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Full Length Article

Hollow fluorescent carbon nanoparticles catalyzed chemiluminescence and its application

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ABSTRACT

In this paper, the chemiluminescence (CL) of luminol-H_2O_2 with cross-linked hollow fluorescent carbon nanoparticles (HFCNs) was reported. The possible CL reaction mechanism was elucidated by means of CL spectra, UV–vis spectra and some radical scavenger experiments. The CL luminophor was 3-aminophthalate, the CL enhancement of luminol-H_2O_2 system was supposed to originate from the intrinsic catalytic activity of HFCNs, which efficiently catalyzed the decomposition of H_2O_2 to generate superoxide radical anion in luminol solution. Dipyridamole (DIP) had an inhibitory effect for the luminol-H_2O_2-HFCNs CL system. The decrease CL intensity was linear with the logarithm of DIP concentration in the range of 2.0×10^{-8}–1.0×10^{-5} mol/L. The detection limit was 3.6×10^{-9} mol/L. The proposed method was applied for the determination of DIP in tablets and urine samples with satisfactory results.

1. Introduction

Chemiluminescence (CL) is defined as the production of light through a chemical reaction, in which some excited species are formed and deactivated to the ground state with light emission. Additionally, CL has proved to be a useful phenomenon in the laboratory, finding ever increasing applications in analytical chemistry for its high sensitivity, wide linear range, simple instrumentation and lack of background scattering light interference. Fluorescent carbon nanoparticles (FCNs) are generally small oxygenous carbon nanoparticles with good water solubility, low toxicity, high chemical stability and low environmental hazard [1,2]. This new nanoparticles have been successfully used as bioimaging [3], photocatalysis [4] and fluorescence probe [5]. Due to the superior emitting properties of FCNs, they have been applied in CL including ultraweak CL systems [6–10] and oxidants induced direct CL systems [11–13]. These investigations open new sight into the optical characteristics of the FCNs and widen their potential optical application.

Dipyridamole (DIP) is widely used for the treatment of cardiovascular diseases because it stimulates a rise in the blood flow through the coronary circulation. It can improve efficiency and decrease tiredness in certain sports, so it is one of the forbidden substances by the International Olympic Committee [14]. Various analytical methods including spectrophotometry [15], photoluminescence [16–18], CL [19,20], electrochemistry [21–23] and chromatography [24–27] have been reported for this purpose.

Water-soluble cross-linked hollow fluorescent carbon nanoparticles (HFCNs) and solid fluorescent carbon nanoparticles (SFCNs) were prepared in an automatic method without external heat treatment by simply mixing glacial acetic acid, water and diphosphorus pentoxide in minutes. Luminol-H_2O_2 CL reaction, a popular CL reaction, has been widely applied for the detection of various substances. In this work, the luminol-H_2O_2 CL reaction was chosen as a model system and the effect of HFCNs and SFCNs on the CL was explored. The results showed that HFCNs and SFCNs could enhance the CL of the luminol-H_2O_2 system and the enhanced capability of HFCNs was superior to SFCNs. The enhancement mechanism of HFCNs on luminol CL was investigated. Furthermore, DIP could inhibit the CL intensity of the luminol-H_2O_2-HFCNs. The analytical application potential for the determination of DIP was exploited.

2. Experimental section

2.1. Materials

All the chemicals were analytical reagent grade. 0.01 mol/L luminol stock solution was prepared by dissolving 0.1771 g luminol (Shaanxi Normal University, Xi'an, China) in 0.1 mol/L NaOH, diluting to 100 mL in a brown calibrated flask. The stock solution of 1.0×10^{-3} mol/L DIP (National Institutes for Food and Drug

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Control, Beijing, China) prepared by dissolving 0.0252 g DIP with a small amount of 0.1 mol/L HCl, diluting with water in a 50 mL volumetric flask. Working solutions of H_2O_2 were prepared daily with 30% (v/v) H_2O_2 (Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., Tianjin, China). Other reagents including glacial CH_3COOH, P_2O_5, NaOH and HCl were purchased from Luoyang Chemical Reagent Co. Ltd. All the solutions were prepared with pure water (Chengdu Ulupure Technology Company, China).

2.2. Apparatus

The experiments were performed on a BPCL ultraweak CL analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China) equipping with the IFIS-C intelligent flow injection sampler (Xi'an Remax Analytical Instrument, Shannxi, China). The UV-vis absorption spectra were studied using a Cary5000 spectrophotometer (Varian, USA). The CL and fluorescence (FL) spectra were measured with a Cary Eclipse fluorescence spectrophotometer (Agilent, Australia). A Fourier transform infrared (FT-IR) spectrum was carried out on a Varian 660-IR spectrometer in the range of 500–4000 cm^{-1} (Varian, USA). Transmission electron microscopy (TEM) image was recorded by a JEM-2100 transmission electron microscopy (JEOL, Japan).

2.3. Synthesis of HFCNs and SFCNs

HFCNs and SFCNs were synthesized according to the literature [28] with some modifications. The reactants for producing HFCNs and SFCNs were the same. For HFCNs, the homogeneous mixture solution of 1 mL glacial acetic acid and 80 μL water was quickly added to 2.5 g P_2O_5 in a 50 mL beaker without stirring. In this system, the upper temperature was mainly controlled by vaporizing the glacial acetic acid at its boiling point (117 °C). The nanobubbles of glacial acetic acid vapor then served as the templates for hollow structures. Finally, the HFCNs in dark brown were collected by dispersing in water, followed by adjustment of the pH to 7.0 with NaOH, diluting to 100 mL in a brown volumetric flask. The obtained HFCNs solution was stable for at least one month in the refrigerator. For SFCNs, a homogeneous mixture solution of 1 mL glacial acetic acid and 5 μL water was quickly added to 1.5 g P_2O_5 in a 5 mL tube with shake. In room temperature, the SFCNs in yellow were collected by dispersing in water, followed by adjustment of the pH to 7.0 with NaOH, diluting to 100 mL in a brown volumetric flask. The concentrations of HFCNs and SFCNs were 0.35 mol/L calculated by C element in glacial acetic acid.

2.4. Procedures

The manifolds of the flow injection CL system were shown in Fig. 1. All solutions were delivered by two peristaltic pumps (P1, P2). P1 was used to deliver HFCNs or SFCNs solution (channel a) and luminol in NaOH solution (channel b) at a flow rate of 2.0 mL/min.

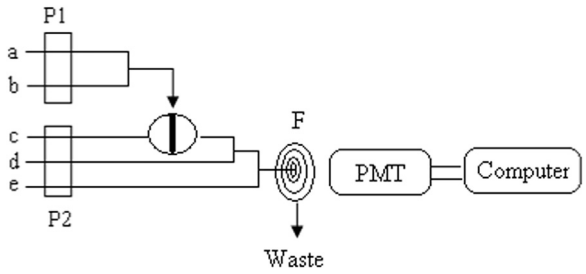

Fig. 1. Schematic diagram of the FI-CL system. a: HFCNs or SFCNs solution; b: luminol solution; c: carrier stream; d: DIP standard or sample solution; and e: H_2O_2 solution. P1 and P2: peristaltic pumps; and F: CL flow-cell.

The carrier water (channel c), DIP standard or sample solution (channel d) and H_2O_2 solution (channel e) were delivered by P2 at a flow rate of 2.5 mL/min. Polytetrafluoroethylene tube was employed to connect all components in the flow system. HFCNs were firstly mixed with luminol at the three-way channel; H_2O was used as the carrier for the mixing of HFCNs and luminol. The mixture of HFCNs and luminol finally mixed with DIP and H_2O_2 solution at the flow cell, in which the CL reaction occurred. The CL signal was detected by the photomultiplier tube (PMT) and recorded with computer. The concentration of DIP was quantified by the relative CL intensity, $\Delta I = I_0 - I$, where I_0 and I denoted CL intensity in the absence and presence of DIP.

3. Results and discussion

3.1. Spectra of HFCNs and SFCNs

Fig. 2(A) showed the UV–vis and FL spectra of HFCNs. A broad absorption around 297 nm and a sharp absorption at 247 nm were observed. The peak at 247 nm was ascribed to π–π^* transition of aromatic C=C bonds [28], while the shoulder at 297 nm attributed to n–π^* transition of C=O bonds [28,29]. The FL spectra of the HFCNs had no shift as the excitation wavelength varied. The maximum FL intensity (~500 nm) was obtained with an excitation wavelength of 400 nm. Fig. 2(B) showed the FT-IR spectrum of the HFCNs. An apparent absorption peak of the −OH group at about 3449 cm^{-1} and an absorption peak of the C=O group conjugated with aromatic carbons at 1658 cm^{-1} appeared. These data showed that the HFCNs were rich in carboxylic groups. A peak at 1542 cm^{-1} from a conjugated C=C stretching vibration was observed, indicating unsaturated carbon bonds formed during the carbonization process. TEM image of HFCNs was displayed in Fig. 2 (C) and the HFCNs were cross-linked with each other. Fig. 2 (D) showed the UV–vis and FL spectra of SFCNs. There were two absorption peaks of SFCNs, one was at 297 nm and another at 247 nm. This was consistent with the absorption of HFCNs. The maximum FL emission (~500 nm) was obtained with an excitation wavelength of 400 nm and the emission shifted with the excitation wavelength. The sizes of prepared SFCNs were less than 10 nm (Fig. 2(E)).

3.2. The effect of HFCNs and SFCNs for luminol CL system

The enhanced effect of HFCNs and SFCNs for luminol-H_2O_2 CL was studied (Fig. 3). Added SFCNs into the luminol-H_2O_2 CL system brought about 2-fold CL intensity enhancement and the HFCNs could enhance the CL intensity about 26 times. The results showed that HFCNs exhibited higher sensitive effect on the luminol-H_2O_2 CL reaction. So, HFCNs was selected as enhancer of luminol-H_2O_2 system in subsequent measurements.

3.3. Measurement of quantum yield of HFCNs

The quantum yield (QY) of the HFCNs was calculated using following function:

$$\Phi = \Phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

Quinine sulfate in 0.1 mol/L H_2SO_4 (literature quantum yield 0.54 at 360 nm) was chose as a standard. Where Φ was the quantum yield, I was the measured integrated emission intensity, η and A was the refractive index and optical density, respectively. The subscript R referred to the reference fluorophore of known quantum yield. In order to minimize re-absorption effects the