



Graphene structure boosts electron transfer of dual-metal doped carbon dots in photooxidation



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ABSTRACT

Carbon dots as a novel photocatalyst have attracted much attention, but they are still limited by their poor electron transfer properties. It is worth noting that graphene structures as a major component of carbon dots, play an important role in the electron transfer properties and photocatalysis. Herein, under different calcination temperature, carbon dots with various graphitization degrees were prepared from the mixture of EDTA-Fe and EDTA-Cu via a facile one-step pyrolysis. The graphitization degree of FeCu-CDs was proved by means of Raman, XRD and XPS spectra. The FeCu-CDs prepared at high temperature have higher graphitization degree and show excellent electron transfer ability. On the other hand, unsaturated metal dopants with mixed valence states (Fe^{2+} , Fe^{3+} , Cu^+ and Cu^{2+}) were fabricated and proved by XPS, ESR and FT-IR spectra, which are beneficial to further enhance both the electron donating/accepting abilities by changing their valence state. This higher graphitization degree and its synergy with dual metal dopants in FeCu-CDs can promote the photocatalytic efficiency in the photooxidation reaction of 1,4-DHP.

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1. Introduction

The development and exploration of renewable and abundant solar energy have attracted widespread attention [1–7]. In this regard, much efforts have been devoted to the exploration of efficient and low cost photocatalyst for solar energy conversion and energy storage [8,9]. Fortunately, carbon dots (CDs), as a relatively new class of nano carbon materials, have broadband absorption ability and abundant functional groups, and they show great potential in the field of photocatalysis [10,11]. For the photocatalysis, they have three key factors: broadband absorption ability, excellent electron transfer and proper photoredox properties [12]. There is still much room left for the improvement of the CDs' properties mentioned above, especially for the electron transfer. Based on the CDs' structure, its electron-transfer improvement could be mainly divided into two parts: CDs' surface and their interior structure. Sun et al. utilized surface attachment with oligomeric ethylene glycol diamine (PEG) to enhance the electron transfer [13]. We have also reported the modification with strong surface groups to improve

the electron transfer properties of CDs derived from raw materials (petroleum coke) [14]. For the improvement of CDs' interior structure, Cu–N dopants in CDs were designed to enhance both electron donating and accepting abilities [15]. Actually, graphene structure is an important component for most CDs' interior structure, which cannot be neglected in the improvement of electron transfer properties.

Graphene has exceptional electronic and optical properties, and to some extent, the graphene degree could strongly influence CDs' electron transfer properties [16–19]. In the metal doping CDs system, graphene is the major component, and it could act as a ligand to chelate with metal in the metal doping CDs system [15]. After irradiation, the graphene may easily accept the photo energy, and promote the electron transfer to the metal dopants through its own pathway. In another point of view, the metal dopants' properties, such as valence state, may change during this process, and it may provide a unique electron transfer pathway for the photocatalysis [20–23]. Moreover, the presence of graphene structure could enhance the extension of light absorption range, the intensity of absorbed light, and chemical stability of photocatalyst [24].

Herein, through a facile one-step pyrolysis, dual-metal doped CDs (FeCu-CDs) with different graphene degree were prepared from the mixture of EDTA-Fe and EDTA-Cu under various

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temperature. It provides an insight into the synergy effect of graphene on the metal dopants and photooxidation. The graphene structure and its degree were carefully studied by TEM, Raman, XRD and XPS spectra. With the assistance of graphene structure, the metal dopants in FeCu-CDs come to mixed valence states (Fe^{2+} , Fe^{3+} , Cu^+ and Cu^{2+}), which were confirmed by X-ray photoelectron (XPS) spectroscopies, FT-IR spectra and Electron spin resonance (ESR). With optimized pyrolysis temperature and mass ratio of EDTA-Fe and EDTA-Cu, the higher graphitization degree and its synergy with metal dopants in FeCu-CDs could enhance the electron transfer abilities and promote extraordinarily high activity for the photooxidation of 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (1,4-DHP), which is the key component in various bioactive compounds and a good substrate for the production of pyridine derivatives [25,26]. And pyridine derivatives have found applications in various fields such as in the synthesis of drugs, herbicides, or insecticides [27–29]. The conversion of 1,4-DHP catalyzed by FeCu-CDs is 8 times higher than that of pure CDs. A possible mechanism of the photocatalytic reaction process was proposed based on the measurements of ESR signal of metal dopants and superoxide anion radical ($\text{O}_2^{\cdot-}$) at different irradiation time.

2. Experimental

2.1. Chemicals

Ethylenediaminetetraacetic acid ferric sodium salt (EDTA-Fe), ethylenediaminetetraacetic acid copper disodium salt (EDTA-Cu) and ethylenediaminetetraacetic acid disodium salt (EDTA-Na) were purchased from Liaoyang Wan Rong Chemical products Co., Ltd., China. All chemicals were directly used without further purification in our experiments.

2.2. Preparation of 350-FeCu-CDs

Typically, the CDs were prepared via a facile one-step pyrolysis that has been reported by our group before [15]. A quartz boat filled with EDTA-Fe and EDTA-Cu (the mass ratio was 1:2, 1:1 and 2:1 named 350-FeCu-CDs-1, 350-FeCu-CDs-2 and 350-FeCu-CDs-3) was put into the center of a quartz tube, and calcined in a tube furnace at 350 °C for 2 h at a heating rate of 5 °C/min under flowing N_2 atmosphere. When the temperature is higher than 350 °C, the polymerization degree is too high to form FeCu-CDs in the nanoscale, resulting instead in the formation of powders on the microscale. So the 350 °C was selected as the highest reaction temperature. The collected target product was grinded and dissolved in water (150 mL), and the mixture was processed by the ultrasonic treatment for 20 min at room temperature. The pre-treated product was filtered with slow-speed quantitative millipore filter (0.22 μm) to remove insoluble substance. After filtering process, the solution was dialyzed with MD34 (3500 Da) dialysis tube for 48 h to remove the remaining salts and small fragments. The solution was dried at 60 °C and 350-FeCu-CDs powder was obtained. The dual metal doping CDs are referred to as 350-FeCu-CDs. In the following introduction, the CDs (Fe: Cu = 1:2) was named as 350-FeCu-CDs uniformly if there is no special description.

Single metal doping CDs was prepared using only EDTA-Fe or EDTA-Cu at 350 °C named Fe-CDs and Cu-CDs. Meanwhile, no metal doping CDs was prepared using EDTA-Na, the product was named as Na-CDs.

2.3. Preparation of 250-FeCu-CDs

The mixture of EDTA-Fe and EDTA-Cu (the mass ratio was 1:2,

1:1 and 2:1 named 250-FeCu-CDs-1, 250-FeCu-CDs-2, 250-FeCu-CDs-3) was calcined at 250 °C for 2 h at a heating rate of 5 °C/min under N_2 atmosphere. Other experiments conditions were unchanged. The CDs (Fe: Cu = 1:2, 250 °C) was named as 250-FeCu-CDs uniformly.

2.4. Photooxidation of 1,4-DHP

Photooxidation was carried out according to a modified literature method [15]. 1,4-DHP, an organic substance, can be dissolved in the mixture of ethanol and water, wherein ethanol could dissolve 1,4-DHP and water could reduce the cost of photooxidation. An ethanol/water (1:1 v/v, 20 mL) mixed solvent containing 1,4-DHP (1.0×10^{-4} M) and the photosensitizer (CDs, 0.15 mg/mL) was put into a 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} , $\lambda > 385 \text{ nm}$) through a cutoff filter (0.72 M NaNO_2 solution, which can filter the wavelength of $\lambda < 385 \text{ nm}$). UV–Vis absorption spectra were used to record at intervals of 10 min. The consumption of 1,4-DHP was monitored by a decrease in the absorption at 374 nm.

2.5. Samples characterization

Transmission electron micrographs (TEM) images were taken on a JEOL JEM-2100UHR microscope with an accelerating voltage of 200 kV. X-ray powder diffraction (XRD) was obtained by using PANalytical X-ray Diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$, 40 kV, 40 mA). Further evidence for the composition of the product was inferred from X-ray photoelectron spectroscopy (XPS), using ESCALAB 250Xi spectrometer equipped with Al X-ray source. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer. Raman spectra measurement was carried out by using Raman Microscopy (Horiba, LabRAM HR Evolution, France) with an excitation wavelength of 532 nm. The Fe and Cu contents in the FeCu-CDs were measured by atomic absorption spectroscopy (AAS, contr AA700), which was produced by Analytikjena. UV–Vis absorption spectra were measured by a UV–Vis spectrophotometer (UV-2700, SHIMADZU). Fluorescence spectra were measured by a spectrofluorometer (F-97 Pro, Shanghai Lengguang Technology Co., Ltd., China). Electron spin resonance (ESR) spectra were recorded at room temperature using a JEOL 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. Structural characterization of FeCu-CDs

The morphology and structure of 350-FeCu-CDs were firstly studied as shown in Fig. 1a and Fig. S1. 350-FeCu-CDs are monodisperse and uniform, and the average diameters of the 350-FeCu-CDs are about 4.2 nm. High-resolution TEM (HRTEM) image (inset image in Fig. 1a) exhibits a good crystallinity of 350-FeCu-CDs with a lattice spacing of 0.2 nm which could be attributed to the lattice fringes of the (100) plane of graphite carbon [30–32]. XRD patterns of 350-FeCu-CDs and 250-FeCu-CDs were shown in Fig. S2a. There is a diffraction peak at 25.5° which is the characteristic peak of carbon corresponding to the (002) plane of graphitic carbon [30]. Compared with 250-FeCu-CDs, the peak of 350-FeCu-CDs is narrower indicating that 350-FeCu-CDs has higher graphitization degree [33]. Fig. S2b reveals the Raman spectra of 350-FeCu-CDs and

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