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Engineering surface structure of petroleum-coke-derived carbon dots to enhance electron transfer for photooxidation

Xiaodong Shao [†], Wenting Wu [*,†], Ruiqin Wang, Jinqiang Zhang, Zhongtao Li, Yang Wang, Jingtang Zheng, Wei Xia, Mingbo Wu [*]

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Qingdao 266580, China

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ABSTRACT

Many abundant and inexpensive materials are being developed for the synthesis of carbon dots. However, the structures of most raw materials are complicated, which inevitably bring difficulties for the optimization of their photocatalytic ability, especially for the electron transfer properties. Herein, petroleum coke was selected as raw material to prepare carbon dots (CDs). The types and contents of the functional groups —C=O and/or —S=O) on CDs surface were finely tuned by facile chemical oxidation, enhancing both of the electron-accepting (11.9 and 3.5 times) and electron-donating abilities (1.7 and 1.4 times). The photocatalytic efficiency of the optimized carbon dots (C-120) in the photooxidation of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (1,4-DHP) is 6.6 times higher than that of CDs with few functionalized groups. The present study demonstrates a feasible and effective strategy to solve the poor electron transfer difficulty of CDs and also helps to understand the regulating strategies and mechanisms of surface structure.

1. Introduction

Since their discovery in 2004, [1] carbon dots (CDs) have become a research hotspot due to their superior properties, such as high aqueous solubility [2,3], outstanding biocompatibility [4–6], broadband absorbing ability [7,8], and others [9,10]. To achieve scalable and cost-effective preparation, many abundant and inexpensive materials have been developed for the synthesis of CDs. For example, Tour et al. [11] reported a facile approach to synthesizing tunable graphene quantum dots from coal. Furthermore, Qiu [12] tailored inexpensive coal to fluorescent CDs via a combined method of carbonization and acidic oxidation etching. Petroleum coke, a byproduct in the oil refining process, has been demonstrated to be good raw material for production of porous carbons [13]. Petroleum coke is rich in benzene rings or aromatic domains and contains a graphene structure that makes it possible to prepare high-performance CQDs. In addition, most of these studies focused on the photoluminescent properties of CDs [14]. Actually, CDs themselves show great potential for photocatalysis, and there is much room left for improvement of the functionalized CDs derived from inexpensive and abundant raw materials for photocatalysis.

Photocatalysis involves three key steps: absorption of photons, electron–hole separation and transfer, and subsequent surface redox reactions [15,16]. Among these steps, electron transfer plays a key role in photooxidation reactions, which has been studied extensively [3,17]. Kang [18] prepared CDs/C_3N_4 composites to improve the efficiency of electron transfer due to the fabrication of heterojunctions. For CDs themselves, the Cu–N dopant was used to enhance the efficiency of electron transfer [3]. However, these strategies are hardly employed with CDs derived from raw materials. Actually, many functional groups, such as —C=O and —S=O, are strong electron-withdrawing groups and can easily be introduced onto the surfaces of CDs by chemical methods. To some extent, they could influence the band structure and the impetus of electron transfer, which has rarely been reported.

Here, petroleum coke, a byproduct in oil refining processes, was selected as the raw material for preparing CDs due to its abundant benzene rings or aromatic domains and graphene structure [14,13]. The surface structures of CDs were tuned by chemical oxidation with a mixture of concentrated H_2SO_4 and HNO_3 (C-120, C-180) or only with HNO_3 (H-120, H-180) at different temperatures (120 and 180 °C), where H_2SO_4 was used to tune —S=O and the temperature was used to alter the content of —C=O. The surface structures of CDs were confirmed by transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman, FT-IR and XPS. After the introduction of —C=O, the electron-accepting ability of C-120

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[*] Corresponding authors.
E-mail addresses: wuwt@upc.edu.cn (W. Wu), wumb@upc.edu.cn (M. Wu).
[†] These authors contributed equally to this work.

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is 11.9 times higher than that of C-180, while the electron-accepting property of C-120 is 3.5 times higher than that of H-120, as a result of the introduction of —S═O. At the same time, the electron-donating ability of C-120 is 1.7 and 1.4 times higher than those of C-180 and H-120, respectively. It is believed that the presence of —C═O and —S═O can influence the electron transfer process, giving rise to distinct photocatalytic performance.

2. Experimental

2.1. Synthesis of carbon dots

Materials synthesis: Petroleum coke (2.0 g) was added into a mixture of concentrated H_2SO_4 (45.0 mL, 18 M) and HNO_3 (15.0 mL, 15.2 M) or into HNO_3 (60 mL, 15.2 M) alone in a flask under ultrasonic conditions for 2 h, and then refluxed under constant stirring in an oil bath at 120 or 180 °C for 12 h, respectively. After the reaction, the mixture was cooled to room temperature and diluted 10 times with deionized water and neutralized with ammonia to pH 7.0. The neutralized mixture was filtered by a filter membrane (0.22 μm) to remove the larger fractions, yielding a solution containing CDs that was further dialyzed with MD 34 (3500 Da) for 72 h to remove the remaining salts and tiny fragments.

Reduction of CDs: Portions of 1 g phenylhydrazine (99%, Aldrich) and 1 mL HCl acid (38%) were dissolved in 200 mL $CHCl_3$, and then 500 mg CDs was added into the solution. After stirring under N_2 for 72 h, the precipitate was filtered out and washed with $CHCl_3$ in Soxhlet extractor for 20 h to remove the physical adsorbed molecules, such as phenylhydrazine. The precipitate was dried under vacuum at 60 °C for 24 h to make R-120.

2.2. Sample characterization

Transmission electron micrograph (TEM) images were taken on a JEOL JEM-2100UHR microscope with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) was performed using a PANalytical X-ray diffractometer equipped with Cu*K*α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA). Further evidence for the composition of the product was inferred from X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250Xi spectrometer equipped with a prereduction chamber. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer. Raman spectroscopy was performed using an Ar^+ ion laser at 514.5 nm (Renishaw in Via 2000 Raman microscope, Renishawplc, UK) to assess the graphitic structure of raw materials and products. UV–vis absorption spectra were measured by a DRSUV-2450 UV–vis spectrophotometer (Shimadzu, Japan). Fluorescence spectra were measured by an F-97 Pro spectrofluorometer (Shanghai Lengguang Technology Co., Ltd., China).

2.3. Photooxidation of 1,4-DHP

Photooxidation was carried out according to a modified method from the literature [19]. An ethanol/water mixed solvent (1:1 v/v, 20 mL) containing 1,4-DHP (1.0×10^{-4} M) and the photosensitizer (CDs) were put into a two-necked round-bottom flask (50 mL). The solution was then irradiated using a xenon lamp with a power of about 35 W (600 W m^{-2}, $\lambda = 385$–800 nm) through a cutoff filter (0.72 M $NaNO_2$ solution, which is transmittal for light with $\lambda > 385$ nm). UV–vis absorption spectra were recorded at intervals of 2–5 min. The consumption of 1,4-DHP was monitored by the decrease in absorption at 374 nm, and the concentration of 1,4-DHP was calculated using its molar absorption coefficient ($\varepsilon = 7744$ M^{-1} cm^{-1}).

2.4. Electron spin resonance spectroscopy

Electron spin resonance (ESR) spectra were recorded at room temperature using a JEO JES FA200 spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis in the dark and illuminated directly in the cavity of the ESR spectrometer. All optical measurements were performed at room temperature.

3. Results and discussion

3.1. Modifying the surface structure of carbon dots

Since the functionalized groups (e.g., —C═O and —S═O) show strong electron-withdrawing ability, they have a great potential to tailor the photooxidation properties of materials. Here, CDs were carefully prepared by chemical oxidation of petroleum coke with a mixture of concentrated sulfuric acid and nitric acid under different temperatures, (120 and 180 °C, namely C-120 and C-180, respectively. The various temperatures provide a facile way to tune the —C═O content of CDs. When the temperature is lower than 120 °C, CDs are difficult to obtain. As the temperature exceeds 180 °C, the functionalized groups (—C═O) easily escape as gaseous byproducts from the solution, causing a decrease in oxygen-containing functional groups on the surface of CDs [20]. At the same time, H_2SO_4 was used to introduce —S═O. For comparison, H-120 and H-180 with no —S═O (in contrast to C-120) were prepared with only HNO_3 at 120 and 180 °C, respectively. To some extent, the number of these functionalized groups on CDs could be finely controlled by the preparation temperature and chemical oxidant. Furthermore, the sizes of CDs were uniformly confined by the dialysis for the sake of eliminating the size-confinement effects. Here, C-120 with rich oxygen-containing functional groups was selected as a good candidate for photooxidation, which is proved in Section 3.3.

3.2. Characterization of the petroleum-coke-derived carbon dots

The morphology and physical structure of CDs were studied by TEM, XRD, and Raman spectroscopy. Fig. S1a in the Supplementary Material shows the particle size distribution of C-120, revealing that the diameter of C-120 is about 1.7 nm. The insets in Fig. S1a are typical high-resolution TEM (HRTEM) images of C-120, which indicates a certain crystallinity with a lattice space of 0.33 nm, corresponding to the lattice fringes of the (002) planes of graphite [21]. The XRD and Raman spectroscopic results are consistent with these results (Figs. S1b and S1c) [22,23], supporting the formation of a graphite-like structure, which is assumed to be beneficial for electron transfer during the photocatalysis.

The functional groups on the surface of C-120 were studied by FT-IR and XPS spectra (Fig. 1b–d). Obviously, they are packed with oxygen functional groups. The small peaks at 1608 cm^{-1} are caused by a carbonyl group (C═O) conjugated with the benzene ring stretching vibration. The existence of sulfonic groups is demonstrated by the characteristic absorption bands at 1065 and 651 cm^{-1}, which are assigned to the symmetric stretching of S═O and the C—S stretching vibration, respectively. As the reaction temperature increases, the content of C═O decreases sharply (Fig. 1b and c). When the temperature reaches 180 °C, there is little C═O in C-180, which could be attributed to the deep oxidation of C═O into carbon dioxide [20]. These results are consistent with those of XPS (Fig. 1b). The XPS spectrum of C1*s* (Fig. 1c) from CDs can be deconvoluted into three smaller peaks, which are ascribed to the following functional groups: sp^3 bonded carbon (C—C,