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Chemiluminescence behavior of the carbon dots and the reduced state carbon dots

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ABSTRACT

Potassium permanganate (KMnO₄) can react with two different carbon nanoparticles, i.e., carbon dots (CDs) and reduced state carbon dots (r-CDs), in a strong acid medium to generate chemiluminescence (CL). Furthermore, the different CL intensities and CL behaviors due to the different surface groups on these two kinds of carbon nanoparticles were confirmed. CL spectra, fluorescence spectra, UV–vis absorption spectra, and electron paramagnetic resonance spectra were applied to investigate the CL mechanism. The main reaction pathways were proposed as follows: for the CL reaction between CDs and KMnO₄, the excited states of CDs (CDs*) and Mn(II) (Mn(II)*) emerged as KMnO₄ could inject holes into CDs, then, the CDs* and Mn(II)* acted as luminophors to yield CL; in the r-CDs-KMnO₄ system, r-CDs were oxidized by KMnO₄ directly, and CDs* and Mn(II)* were produced, at the same time, CL occurred. What is more interesting is that the CL intensity of the r-CD system is stronger than that of the CD system, which confirms that functional groups have strong effect on the CL behavior. It inspired us that new carbon nanoparticles with excellent luminous performance can be designed by tuning their surface groups.

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1. Introduction

Fluorescent quantum dots (QDs) have been widely investigated for their unique optical properties and their potential applications in sensing [1,2], catalysis [2,3], imaging [4], and optoelectronic devices [5]. However, most conventional QDs contain heavy metals, such as Cd, which is potentially toxic and hazardous to environment and their applications are limited [6–8]. Recently, carbon dots (CDs) emerged as a new kind of fluorescent carbon nanomaterial [9], have received much attention due to their high photostability against photo-bleaching, no blinking, biocompatibility, low toxicity, and environmental friendliness as compared with the metal-based QDs [10–14]. Therefore, they have been successfully used in bioimaging [10,11], catalysis [12–14], and sensing [15,16]. However, the range of CDs practical applications is also scarce and further work is still necessary.

Particularly, the application of CDs as luminophor still remains sparse. The chemiluminescence (CL) properties of CDs have gained more attention recently [17–20]. For example, Lin et al. and Xue et al. [17–19] reported the CL of CDs in the presence of ONOOH or

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classical oxidants, and they found that the CDs could enhance the CL of H₂O₂–HSO₃[−]. Jiang et al. [20] demonstrated that the CDs could greatly enhance NaIO₄–H₂O₂ CL reaction. In these systems, the CDs were passivated by poly (ethylene glycol) (PEG) [17–19] or doped with nitrogen atoms [20] and the CDs acted as reductant [17], luminophors [18], or energy acceptors [19,20]. However, the CL of bare CDs without passivation or doping and the effect of surface groups on the CDs CL properties were rarely investigated. Detailed investigation of these surface properties of CDs is still an interesting challenge inspiring intensive research effort.

We have used a simple reduction pathway to change the surface groups of bare CDs and found that the surface groups of CDs played an important role in their photoluminescence behavior [21]. The reduction pathway can prepare the reduced state CDs (r-CDs) without any passivating or doping treatment. Herein, we chose the bare CDs and r-CDs as models to investigate the surface group effect on the CL behaviors of CDs for the first time. CL signals can be observed after mixing these two kinds of CDs with KMnO₄. The mechanism of the CL was investigated by CL spectra, fluorescence spectra, UV–vis absorption spectra, and electron paramagnetic resonance (EPR) spectra. Our results demonstrated that the CL behavior of the two systems is different and the CL intensity of r-CD system is much stronger than that of the CD system. We believe our research will be valuable both for understanding the relationship of CL behavior and the surface

groups of CDs, and for design and synthesis of the CDs with excellent CL properties.

2. Experimental section

2.1. Materials and reagents

Lamp black was purchased from Anhui Jixi Hukaiwen Ink Industry Co. (Jixi, China). Sodium borohydride (NaBH_4) was purchased from Kelong Chemical Reagent Factory (Chengdu, China). Potassium permanganate (KMnO_4), nitric acid (HNO_3), hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) were from Chuandong Chemical Reagent Company (Chongqing, China). *L*-histidine was obtained from Beijing Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Dialysis bags (molecular weight cut off=3500) were purchased from Green Bird Science & Technology Development Co., Ltd. (Shanghai, China). Ultra-pure water was prepared by a Milli-Q-Plus system (USA) and used throughout.

2.2. Synthesis of CDs and r-CDs

The CDs were prepared as Liu et al. [22] and Mao et al. [23] had reported. Briefly, lamp black (0.5 g) was added to HNO_3 solution (5 mol/L, 150 mL) and the mixture was heated under reflux at 140 °C for 12 h. The dark-brown CD solution was neutralized with sodium carbonate. The supernatant was collected by centrifugation at 12,000 rpm for 15 min and it was then loaded into dialysis bags for dialysis against ultra-pure water for 48 h. The purified CD solution was stored at 4 °C for further use. To prepare r-CDs, excessive NaBH_4 was mixed with the aqueous solution of CDs and then stirred gently overnight at room temperature. Excess reductant was removed by dialysis mentioned above, and the obtained r-CD solution was stored at 4 °C.

2.3. High-resolution transmission electron microscopy (HRTEM)

CD and r-CD samples were prepared by dropping the CD and r-CD aqueous solution onto 400-mesh carbon coated copper grids (SPI, USA) and dried in a vacuum oven, respectively. The size and dispersivity were determined by HRTEM (Tecnai G2 F20 S-TWIN, FEI, USA) operating at 200 kV. The size distribution was determined by measuring 100 particles.

2.4. CL measurement

A diagram of the flow injection CL detection system was showed in Fig. 1. For CL measurement, the flow lines were inserted into the KMnO_4 , water, and CDs or r-CD solution, respectively. Then the pumps were started until a stable baseline was recorded. Injection was made by using an eight-way injection valve. The CL signals were recorded by an IFFL-D flow injection CL Analyzer (Ruimai Electronic Equipment Company Ltd., Xi'an, China).

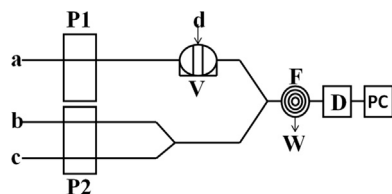


Fig. 1. Diagram of the flow injection CL system. a: water carrier; b: KMnO_4 ; c: H_2SO_4 ; d: r-CDs; V: injection valve; P1 and P2: peristaltic pumps; F: flow cell; W: waste; D: detector; and PC: personal computer.

2.5. Spectra measurements

The CL spectra of these systems were measured by using an F-7000 fluorescence spectrophotometer (Hitachi, Japan) with the xenon lamp turned off. Fluorescence spectra, UV–vis absorption spectra, and electron paramagnetic resonance (EPR) spectra were measured on an F-7000 fluorescence spectrophotometer, a UV-2450 UV–vis spectrophotometer (Shimadzu, Japan), and an ESP-300 E spectrometer (Bruker, Germany). X-ray photoelectron spectroscopy (XPS) spectra were measured using a XSAM-800 X-ray photoelectron spectroscope (KRATOS, UK).

3. Results and discussion

3.1. Characterization of CDs and r-CDs

HRTEM images (Fig. 2, Fig. S1) show that the CDs and r-CDs are near spherical and well dispersed. The average diameters of the CDs and r-CDs were about 3.1 ± 0.6 and 3.4 ± 0.8 nm, respectively (Fig. 2C, D). The UV–vis absorption spectra and photoluminescence spectra of the CDs and r-CDs were also recorded. No appreciable absorption peak is observed for the CDs (Fig. S2A). However, a new absorption peak at 280 nm for the r-CDs appears in the UV–vis spectrum (Fig. S2B). The CDs present yellow emission while the r-CDs present blue emission under the ultraviolet radiation (360 nm) (Fig. S2).

The maximum fluorescence emission of the CDs is located at 520 nm with an excitation wavelength of 470 nm. However, the r-CDs exhibit maximum excitation and emission wavelength near 280 and 440 nm, respectively (Fig. 3). The pH effects on the fluorescence of CDs and r-CDs were investigated. And we find that the fluorescence intensity from both CDs and r-CDs are higher at neutral solutions and lower at acidic or basic solutions (Fig. S3) [22]. The CDs were rich in oxygen-containing surface groups (carbonyl, carboxyl and epoxy) [21]. NaBH_4 could selectively reduce the carbonyl and epoxy moieties to hydroxyl groups and significantly enhance the fluorescence of CDs. XPS analysis (Fig. S4) also shows that the carbonyl peak at 288.4 eV decreased in intensity after reduction. The quantum yields of CDs ($\lambda_{\text{ex}}=470$ nm) and r-CDs ($\lambda_{\text{ex}}=280$ nm) are 0.59% and 3.1%, obtained by using fluorescein and quinine sulfate as the reference, respectively (Fig. S5) [21].

3.2. Optimization of the reaction conditions

Acidic media have been reported to be very important for the KMnO_4 induced CL systems [24,25]. Thus, H_2SO_4 , HCl , HNO_3 and H_3PO_4 in 1 mol/L concentration were tested as the acidic medium for the r-CDs- KMnO_4 system. The strongest CL signal is observed in H_2SO_4 medium (Fig. S6A). Concentrations of H_2SO_4 were optimized in a range from 0.01 to 5.0 mol/L and 1/1.0 mol H_2SO_4 was chosen for further work as the Fig. S6B showed. Concentrations of KMnO_4 were optimized in a range from 5.0×10^{-7} to 1.0×10^{-3} mol/L. CL intensity enhances with the increasing of KMnO_4 concentration, and the CL intensity levels off as KMnO_4 concentration reached 1.0×10^{-4} mol/L (Fig. S6C). However, higher concentration of KMnO_4 cause a CL intensity decrease because the CL signal can be severely absorbed by high concentration of KMnO_4 [26].

Meanwhile, the CL intensity was dependent on the concentration of the r-CDs in a certain range (Fig. S6D). The reaction conditions of the CDs- KMnO_4 system were optimized (Fig. S7) and they are the same to that of the r-CDs- KMnO_4 system. For comparison, the same concentration of CDs and r-CDs were selected for further experiments in the CDs system and the r-CDs system.

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