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Determination of catechol in water based on gold nanoclusters-catalyzed chemiluminescence

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ABSTRACT

In this paper, a novel chemiluminescence (CL) system is introduced based on the reaction of fluorescein and H_2O_2 in alkaline medium. Gold nanoclusters (Au NCs) were synthesized using a facile BSA-stabilized method and were then applied to the fluorescein-H_2O_2 system for the first time, which effectively enhanced the intensity of the CL system. The addition of trace level of catechol into the CL system caused significant quenching of luminescence intensity. At optimal experimental conditions, the decreased CL intensity exhibited a favorable linear relation with catechol concentration. Based on this inhibitory phenomenon, a flow injection CL method with good selectivity was developed for determining catechol. A possible reaction mechanism was also proposed according to results of the kinetic curves of Au NCs in fluorescein-H_2O_2 CL system, radical scavengers and the spectra of CL, fluorescent and UV-visible. Finally, this method has been successfully used for the analysis of catechol in environmental water samples.

1. Introduction

Catechol (1,2-dihydroxybenzene) is a representative polyphenolic compound which widely exists in higher plants such as vegetables, fruits, teas, nicotiana tabacum plants and some traditional Chinese medicines. It is extensively used in the field of food chemistry, cosmetics, tanning, pesticides, pharmaceuticals, photography chemicals and so forth [1]. However, catechol is harmful to humans, natural environments, especially for the water pollution even at quite low concentration. As far as we know, the absorption of excessive catechol could induce vasoconstriction, renal tube degeneration, liver function decrease, cancers and neurodegenerative diseases.

Due to the harmfulness of catechol to the environment and human health, a series of analytical methods have been employed to determine catechol, including electrochemiluminescence [2,3], spectrophotometry [4], liquid chromatograph [5], gas chromatography [6], electrochemistry [7–12], capillary electrophoresis [13] and high performance liquid chromatography (HPLC) [14]. However, these methods suffer from sophisticated operations and expensive instrumentations. For example, the ECL and electrochemistry detection for catechol may require a complicated electrode preparation procedure. The capillary electrophoresis methods probably possess complex manipulations. The HPLC separations might be time-consuming. Herein, the development of simple, rapid, low-cost methods for detecting catechol is highly demanded.

Chemiluminescence has been put to employ in plenty of fields for its advantages of wide linear range and simple instrumentation [15–22]. Moreover, chemiluminescence mainly arises from its ability to produce photons without an excitation source, avoiding problems generating from background scattering light interference [23]. Unfortunately, the sensitivity of many traditional chemiluminescence systems cannot satisfy trace detection of certain substances, or some luminescent reagents are expensive or toxic, which restricts its application. In recent years, the research of CL mainly focused on hunting for new chemiluminescence reaction systems or combining traditional CL systems with new nanomaterials or techniques, thus constructing cheap, high luminous efficiency and green environmental protection system to expand the range of application and sensitivity of CL. Recently, nanomaterials has been extended to the chemiluminescence research field, mainly producing amplified CL emission. Noble metal nanoclusters (NCs), especially Au NCs have gained great attention on account of their remarkable features, such as easy synthesis, desirable water solubility and good stability. Up to now, the application of Au NCs primarily concentrated on their excellent fluorescence properties. To the best of our knowledge, the previous reported papers about Au NCs application to CL system are extremely finite [24–27]. You et al. have described a gold nanoclusters-based chemiluminescence resonance energy transfer [24]. Deng et al. have presented a method based on BSA-stabilized Au nanoclusters enhanced chemiluminescence of the luminol system

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[25]. Sui et al. have proposed gold nanoclusters-enhanced ultra-weak chemiluminescence systems [26,27]. However, there are no reports about the exploration of Au NCs in fluorescein CL reactions.

Fluorescein as one of common dyes, hitherto, few researches have shown fluorescein chemiluminescence reaction. It is said that fluorescein is low cost and available, making the study of fluorescein and H_2O_2 system become attractive and meaningful. In the study, it was highly desirable to find that Au NCs have effect on the CL reaction of fluorescein and H_2O_2, and the weak CL emission of the system was greatly enhanced by Au NCs. The trace of catechol-induced reduction of the CL signal from the Au NCs-enhanced fluorescein-H_2O_2 system. Through discussing the possible reaction mechanism of this system, we discovered that Au NCs exist in the system as the catalyst. In this work, the combination of Au NCs with new chemiluminescence system fluorescein-H_2O_2 not only introduces Au NCs to the liquid phase chemiluminescence, but also broadens the application of chemiluminescence.

2. Experimental

2.1. Apparatus

The CL experiments were carried out with a traditional Ultra-Weak Luminescence analyzer (Xi'an Remax company, Xi'an, China). CL spectra was obtained by a photomultiplier tube (opened at −800 kV). UV–vis absorption spectra were taken on a Model UV-2550s Spectrophotometer (Shimadzu, Japan). Fluorescencespectra were obtained by means of F-4500 spectrouorophotometer (Hitachi, Japan).

2.2. Reagents and materials

All chemicals and reagents were of analytical grade and used as received without further purication, and ultrapure water was used throughout. Bovine serum albumin (BSA) was purchased from Sangon Biotech Co., Ltd (Shanghai, China). Chloroauric acid ($AuCl_3 \cdot HCl \cdot 4H_2O$) and fluorescein were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nitro blue tetrazolium (NBT) was purchased from Kelong Reagent Co. Ltd. (Chengdu, China). Thiourea and ascorbic acid (AA) were commercially obtained from Chongqing Chemical Regent Company (Chongqing, China). 30% H_2O_2 and catechol were purchased from Chongqing Chuan dong Chemical (Group) Co., Ltd (Chongqing, China).

The 1×10^{-4} mol/L stock solution of catechol was prepared in water. The 0.01 mol/L stock solution of fluorescein was prepared by dissolving fluorescein in 0.1 mol/L NaOH and diluting to 100 mL with water. The working solution of fluorescein was prepared by diluting the stock solution with suitable concentration of sodium hydroxide. Working solutions of H_2O_2 were prepared fresh daily by dilution of 30% H_2O_2 with water. All the reagents used were of analytical reagent grades and doubly distilled water was used throughout the whole experiment.

2.3. Procedures

The chemiluminescence detection was carried out on a flow injection CL system, consisting of two peristaltic pumps to deliver the reactants to the flow cell (Fig. 1). The PTFE tubing (0.8 mm i.d.) was used to connect all components in the flow system. A six-way injection valve equipped with an 8 cm long sampling loop was used to inject. The CL signal produced was detected by a photomultiplier tube, and was then recorded by a computer equipped with a data acquisition interface. Data acquisition and treatment were performed with BPCL software running under Windows XP. Determination of catechol was performed based on the net CL

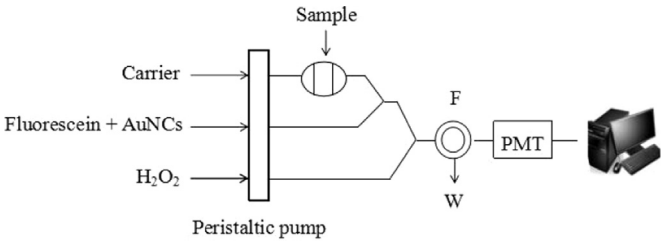

Fig. 1. Schematic diagram of the flow injection chemiluminescence system.

intensity of $\Delta I = I_0 - I_S$, where I_0 and Is denote the CL intensity in the absence and presence of catechol, respectively.

2.4. Sample preparation

Tap water and bottled drinking water were analyzed without any preprocessing. River water sample was filtered through a membrane filter of 0.22 μm pore size and added with 1.0×10^{-5} mol/L EDTA as a masking reagent for metal ions before the CL determination. The above solutions were then used for catechol detection.

2.5. Preparation of BSA–Stabilized Au Nanoclusters

BSA modified Au NCs were prepared according to the previous literature [28]. $HAuCl_4$ solution (15 mL, 10 mmol/L, 37 °C) introduced into BSA solution (15 mL, 50 mg/mL, 37 °C), stirring for 2 min. Then NaOH solution (1.5 mL, 1 mol/L) was added to the mixture. The mixture reaction allowed incubating at 37 °C for 24 h. The color of the solution changed from light yellow to light brown, and then to deep brown. The as-prepared Au NCs were then dialyzed in ultra-pure water for 48 h with dialysis membrane, and the cut off molecular weight of this dialysis membrane is 3500 Da. The final solution was stored at 4 °C refrigerator for further work. The synthesized Au NCs indicated with the appearance of red color under the uv lamp with naked eye as well as the UV–vis spectrophotometer and Fluorescence spectrophotometer which confirms the formation of Au NCs (Fig. 2).

3. Results and discussion

3.1. Kinetic characteristic of CL system

The weak CL emission resulting from the reaction of fluorescence and H_2O_2 was recorded in Fig. 3A, curve a. Then, the CL

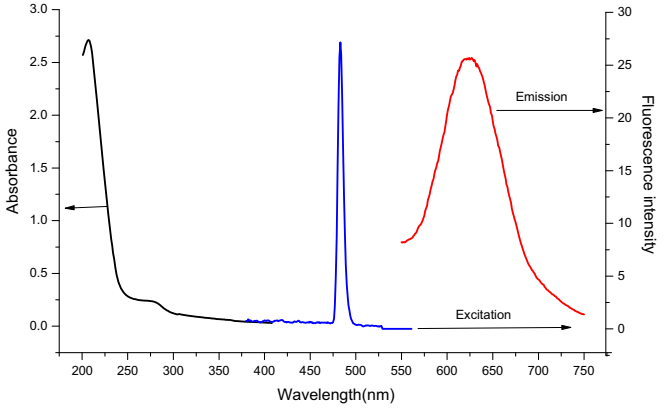

Fig. 2. UV–vis spectra and Fluorescence spectra of the synthesized Au NCs. Au NCs: 1×10^{-4} mol/L. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)