



Solvothermal conversion of coal into nitrogen-doped carbon dots with singlet oxygen generation and high quantum yield



Mingyu Li^{a,1}, Chang Yu^{a,1}, Chao Hu^b, Wenbo Yang^c, Changtai Zhao^a, Shuai Wang^a, Mengdi Zhang^a, Jianzhang Zhao^c, Xiuna Wang^a, Jieshan Qiu^{a,b,*}

^aState Key Lab of Fine Chemicals, School of Chemical Engineering, Liaoning Key Lab for Energy Materials and Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

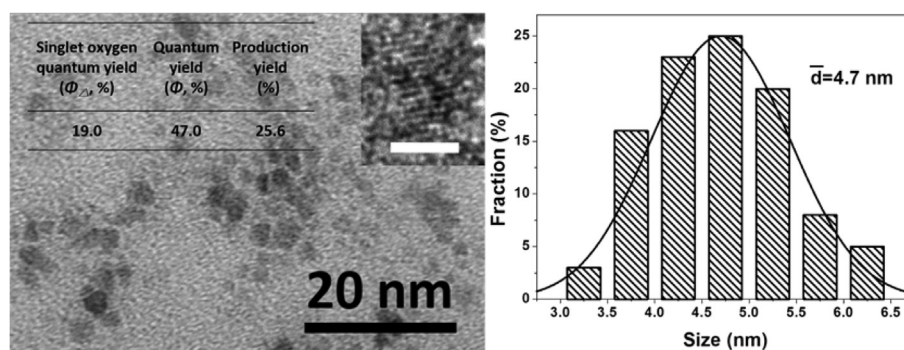
^bSchool of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

^cState Key Lab of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling Gong Road, Dalian 116024, China

HIGHLIGHTS

- Controlled synthesis of nitrogen-doped carbon dots from coal is achieved by a facile solvothermal process.
- The carbon dots feature a high quantum yield up to 47%, as well as singlet oxygen generation behavior.
- The possible mechanism involved in the formation of nitrogen-doped carbon dots is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorescent nitrogen-doped carbon dots (N-CDs) are synthesized by a facile one-pot solvothermal approach from Taixi anthracite in the presence of dimethyl formamide (DMF). Benefiting from superior dispersion of light components in DMF and easy exfoliation of smaller sp^2 -carbon structures from the anthracite, the as-prepared N-CDs show a strong photoluminescence (PL) with a high quantum yield (QY) of 47.0% and production yield of 25.6 wt%. Besides, the N-CDs also exhibit a singlet oxygen (1O_2) generation behavior with a 1O_2 generation QY of 19.0%. Moreover, the as-obtained N-CDs emit blue PL under the excitation wavelength of 365 nm, and can be easily dispersed in polymethyl methacrylate (PMMA), retaining the inherent advantages of the N-CDs and the PMMA matrix. The possible mechanism involved in the formation of N-CDs is proposed and discussed in terms of the macromolecular structure of the anthracite and the solvothermal approach adopted in the study.

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* Corresponding author at: State Key Lab of Fine Chemicals, School of Chemical Engineering, Liaoning Key Lab for Energy Materials and Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China.

E-mail addresses: jqiu@dlut.edu.cn, jasonqiu@xjtu.edu.cn (J. Qiu).

¹ These authors contributed equally to this work.

1. Introduction

Carbon dots (CDs), a kind of newly emerged fluorescent nanomaterial, have been synthesized from various kinds of carbon sources including fullerene, graphite, graphene oxide, carbon

nanotubes and carbohydrates by top-down methods [1–9]. Among these carbon sources available now, low-cost and earth-abundant coal has demonstrated a unique and charming superiority [10–13]. For example, Ye et al. have adopted a wet-chemistry route to fabricate graphene quantum dots by heat treatment of coal via acidic oxidation [13]. In our previous work, ethylenediamine-grafted CDs were synthesized by acidic oxidation of coal coupled with surface grafting of the as-obtained CDs, delivering a high quantum yield (QY) [14]. And the size-controlled fluorescent coal-based CDs were also produced by the combined method including carbonization and acidic oxidation etching [12]. However, all of the approaches mentioned above are carried out in the presence of concentrated acid, which are time-consuming, environmentally unfriendly along with a relatively low QY. On one hand, the subdomains formed by acidic oxidation treatment are energetically unfavorable, thus leading to weakly intrinsic emission [15]. On the other hand, the acidic oxidation produces various oxygen-containing functional groups on CDs, which will provoke nonradiative recombination of electron-hole pairs, thus leading to a relatively low QY [16,17].

It should be noted that the defects and free radicals on the surface of CDs can promote the transfer of light energy from CDs to oxygen, finally leading to the generation of reactive oxygen species such as singlet oxygen ($^1\text{O}_2$) [18]. Such a unique characteristic is capable of extending the practical application of CDs such as in photodynamic therapy field [19]. With this information in mind, the $^1\text{O}_2$ generation ability of CDs is highly concerned.

Herein, we firstly synthesized fluorescent nitrogen-doped CDs (N-CDs) from Taixi anthracite via a facile one-pot solvothermal route in the presence of dimethyl formamide (DMF). The N-CDs can be obtained by rotary evaporation rather than dialysis, and the solvent can be retrieved and recycled, indicative of a simple, green and sustainable process. The as-prepared N-CDs show a strong photoluminescence (PL) with a high QY of 47.0%. Besides, $^1\text{O}_2$ generation behavior is also delivered in N-CDs, with a $^1\text{O}_2$ generation QY up to 19.0%. The present work is an efficient strategy for fabricating N-CDs with high QY, which will provide a new impetus for practical application of the CDs [20–22].

2. Materials and methods

2.1. Materials

One kind of Chinese anthracite from Taixi coal mine was used. Its scanning electron microscopy (SEM) image and analysis data are shown in Fig. S1 and Table S1, respectively. The coal sample without pretreatment was crushed and sieved with a 200 mesh sieve, and fully dried before use. DMF was ordered from Tianjin Fuyu Chemical Reagent Factory of China. Azobisisobutyronitrile (AIBN) was purchased from Tianjin Damao Chemical Reagent Factory of China. Methyl methacrylate (MMA) was bought from Tianjin Bodi Chemical Reagent Factory of China. Dialysis bags (molecular weight cut off = 3500 Da) were purchased from the Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without any further purification. Deionized water was used throughout the experiments.

2.2. Synthesis of N-CDs, carbogenic dots and single coal-based CDs

Pristine anthracite was crushed and dispersed in 20 mL of DMF with a concentration of 2.5 mg/mL. After ultrasonication for 1 h, the mixture was transferred to a Teflon-lined stainless steel autoclave (50 mL) and kept at 180 °C for 12 h. After cooling down, a supernatant brown colloid was achieved by centrifuging at 9000 rpm for 30 min. The powder of CDs can be obtained by rotary

evaporation of the solution, denoted as N-CDs. The comparison experiment was carried out in the absence of the anthracite, yielding the carbogenic dots. Single coal-based CDs were also prepared by chemical oxidation of anthracite following our previous work [12,14].

2.3. Synthesis of N-CDs-polymethyl methacrylate (N-CDs-PMMA) composites

300 mg of AIBN was ultrasonically dispersed into methyl methacrylate (5 mL). After adding the N-CDs, the N-CDs-PMMA composite monoliths were synthesized by solidifying at 50 °C for 24 h, in which the loading fractions of N-CDs in PMMA were controlled to be 0, 2.5, 25, 50, 100, and 200 ppm, respectively.

2.4. Characterization

The morphology of coal was characterized by SEM (QUANTA 450 microscope). The structure of CDs was examined by transmission electron microscopy (TEM, Philips Tecnai G220) and high-resolution TEM (TF30). The Fourier transform infrared (FTIR) spectra were scanned by Thermo Scientific Nicolet iN10. The UV–vis absorption and fluorescence spectra were recorded on a ThermoFisher UV–vis spectrophotometer and ThermoFisher spectrophotometer, respectively. The data of X-ray photoelectron spectroscopy (XPS) were obtained using a Thermo ESCALAB 250 spectrometer with an Al-K α X-ray source. Raman measurements were carried out on Thermo Fisher Scientific DXR Raman Microscope using laser excitation at 780 nm.

2.5. QY measurement

QY determination was achieved according to the previously established procedure [23,24]. Rhodamine B (literature QY 0.31 at 340 nm) was selected as a reference. The QYs were calculated by comparing the integrated PL intensity (excited at 340 nm) and the absorbance value (at 340 nm) of the standard with each of the coal-based CDs, based on the following equation:

$$\Phi = \Phi_r \times \frac{A_r}{I_r} \times \frac{I}{A} \times \frac{n^2}{n_r^2}$$

where Φ is the QY, I is the measured integrated emission intensity, n is the refractive index, and A is the optical density. The subscript “r” refers to the reference fluorophore of a known QY. In order to minimize re-absorption effects, absorbance in the 10 mm fluorescence cuvette was kept under 0.1 at the excitation wavelength of 340 nm.

2.6. $^1\text{O}_2$ generation QY (Φ_Δ) measurement

Φ_Δ value of the triplet photosensitizer was determined according to a modified literature method with the Ir(ppy) $_2$ bpy ($\Phi_\Delta = 0.92$ in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (9:1, v/v)) as the standard [25]. 1, 3-Diphenylisobenzofuran (DPBF) was used as the $^1\text{O}_2$ scavenger due to its fast reaction with $^1\text{O}_2$. The absorbance of DPBF was adjusted around 1.0 at the maximum absorbance wavelength of 414 nm by changing the amount of the air-saturated $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solvent. The photosensitizers Ir(ppy) $_2$ bpy and the N-CDs were added to the cuvette, respectively, and the absorbance was adjusted to around 0.2–0.3 by increasing the proportion of the solvent. The crossover wavelength of the photosensitizers Ir(ppy) $_2$ bpy and the N-CDs was at 355 nm. In this case, 355 nm was chosen as the excitation wavelength of the samples to exclude the effects of the absorption correction factor (Fig. S2). Then the cuvette was exposed to monochromatic light with an energy of

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