



Quantum dots in organo-modified layered double hydroxide framework-improved peroxyntrous acid chemiluminescence for nitrite sensing



Shichao Dong, Weijiang Guan, Chao Lu*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:

Received 9 June 2013

Received in revised form 15 July 2013

Accepted 17 July 2013

Available online 25 July 2013

Keywords:

Quantum dots

Organo-modified layered double hydroxides

Chemiluminescence

Nitrite

Peroxyntrous acid

Nanocomposites

ABSTRACT

In this study, the directional luminescent quantum dot (QD)-layered double hydroxide (LDH) assembly was fabricated by embedding the trace QDs onto the exterior surface of the organo-modified LDHs. It was found that this novel nanomaterial was able to extraordinarily improve an ultra-weak chemiluminescence (CL) emission from peroxyntrous acid (ONOOH). The enhanced CL emission was attributed to the electrostatic concentration of peroxyntrite (ONOO⁻) onto the orderly surface of the QD-organo-modified LDHs as well as the hydrophobic microenvironment of the organo-LDHs, facilitating the production of superoxide radical ($\bullet\text{O}_2^-$) and hydroxyl radical ($\bullet\text{OH}$). In addition, the CL intensity increased with increasing the concentration of nitrite in a wide range of 1.0–1000 μM with a detection limit of 0.3 μM (S/N = 3). Therefore, the proposed method was applied for the selective and sensitive detection of nitrite in sausage samples. Recoveries from spiked real samples were in the range of 96–103%. The results of the proposed method for sensing nitrite in real samples were agreed with those obtained by the standard spectrophotometric method.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nitrite widely exists in food as preservatives and fertilizing agents [1]. High intake of nitrite can cause the dangerous methemoglobinemia due to its reaction with hemoglobin to form methemoglobin by oxidation of ferrous iron to the ferric state, reducing or preventing the blood to transport oxygen [2]. Moreover, nitrite can interact with secondary amines to form carcinogenic, teratogenic, and mutagenic nitrosamines which can induce stomach and esophagus cancer [3,4]. Moreover, it also plays a key physiological role in signaling, blood flow regulation and hypoxic nitric oxide homeostasis [5]. Therefore, it is very important to quantitatively detect nitrite in public health. Some methods, such as spectrophotometric [6], chromatographic-mass spectrometry [7], electrochemical [8], fluorescence [9] and chemiluminescence (CL) [10–14] methods, have been developed for the analysis of nitrite. However, each method has its advantages and disadvantages. For instance, spectrophotometric methods suffer from poor sensitivity and selectivity. Chromatographic-mass spectrometry methods possess high sensitivity, but they are time-consuming. Fluorescent detections need fluorescent dyes, and thus they suffer the interferences from background fluorescent matrix in real samples.

Recently, CL methods have attracted more attention with their simplicity, speed, low cost and high sensitivity [10–15]. Therefore, it is necessary for developing a simple, selective and rapid CL method for sensing nitrite.

Peroxyntrous acid (ONOOH) is a fairly strong acid ($\text{pK}_a = 6.8$) [16]. It was reported that the decomposition of ONOOH can produce a spontaneous weak CL emission [17]. In the recent years, there is an increased interest in a flow injection method for nitrite determination in the presence of some CL amplifiers [11–13] where the high concentration of the amplifiers were used, resulting in the quenching of the CL intensity. Fortunately, we found that a strong CL was obtained by assembling organic molecules (CL amplifiers) on the surface of layered double hydroxides (LDHs) due to the suppression of the intermolecular π – π stacking interactions among aromatic rings and the improvement of molecular orientation and planarity in the LDH matrix, enabling a remarkable increase in fluorescence lifetime and quantum yield of organic molecules [10]. These interesting results inspire us to investigate the CL properties of other CL amplifiers assembled onto the surface of LDH matrix.

Quantum dots (QDs) have received much attention over the past decades as a promising luminescent material due to their unique optical properties [18,19]. QDs exhibit a strong sensitivity toward surface interactions, and thus the optical properties can be tailored to meet specific wavelength requirements by tuning the composition and size [20]. These inherent advantages of QDs are attractive for various prospective applications in chemical

* Corresponding author. Tel.: +86 10 64411957.

E-mail addresses: luchao@mail.buct.edu.cn, luchaohanghang@126.com (C. Lu).

analysis, optoelectronic devices, medical treatments, and biological labeling [21,22]. However, photoluminescence quantum yield of QDs can be reduced upon their exposure to moisture, oxygen, heat, or light by surface degradations. Furthermore, QDs can be irreversibly agglomerated upon their isolation from the colloidal suspensions, leading to the changes of their optical absorption and emission [23]. To solve these problems, the incorporation of QDs into various matrices such as polymers and inorganic materials has been reported [24]. Among them, LDHs are an important class of host–guest materials consisting of positively charged metal hydroxide sheets with charge-balancing intercalated anions and water molecules. These properties of LDHs can be tuned by adopting different kinds of metal ions and interlayer anions [25]. Recently, the noticeable properties of LDHs make them become the promising candidate for guaranteeing the chemical properties and photostability of QDs and preventing their aggregation [26,27].

In this paper, the orderly QDs were prepared by assembling them upon the exterior surface of the organo-modified LDHs. Interestingly, the weak CL emission from ONOOH was greatly enhanced by such QDs. The CL enhancement mechanism of the present system was confirmed by some techniques, such as CL spectrum, radical scavengers, and fluorescence spectra. In addition, the CL intensity increased with increasing the concentration of nitrite. The proposed CL system was applied for the selective and sensitive detection of nitrite in real sausage samples.

2. Experimental

2.1. Reagents

Analytical grade chemicals including NaOH, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, H_2O_2 , HCl, 1,4-diazabicyclo[2.2.2]octane (DABCO), and ascorbic acid were purchased from Beijing Chemical Reagent Company. Thiourea was purchased from Tianjin Fuchen Chemical Reagents Factory. Sodium dodecyl benzene sulfonate (SDBS) was purchased from Tokyo Chemical Industry Co., Ltd. Tellurium powder (Te, 99.999%), thioglycolic acid (TGA), cadmium chloride (CdCl_2) and sodium borohydride NaBH_4 were obtained from Tianjin Chemical Reagent Company. Nitro blue tetrazolium chloride (NBT) was purchased from Nacalai Tesque Inc. (Tokyo, Japan). All reagents were used without further purification. A 0.1 M nitrite stock solution was prepared by dissolving 0.69 g NaNO_2 (Tianjin Chemical Reagent Company) in 100 mL of deionized water. Working solutions of nitrite were freshly prepared by diluting the nitrite stock solution with deionized water. A mixed working solution of 0.03 M H_2O_2 and 0.01 M HCl was freshly prepared by volumetric dilution of commercial 30% (v/v) H_2O_2 and 36% (v/v) HCl with deionized water, respectively.

2.2. Apparatus

The powder X-ray diffraction (XRD) measurement was performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized $\text{Cu}/\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The 2θ angle of the diffractometer was stepped from 2° to 70° at a scan rate of $0.02^\circ/\text{s}$. The particle sizes and external morphology of the samples were observed on a transmission electron microscope (TEM, Tecnai G220, FEI Company). S-4700 field-emission SEM was used for obtaining the scanning electron microscopy images. The fluorescence spectra was obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at a scanning rate of 1500 nm/min. The excitation slit and the emission slit were maintained at 5.0 nm and 2.5 nm, respectively. Nicolet 6700 FT-IR (Thermo, America) was used for infrared spectroscopy. The CL spectrum of this system was measured with high-energy

cutoff filters from 490 to 640 nm between the flow CL cell and the photomultiplier tube (PMT). The CL detection was conducted on an Ultra-Weak Luminescence Analyzer, which was purchased from institute of Biophysics, Chinese Academy of Science, Beijing, China (Biophysics Chemiluminescence, BPCL).

2.3. Synthesis of Mg-Al- NO_3 LDHs

The co-precipitation method was carried out to synthesize Mg-Al- NO_3 LDHs. The precipitation process was taken under low supersaturation conditions at constant pH. The NaOH solution was prepared by dissolving NaOH (0.16 mol) in 80 mL of degassed and deionized water. The salt solution was prepared by dissolving $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.06 mol) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.02 mol) in 80 mL of degassed and deionized water with a Mg/Al ratio of 3. The two solutions were dropwise added into a 250 mL four-necked flask under vigorous stirring maintaining pH 9.5–10 at room temperature. The resulting white precipitate was aged for 24 h at 65°C . The whole procedure was performed under a nitrogen atmosphere to exclude the aqueous CO_2 . The resulting slurry was centrifuged and washed with degassed and deionized water for several times, and dried in vacuo at 65°C for 24 h.

2.4. Synthesis and characterizations of Mg-Al-DBS LDHs

Mg-Al-DBS LDHs (one of the organo-modified LDHs) were synthesized by using a simple ion exchange method. The Mg-Al- NO_3 LDH powder (2.0 g) was mixed with a 0.2 M DBS aqueous solution (50 mL) prepared by degassed and deionized water. After vigorous stirring at 80°C for 24 h in an N_2 atmosphere, the prepared Mg-Al-DBS LDHs suspension was centrifuged and washed with degassed and deionized water for several times before it was stored at 4°C for further use. The representative XRD pattern of DBS-LDHs was displayed in Fig. S1. A series of peaks were clearly shown at lower diffraction angles ($2\theta = 3.01^\circ$) with $d_{(003)}$ value of 29.63 Å. The basal spacing of LDHs is the sum of the interlayer height and the thickness of a Mg/Al-hydroxide sheet (about 4.8 Å) [28]. In this case, the basal spacing of 29.63 Å is larger than the sum of the thickness of a Mg/Al-hydroxide sheet (ca. 4.8 Å) and the length of the alkyl chain of DBS anion (ca. 21.40 Å), indicating that the intercalated surfactants adopt a paraffin bilayer arrangement model.

2.5. Synthesis of CdTe QDs

The colloidal CdTe QDs were prepared using the reaction between Cd^{2+} and NaHTe solution. NaHTe solution was obtained by the reaction of tellurium and sodium borohydride under N_2 atmosphere to exclude the aqueous O_2 at 60°C . CdTe QDs were synthesized by adding freshly prepared NaHTe solution to N_2 -saturated CdCl_2 solution at pH 11 in the presence of TGA as a stabilizer. The molar ratio of $\text{Cd}^{2+}/\text{Te}^{2-}/\text{TGA}$ was fixed at 1:0.5:2.5. The precursors were converted to CdTe nanocrystals by refluxing the reaction mixture at 96°C under open-air conditions with condenser attached. The size of the CdTe QDs growing further was controlled by the duration of reflux and could easily be monitored by absorption and fluorescence spectra. For purifying CdTe QDs, the unreacted CdCl_2 and TGA were removed via dialysis for 24 h in 0.01 M NaOH solution by the dialysis membrane with a molecular weight of cutoff 7000. The obtained CdTe QDs remained stable for several months in a refrigerator at 4°C .

2.6. Preparation of QD-LDH assembly

A mixed suspension composed of 2.5 mL 0.2 mM CdTe QDs solution and 2.5 mL NO_3 -LDHs or organo-modified LDHs was stirred for 10 min at room temperature for further use. The as-prepared

Download English Version:

<https://daneshyari.com/en/article/7148639>

Download Persian Version:

<https://daneshyari.com/article/7148639>

[Daneshyari.com](https://daneshyari.com)