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# Nitrite sensing based on the carbon dots-enhanced chemiluminescence from peroxyntrous acid and carbonate

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## ABSTRACT

In this work, chemiluminescence (CL) from peroxyntrous acid (ONOOH)–carbonate system greatly amplified by carbon dots was observed. The CL mechanism of the ONOOH–carbonate–carbon dots system has been investigated and the results reveal that the carbon dots could serve as the energy acceptor, which gives us new insight into the optical properties of the new emerging carbon nanomaterial. There is a good linear relationship between the CL signal and the concentration of the nitrite using for ONOOH formation, which provides us a nitrite sensing method with sensitivity as high as  $5.0 \times 10^{-9}$  M (S/N=3). The method has been successfully applied to the determination of nitrite in tap water with the recovery of 98%. The standard deviations are within 2.5%.

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## 1. Introduction

Peroxyntrite is a powerful oxidizing agent of biological importance, which exists in many forms, such as *trans*-peroxyntrous acid (ONOOH), *cis*-ONOOH, activated form of ONOOH, and peroxyntrous anion [1–3]. ONOOH, as a weak acid with a pKa of 6.8, is an important form of peroxyntrite [4]. In acid solution, ONOOH is an unstable compound with lifetime less than 1 s [5]. In basic solution, ONOOH could be converted to peroxyntrous anion (ONOO<sup>-</sup>) that is fairly stable and can decompose slowly to nitrite and superoxide anion radical. The oxidation reaction by peroxyntrite is beneficial for destroying invading organism. However, peroxyntrite is also involved in protein and lipid nitration, which has been found to be an early event in the etiology of some pathologies. The study concerning peroxyntrite has attracted many attractions.

Certain chemical reactions released their energy through light emission, which was called as chemiluminescence (CL). Large amount of excited species with short life are involved in CL reaction. Hence, CL could be a useful tool in reactive species investigation. Since 1999, Starodubtseva et al. had reported weak CL emission from excited ONOOH. ONOOH/ONOO<sup>-</sup> also oxidized pholasin [6], chloroquine [7,8] and bilirubin [9] to produce strong CL. There are some reports concerning the CL from the decomposition of ONOO<sup>-</sup>, which is enhanced by some energy acceptors,

such as fluorescent compounds [10], CdTe quantum dots [11]. Materials, including Mg–Al–carbonate layered double hydroxides [12] and gold nanoparticles [13], could increase the CL from ONOOH related system. Carbonate solution was reported to react with ONOO<sup>-</sup> to produce ONOOCO<sub>2</sub><sup>-</sup> that had a lifetime less than 3 ms and decomposed rapidly into •NO<sub>2</sub> and carbonate radical (•CO<sub>3</sub><sup>-</sup>) [14,15]. •CO<sub>3</sub><sup>-</sup> changed to carbon dioxide in its excited form that brought in the CL emission [16].

Carbon dots, as a new type of fluorescent carbonaceous nanoparticle, owned lots of advantages, such as environmental benign, optical stability, low cost and easy preparation. Nowadays, fluorescent carbon dots have been successfully applied in bio-imaging for cells [17,18]. The new properties of carbon dots, such as catalytic activity [19,20], fluorescent probe [21,22] and photocatalyst [23,24], have been reported recently by several groups. The CL enhanced role of carbon dots was firstly reported in our group and the CL mechanism was revealed. There are several possible mechanisms explaining the enhancing effect of carbon dots: (1) Carbon dots have catalysis effect on the reaction [25]. (2) Carbon dots concentrated the excited CL emitter, which facilitated the CL emission [26]. (3) Carbon dots were involved in the CL reaction and the CL emission was through the annihilation of hole-injected and electron-injected carbon dots [27].

We firstly found that carbon dots had enhancing effect on the ONOOH system [27]. In the present work, we further find that carbon dots could greatly amplify the CL from ONOOH–carbonate system. Furthermore, the carbon dots–ONOOH–carbonate CL system has higher CL intensity than that from carbon dots–ONOOH system. More interestingly, a linear relationship between the

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nitrite for the formation of ONOOH and CL signal produced from the carbon dots–ONOOH–Na<sub>2</sub>CO<sub>3</sub> system was found. Hence, the proposed method can be employed for the determination of nitrite with improved sensitivity. The CL enhanced mechanism of carbon dots on ONOOH–Na<sub>2</sub>CO<sub>3</sub> system was also illustrated in details, and its role of energy acceptor was further discussed.

## 2. Experimental

### 2.1. Reagents and materials

All chemicals were of analytical grade and were used as received. Sodium nitrite (NaNO<sub>2</sub>) was from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35%) was obtained from Alfa Aesar China Ltd. Serine and polyethylene glycol 1500 (PEG 1500) were purchased from Merck Company (Darmstadt, Germany). 5, 5-Dimethyl-1-pyrroline N-oxide (DMPO) was from Sigma-Aldrich Chemical Co. (St. Louis, USA). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) and glycerine were bought from Beijing Chemical Reagent Co. (Beijing, China).

### 2.2. Apparatus

Flow injection experiments were performed with a LumiFlow LF-800 detector (NITI-ON, Funabashi, Japan). Batch CL experiment was performed with a BPCL ultraweak CL analyzer (Institute of Biophysics, Chinese Academy of Science, Beijing, China). Two peristaltic pumps (SJ-1211, Atto, Tokyo, Japan) were used to deliver the solution into the spiral flow CL cell, which was installed in front of the photomultiplier tube (PMT). The fluorescent spectra were performed using a FL-7000 spectrofluorometer (Hitachi, Japan). Electron paramagnetic resonance (EPR) spectra were measured on a JEOL spectrometer (JES-FA200, Japan).

### 2.3. CL system

Carbon dots were prepared by microwave heating of serine in the presence of 15 mL glycerine and 1.0 g PEG 1500 by microwave oven for 10 min. Carbon dots were dialyzed against pure water before the batch experiment. While in the flow injection experiment, carbon dots were used without any further treatment. CL kinetic curves were obtained by batch experiments, which were carried out in the glass cuvette. The CL profiles were displayed and integrated for 0.1 s interval. A microliter syringe was used for the injection of the solution from the upper injection port. The addition orders of the reagent and design the CL flow injection analysis system.

The manifolds of the flow injection system were shown in Fig. S1. The solution of NaNO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> was mixed at the three-way channel, where HNOOH was produced and reached the flow cell through channel AB. Carbon dots and Na<sub>2</sub>CO<sub>3</sub> were pumped by pumps 1 and 2 to mix with HNOOH in the flow cell. The CL signal was collected by the LF-800 detector. The peak height of the signal recorded was measured as CL intensity.

### 2.4. Sample preparation

For the determination nitrite in tap water, the water was firstly filtered by 0.25 μm and then was passed through a cation-exchange resin to eliminate interferences from metal cation.

## 3. Results and discussions

### 3.1. CL from carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> system by flow injection system

Flow injection system with precise control of the sample volume, flow rate and mixing time of the reagent has been employed to compare the CL intensity from several systems. The manifolds of the flow injection system were shown in Fig. S1. The interaction of NaNO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in acid medium produced ONOOH [28]. The solution of NaNO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> was mixed at the three way channel AB to generate HNOOH. Carbon dots enhanced the CL from ONOOH system, and its CL has been recorded in Fig. 1a. The baseline of curves b and c in Fig. 1 stands for the CL intensity caused by the reaction of ONOOH–NaOH and ONOOH–Na<sub>2</sub>CO<sub>3</sub> systems. The introduction of carbon dots further increased the CL intensity from ONOOH–NaOH and ONOOH–Na<sub>2</sub>CO<sub>3</sub> system (Fig. 1b and c). ONOOH, as a weak acid with pKa of 6.8 [4], is suggested to be turned to ONOO<sup>−</sup> related species in alkaline medium. The CL enhancement of carbon dots in alkaline medium is suspected to be attributed to the interaction between carbon dots and ONOO<sup>−</sup> related species [29]. Compared with the CL from carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> system (Fig. 1d), the CL from carbon dots–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> system in the absence of NaNO<sub>2</sub> was rather low, which confirmed the main role of nitrite and its related species (ONOOH, ONOO<sup>−</sup>, and ONOOCO<sub>2</sub><sup>−</sup>) in the CL reaction.

### 3.2. CL from carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> system by batch experiment

The CL dynamic curves under different reagent injection orders have been obtained by batch experiment. The injection of solution of Na<sub>2</sub>CO<sub>3</sub> and carbon dots together into ONOOH was accompanied by very strong CL (Fig. 2), which was stronger than the CL intensity obtained when Na<sub>2</sub>CO<sub>3</sub> and carbon dots were added in that order into ONOOH. In the absence of nitrite, very weak CL emission as low as 120 count was observed in Fig. 2, which further verified the important role of ONOOH, ONOO<sup>−</sup> and ONOOCO<sub>2</sub><sup>−</sup> in the CL system.

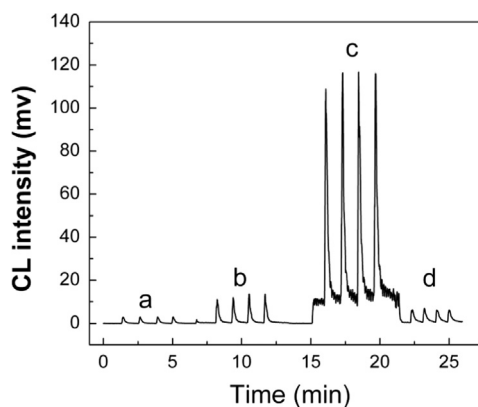


Fig. 1. The CL signal in the flow injection system for carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>, carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–NaOH, carbon dots–NaNO<sub>2</sub>–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> and carbon dots–H<sub>2</sub>O<sub>2</sub>–Na<sub>2</sub>CO<sub>3</sub> systems. Conditions: 0.1 M H<sub>2</sub>O<sub>2</sub> in 0.025 M H<sub>2</sub>SO<sub>4</sub>, 1.0 × 10<sup>−5</sup> M NaNO<sub>2</sub>, 0.1 M Na<sub>2</sub>CO<sub>3</sub>, carbon dots with a dilution of 1: 1000.

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