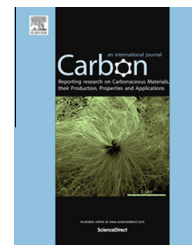


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Organic amine-grafted carbon quantum dots with tailored surface and enhanced photoluminescence properties

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ABSTRACT

A facile one-step synthesis strategy has been developed for producing fluorescent carbon quantum dots (CQDs) from a kind of Chinese coal, Jincheng anthracite. Surface grafting of the CQDs was completed and systematically investigated by grafting with a series of organic amino molecules. It was found that the solubility and the optical properties of CQDs vary with and depend on its surface chemistry to some degree. Of organic amine-grafted coal-derived CQDs available now, ethylenediamine-grafted CQDs (EDA-CQDs) possess an obviously enhanced photoluminescence (PL) with the quantum yield (QY) as high as 18.6%, being an increase of 24.5 times in comparison with that of the pristine CQDs (0.73%), and have a capability of well dispersing within other polymer matrixes due to their good compatibility after amine-grafting. The hybrid monolith made of amine-grafted CQDs and polymer gelatin exhibits excellent PL properties even at a relatively high concentration of CQDs, indicative of great potential applications in various optical materials and devices.

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1. Introduction

Carbon quantum dots, as an emerging new class of fluorescent nanomaterials, have drawn an increasing attention due to their high photostability against photobleaching, tunable excitation and emission wavelengths, good biocompatibility and low molecular weight in comparison with semiconductor quantum dots and other fluorescent nanoparticles [1–4]. So far, various methods have been explored to prepare CQDs, such as electrochemical synthesis [5–9], acidic oxidation [10,11], supported synthesis [12,13], microwave assisted methods [14–16], ultrasonic synthesis [17], arc discharge [18] and laser ablation [1,19–22]. Among these methods available now, chemical oxidation with strong acids or oxidants has

become a popular strategy, in which high-quality CQDs can be prepared at low cost and large-scale production. Besides, a series of carbon sources, including graphite oxide [14], carbon nanotubes [23], ammonium carboxylate salts [24], carbon soot from natural gas [25] and burning candles [11] and carbohydrates [15] have been used to prepare CQDs. It was found that, coal, as a kind of abundant and affordable carbon source, has demonstrated a charming superiority in comparison with other carbon sources [26]. In addition, although various methods and carbon sources have been investigated in the preparation of CQDs, the CQDs with a high quantum yield (QY) are still sought after and highly desirable. It is believed that surface grafting with organic agents is a feasible strategy to improve and tailor the PL properties of CQDs and provide

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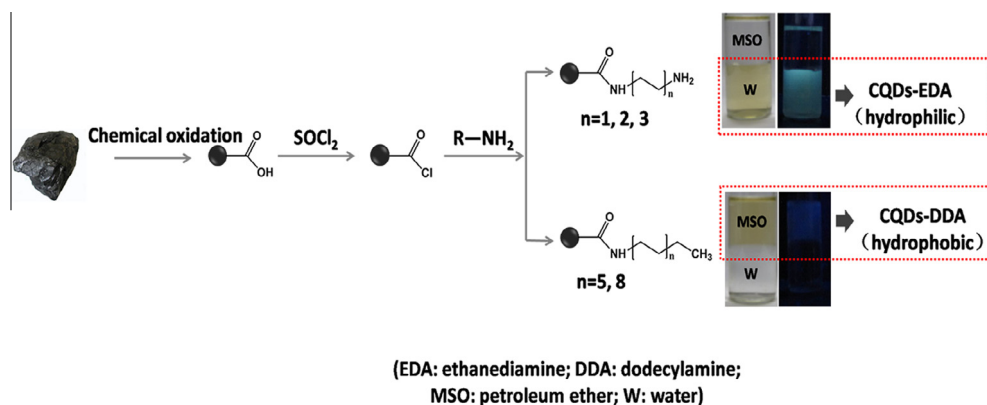


Fig. 1 – The schematic diagram for the surface grafting of CQDs. (A color version of this figure can be viewed online.)

an important method for modification of fluorescent nanoparticles [27–30]. Gogotsi and his co-workers have successfully reported the synthesis of fluorescent nanodiamond by covalent linking of octadecylamine to the surface of nanodiamond. The surface-modified nanodiamond shows a remarkably blue fluorescence and enhanced dispersion property [28]. However, the influences of various grafting agents on the properties of coal-based CQDs and their sensitivity to organic amino agents have never been explored systematically.

Herein, we first synthesized fluorescent CQDs from Jincheng anthracite via an inexpensive and facile one-step wet chemistry route. Besides, the as-obtained CQDs were grafted with various organic amino molecules. The influences of the amino groups with different lengths of the hydrocarbon chains on the PL properties of the coal-based CQDs were systematically investigated and compared. Fig. 1 illustrates the schematic of the surface grafting process, which was carried out by refluxing CQDs in the presence of sulfoxide chloride, followed by stirring with different amides under N₂ protection to link the amino group on the edge of CQDs. The modified CQDs demonstrate enhanced PL properties with high QY, and its surface hydrophilicity and hydrophobicity can be tuned and controlled due to the existence of surface amino groups, leading to controllable stabilization of CQDs in the water or organic phase. CQDs/gelatin hybrid monoliths can be produced by homogeneously dispersing amine-grafting CQDs in gelatin. It is believed that such unique characteristics will provide potential possibilities for various optical materials and devices [29,31].

2. Experimental

2.1. Materials

The carbon source is anthracite from Jincheng, China. Its analysis data are shown in Table S1. The coal sample without pre-treatment was crushed and sieved to 74 μm, and fully dried before use. Dialysis bags (molecular weight cut off = 3500 Da) were purchased from the Sinopharm Chemical Reagent Co., Ltd. Concentrated nitric acid (65–68 wt.%) and sodium hydroxide were ordered from Tianjin Damao Chemical Reagent Factory of China. Gelatin was bought from Tianjin Bodi Chemical Reagent Factory of China.

2.2. Synthesis of the CQDs

Pristine CQDs were prepared by chemical oxidation and etching from the Jincheng anthracite, which had been reported in our previous work [32]. For a typical run, 120 mg coal was dispersed in a 30 mL of concentrated nitric acid under ultrasonication for 1 h, keeping stirring at 140 °C for 24 h. The reaction system was then cooled down to room temperature, followed by continuously dropping sodium hydroxide into the above solution to turn it to neutrality, yielding a supernatant yellow colloid that was separated from the sediment by centrifuging at 9000 rpm for 30 min, and then dialyzed (3500 Da) for 3 days to remove the nitrate, yielding the CQDs.

2.3. Synthesis of the surface-modified CQDs

For a typical procedure, 30 mL thionyl chloride was mixed with the solid of as-made CQDs, and after ultrasonic treatment for 1 h, the excess thionyl chloride was removed by evaporation. The acyl chloride derivative was stirred in a sealed flask with a series of organic amino groups including EDA, butanediamine (BDA), hexanediamine (HMDA), dodecylamine (DDA) or octadecylamine (ODA) in N₂ atmosphere at 110 °C, yielding a series of grafted CQDs, respectively, such as EDA-CQDs, BDA-CQDs, HMDA-CQDs, DDA-CQDs, and ODA-CQDs. The as-obtained hydrophilic CQDs, including EDA-CQDs, BDA-CQDs and HMDA-CQDs were vacuum-distilled to remove the solvents, then washed with ethanol several times, and finally vacuum-dried overnight. Besides, the DDA-CQDs and ODA-CQDs were purified by extraction with hot methanol in a Soxhlet apparatus [28].

2.4. Characterization

Scanning electron microscopy (SEM) of the coal structures was performed by a QUANTA 450 microscope. The CQDs were examined by X-ray diffraction (XRD) (Cu Kα, λ = 1.5406 Å) and transmission electron microscopy (TEM, Philips Tecnai G² 20). The UV–vis absorption spectra were recorded on a Thermofisher UV–vis spectrophotometer. Fluorescence spectra were recorded by a Hitachi F-7000 spectrophotometer. The Fourier transform infrared (FTIR) spectra were scanned on a Bruker EQUINOX 55 and Thermo Scientific Nicolet iN10.

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