fig. 6.

We can determine that the carbon dots are amorphous by peak type of the XRD spectrum, diffraction peak of its is $2\theta = 28°$, according to Xie Le (Scherrer) equation, the expression is $D = K\lambda/B\cos\theta$, K is Scherrer constant, the value is 0.89; D is grain size (nm); B is the integral half high width, it will be converted to a radians (RAD) in the calculation; θ is the diffraction angle; λ is X wavelength, which is 0.154056 nm. After the calculation, the particle size of carbon dots is about 4.6 nm. The result is consistent with the result of the TEM image.

FTIR spectra of carbon quantum dots: The characterization of surface properties of carbon quantum dots *via* TENSOR 27 infrared spectrometer (Germany BRUKER company), the

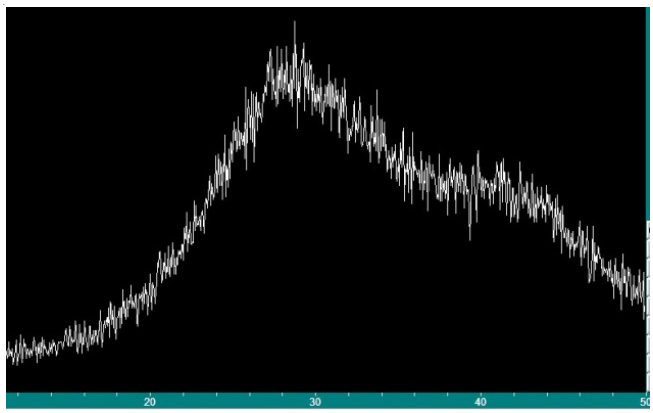

Fig. 6 XRD spectra of carbon dots

result is shown in Fig. 7. There is a strong carbonyl characteristic absorption peak at 1637 cm^{-1} and a strong hydroxyl characteristic absorption peak at 3284 cm^{-1}, we can know that there is formation of hydrogen bonds from its peak shape becoming wide. There is a hydroxyl in-plane bending vibration peak at 1400 cm^{-1}, there is a C-O stretching vibration peak at 1110 cm^{-1}. Through the analysis of the spectrum, we can know that the surface of the carbon dots may contain hydroxyl, carbonyl and carboxyl functional groups. The surface of carbon dots contain many hydrophilic groups, so it is easy to dissolve in the water.

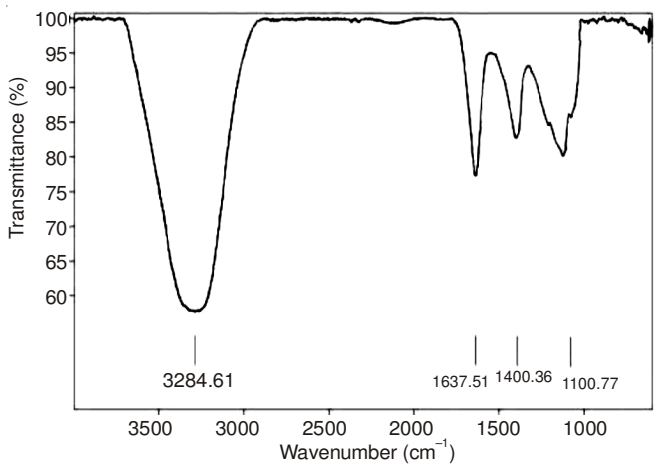

Fig. 7 FTIR spectra of carbon dots

Conclusions

• This experiment has got the best experimental conditions, the best reaction time is 13 h, nitric acid volume mL number and mg ratio of charcoal activated is 3:1.

• A small amount of hydrogen peroxide has fluorescence quenching influence on carbon quantum dots, when the amount of hydrogen peroxide is larger than 25 mL, it will contribute to the synthesis of carbon quantum dots.

• Through the fluorescence spectra of carbon quantum dots we can arrive at such a conclusion that with the incense of excitation wavelength,the fluorescence intensity gets attenuated, the fluorescence emission peak of carbon quantum dots gets lower and has a tendency of red shift.

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