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Carbon nanodots sensitized chemiluminescence on peroxomonosulfate–sulfite–hydrochloric acid system and its analytical applications

Yun Zhou [a], Gaowa Xing [a], Hui Chen [a], Nobuaki Ogawa [b], Jin-Ming Lin [a,*]

[a] Beijing Key Laboratory of Microanalytical Method and Instrumentation, Department of Chemistry, Tsinghua University, Beijing 100084, China
[b] Faculty of Engineering and Resource Science, Akita University, Tegata Gakuencho, Akita 010-8502, Japan

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ABSTRACT

In the present work, new water-soluble fluorescent carbon nanodots (C-dots) were prepared in a facile microwave pyrolysis approach in minutes by combining glycine and polyethylene glycol 200 (PEG 200). Transmission electron microscopy (TEM) measurements showed that the resulting C-dots had diameters of about 3 nm. ^{13}C NMR spectra further confirmed the presence of carbons (sp^2 and sp^3) indicating a nanocrystalline core of the resulting C-dots with hydroxyl of PEG 200 covered outside. It was discovered that the prepared C-dots could dramatically enhance the chemiluminescence (CL) intensity of potassium peroxomonosulfate–sodium sulfite–hydrochloric acid (PSHA) reactions. UV–vis absorption and photoluminescence (PL) spectra indicated that the C-dots sensitized enhancements originated from their energy transfer and electron-transfer annihilation effects on the CL system. When the concentration of C-dots was 4×10^{-5} M, and those of $KHSO_5$, Na_2SO_3 and HCl were 1×10^{-2} M, an excellent performance was obtained. The C-dots sensitized CL system was successfully applied to the determination of aliphatic primary amines in real water samples with satisfactory results.

1. Introduction

Recently, C-dots have been paid great attention in many fields [1–5]. They are discrete and almost spherical nanoparticles with sizes below 10 nm. They can be bought inexpensively and easily in bulk by many methods (for example, electrochemical oxidation of graphite or multiwalled carbon nanotubes, one-step pathway of microwave pyrolysis approach, etc.) [6–13]. They have many luminescent properties such as strong optical absorption in the UV region [14–16], photoluminescence produced with photoexcitation [17–19], and electrochemiluminescence (ECL) generated by electron injection [8,15,20]. They have many other amazing characteristics: size and wavelength-dependent luminescence emission, resistance to photobleaching, and ease of bioconjugation without toxicity and environmental hazard. Besides these outstanding advantages, the most commendable fact is that they are covered with hydrophilic hydroxyl of PEG 200 from outside. Therefore they have good solubility in water, which greatly deepens their applications as many reactions occur in aqueous phase systems [21–26].

Water soluble aliphatic primary amines (i.e. C1: methylamine, C2: ethylamine, C3: n-propylamine, C4: n-butylamine, and C5: n-pentylamine) are degradation products of biological systems, such as amino acids and proteins. They are widely distributed in the environment as the byproducts of industrial and agricultural activities. Residues of these amines are hazardous to human health due to their pungent and irritant odor to skin, eyes, etc. [27–29]. But in certain environmental water, the quantities of aliphatic primary amines are too small to be detected. Thus, a rapid and sensitive technique for the detection of aliphatic primary amines in water samples is very necessary.

CL technique is a cheap and simple optical detection system. It has low background noise, low detection limit, and wide working range [30–33]. It has been proven effective in rapid and sensitive measurements at ultra-trace levels. Recently, the CL detection technique has widely incorporated C-dots in many CL systems, which broadens its application fields [34–38].

In this paper, water-soluble C-dots were prepared easily in a facile microwave pyrolysis approach in minutes. Incorporated with these C-dots, a novel PHSA CL system was developed. It consists of C-dots, sulfite, hydrochloric acid and peroxomonosulfate ($KHSO_5$). $KHSO_5$ is an inexpensive, commercially available potassium carotate. It acts as a provider of excited singlet oxygen ($^1O_2$) in many CL systems [39–41]. Investigation indicated that C-dots had apparent sensitization effects on the PHSA CL system. Possible mechanism of C-dots sensitized PHSA CL system was proposed. Further investigation indicated that the CL enhancements of C-dots could be inhibited by the addition of aliphatic primary amines. This inhibited method exhibited a linear range

* Corresponding author. Tel./fax: +86 10 62792343.
E-mail address: jmlin@mail.tsinghua.edu.cn (J.-M. Lin).

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from 1×10^{-9} to 1×10^{-5} M with detection limits from 2.5×10^{-10} to 3.3×10^{-9} M. The proposed CL system was successfully applied for the determination of aliphatic primary amines in water samples.

2. Experimental

2.1. Chemicals and materials

Ultra-purification water was prepared with a Compact Ultrapure water system (18.3 MΩ cm). The analytical reagent-grade chemicals were used throughout. A solution of $KHSO_5$ was prepared daily by dissolving a triple salt ($K_2SO_4\cdot KHSO_4\cdot 2KHSO_5$, Alfa, Ward Hill, USA) in water. Na_2SO_3 and HCl were obtained from Tianjin Kaitong Chemicals Co. (Tianjin, China). They were also prepared daily. PEG 200 and glycerol were obtained from Shantou Xilong Chemical Factory (Guangdong, China). Glycine (assay ≥ 99%) was from Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Aliphatic primary amines (i.e. methylamine, assay 30–33%; ethylamine, assay 65–70%; n-propylamine, assay ≥ 98.5%; n-butylamine, assay ≥ 99%; and n-pentylamine, assay ≥ 97%) were from Sigma-Aldrich Co. (USA).

2.2. Apparatus

C-dots were synthesized within an 800 W microwave oven (Galanz G8023CSL-K3, Galanz Group, Guandong, China). Static CL measurements were performed with an ultra-weak CL analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). A flow CL analyzer (Lumiflow LF-800, Microtech NITI-ON, Funabashi, Japan) was used in flow injection CL measurements. PL spectra were examined by a F-7000 fluorescence spectrophotometer (Hitachi, Japan). UV–vis absorption spectra were achieved with a Model UV-2100s Spectrophotometer (Shimadzu, Japan). Particle sizes and morphologies of C-dots were measured by a transmission electron microscope (TEM, Tecnai G^2 20S-Twin, FEI Company, USA) at 200 kV. The TEM samples were prepared by casting a drop of C-dots solution in nanopure water onto a 300-mesh holey carbon-coated copper grid for observation. ^{13}C NMR spectra were collected with a JNM-ECX 400 MHz spectrometer (JEOL Ltd., Japan) by dissolving 30 mg of C-dots in 0.5 mL deuterated water. Ultrasonic instrument (KQ-500DB, 500 W, Kun Shan Ultrasonic Instruments Co., Ltd.) was used for mixing solutions well.

2.3. Synthesis of C-dots

C-dots were synthesized according to Ref. [10] with little modification. Briefly, PEG 200 (1 mL) and glycine (1 mM) were added into glycerin (5 mL). Then they were mixed well by an ultrasonic instrument. Next, the mixture was heated for 6 min in a microwave oven. Increasingly, the color of the heated solution changed from colorless to dark brown. Then the solution was dialyzed for 4 days. Finally, a light green powder was prepared and labeled as C-dots. It was then dried in a vacuum rotary evaporator and stored in a refrigerator at 4 °C for future use (Fig. 1).

2.4. Procedure for PSHA dynamic CL

To investigate the dynamic properties of the PSHA CL system, a static injection CL analysis was carried out in a 3 mL quartz glass cuvette by a batch method. Every time before static CL measurement was taken, the analyzer was run for 10 min in order to obtain a good mechanical and thermal stability. After that, a solution of Na_2SO_3 (100 μL) was added to the mixture of $KHSO_5$ (100 μL) and C-dots (100 μL) in the cuvette. Immediately, a solution of HCl (100 μL) was injected into it too. The CL intensity was displayed and integrated instantly with the luminescence analyzer. The analyzer was run at a 0.01 s sample interval and −1.2 kV PMT work voltage.

2.5. Procedure for PSHA CL

A flow injection analysis (FIA) was employed to perform the C-dots sensitized PSHA CL system (Fig. 2). Two peristaltic pumps were used to deliver four flowing streams in this FIA method. PTFE (polytetrafluoroethylene) tubing (0.8 mm i.d.) was used as the delivery channel. The sample injection part was a six way valve which was equipped with a 100 μL sample loop. A spiral

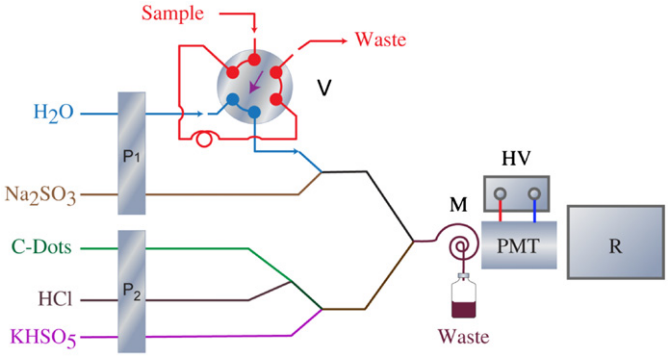

Fig. 2. Schematic diagram of FIA CL system. P_1 and P_2, peristaltic pump; V, six-way injection valve; M, CL flow cell; W, waste; HV, negative high-voltage power supply; PMT, photomultiplier tube detector; and R, luminescence analyzer controlled by personal computer.

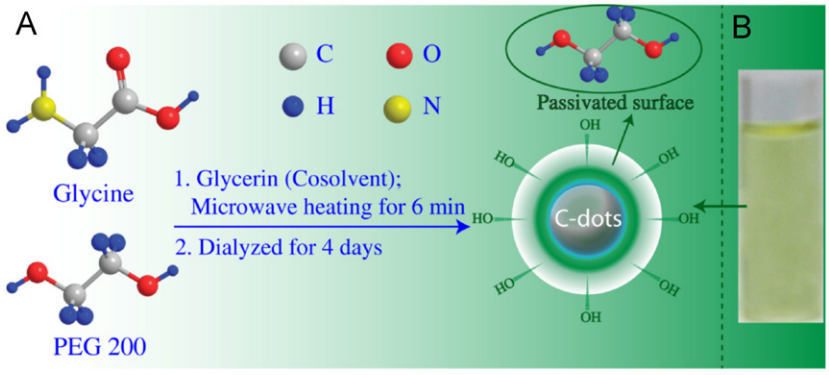

Fig. 1. (A) Schematic illustration for the synthesis of C-dots and (B) photo of light green product after being dialyzed for 4 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)