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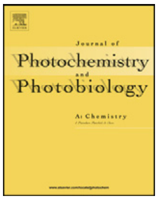

Platinum nanoparticle-catalyzed lucigenin–hydrazine chemiluminescence

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ABSTRACT

It was found that lucigenin alkaline solution could react with hydrazine in the presence of Pt nanoparticles to generate strong chemiluminescence (CL) centered at 480 nm. In order to explore the CL mechanism, UV–visible spectra, X-ray photoelectron spectra studies before and after the CL reaction were carried out. The effects of O_2 and superoxide dismutase (SOD) on the CL reaction were examined. The catalytic effect of Pt NPs on the hydrazine–O_2 reaction was studied. A possible mechanism is proposed to be due to that Pt NPs catalyzed the reaction between hydrazine and the dissolved oxygen under alkaline conditions to yield hydroperoxide species and superoxide radical anion, which further oxidized lucigenin to produce CL emission. Moreover, the effects of some organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), or sulfur groups on the lucigenin–hydrazine–Pt NPs CL system were tested. Thiol-containing compounds such as cysteine (Cys), glutathione (GSH), homocysteine (Hcy), and 6-mercaptopurine (6-MP) were observed to greatly enhance the CL intensity. It is suggested that the CL enhancement might be due to the fact that thiol-containing compounds could facilitate the electron transfer process under the catalysis of Pt nanoparticles and accelerate the generation of $OH^\bullet$ and $O_2^{\bullet-}$ radicals, leading to the strong CL.

1. Introduction

In recent years, metal nanoparticle (NP)-involved chemiluminescence (CL) has received considerable interest because of their unique chemical reactivity, catalytic properties and surface property [1]. For example, metal NPs such as Au NPs, Ag NPs and Pt NPs can participate in CL reactions as reductants, catalysts, luminophors and nano-sized reaction platforms. Among them, metal NPs-catalyzed CL has become an important subject. It has been reported that Au NPs, Ag NPs and Pt NPs could catalyze the luminol–H_2O_2 CL reaction [2–4]. Au NPs and Ag NPs could catalyze the luminol–ferricyanide CL reaction [5,6], and Au NPs could catalyze the luminol–$AgNO_3$ CL reaction and luminol–hydrazine CL reaction [7,8]. It was also found that Au–Ag alloy nanoparticles could catalyze the Rhodamine 6G-Cerium(IV) CL reaction [9]. However, for metal nanoparticle as CL catalysts, the used metal NPs are focused on Au NPs and Ag NPs, and other metal NPs are rarely studied. Besides, the studied CL system is mainly limited to luminol reactions. For other famous CL reactions such as lucigenin CL reactions, metal NPs seem to be inefficient for catalysis. There are few reports about catalysis of metal NPs in lucigenin CL reactions. Recently, it was found that ethanol can initiate Pt NPs to catalyze the lucigenin CL reaction in an alkaline solution, leading to a visible light emission with autocatalytic property [10]. The CL emission was also time-tunable by adjusting the concentration of Pt NPs injected. Both Pt NPs and ethanol were necessary for autocatalytic CL. Pt NPs were general catalysts for the oxidation of ethanol to acetaldehyde and the CL enhancement by acetaldehyde. Ethanol in this system was an initiator for catalysis.

In the present study, it was found that Pt NPs could directly catalyze the reaction of lucigenin with hydrazine in an alkaline solution, accompanying with a strong CL. The effects of Pt NPs with different protecting agents synthesized by the citrate on the lucigenin–hydrazine CL system were explored. UV–visible spectra and X-ray photoelectron spectra (XPS) studies were conducted before and after the CL reaction. The effects of O_2 and superoxide dismutase (SOD) on the CL reaction were examined. The catalytic effect of Pt NPs on the hydrazine–O_2 reaction was studied. A possible CL mechanism is proposed. Moreover, the effects of 30 organic compounds containing hydroxyl (OH), carboxyl (COOH), carbonyl (CO), amino (NH_2), or sulfur groups on the lucigenin–hydrazine–Pt NPs CL system were explored. It was found that thiol-containing compounds could greatly enhance the CL. The CL enhancing mechanism is discussed.

2. Experimental

2.1. Chemicals and solutions

Lucigenin was obtained from TCI (Japan). Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 37.0%, w/w), trisodium citrate ($Na_3C_6O_7$), NaOH, poly-(vinylpyrrolidone) (PVP, MW 36000), hydrazine

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($N_2H_4{\cdot}H_2O$), NaCl, hydrogen peroxide (H_2O_2), superoxide dismutase (SOD), horseradish peroxidase (HRP), and 2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) were obtained from Shanghai Reagent Co., Ltd (Shanghai, China). 6-Mercaptopurine (6-MP), adenine, tripropylamine, ethylenediamine, adrenaline, norepinephrine, aniline, o-diaminobenzene, m-phenylenediamine, p-phenylenediamine, phenol, catechol, resorcinol, hydroquinone, methanol, ethanol, acetaldehyde, and formic acid were purchased from Sangon Biological Engineering Technology & Services Co., Ltd. (Shanghai, China). Homocysteine (Hcy), glutathione (reduced) (GSH), cysteine (Cys), cystine, glutathione (oxidized) (GSSG), glycine (Gly), histidine (His), tryptophan (Trp), arginine (Arg), and methionine (Met) were obtained from Solarbio (Beijing, China). All the reagents were of analytical grade, and Milli-Q water (18.2 MΩ) (Millipore, USA) was used throughout.

The stock solution of lucigenin (1.0×10^{-3} mol/L) was prepared by dissolving lucigenin in water. Working solutions of lucigenin were prepared by diluting the stock solution with water. The stock solution of (1.0×10^{-3} mol/L) 6-MP was prepared in 0.01 mol/L NaOH and stored in 4 °C. Working solutions of 6-MP were prepared by diluting appropriate amount of stock solution with water and stored at 4 °C in the dark during the day.

2.2. Synthesis of citrate- and PVP-protected Pt colloids by the citrate reduction method

The citrate-protected colloidal platinum nanoparticles were prepared as described by Henglein et al. [11]. The procedure is as follows: $H_2PtCl_6{\cdot}6H_2O$ (0.03 mmol) was added to 50 mL water and heated to boiling with stirring in a 100 mL round-bottomed flask. After adding 5.0 mL trisodium citrate (1.0% aqueous solution), the resulting solution was maintained at boiling for 1 h. Brown-colored colloidal platinum colloids were then obtained and cooled to room temperature. PVP-protected Pt NPs were prepared by the citrate reduction method according to the same procedure as above, except for 33 mg PVP (0.3 mmol as monomeric unit) was added as a protective agent.

2.3. Chemiluminescence measurements

The chemiluminescence detection was conducted on a laboratory-built flow injection chemiluminescence system, consisting of a model IFFM-D flow injection system (Ruimai Electronic Science Co.), a model IFFS-A luminometer, and a computer, as shown in Fig. 1. Water carrying the colloidal solution of Pt NPs was mixed with hydrazine and then with NaOH–lucigenin solutions. The CL signals were monitored by the PMT adjacent to the flow CL cell. When the CL system was used to study the effect of organic compounds, the sample solution containing organic compounds and the Pt colloids were mixed offline, which was combined with hydrazine and then with NaOH–lucigenin solutions. The value of $\Delta I = I - I_0$ showed the effect of organic compounds on the CL intensity of lucigenin–hydrazine–Pt NPs system, where I_0 stands for the signal in the absence of organic compounds and I stands for the signal in the presence of organic compounds.

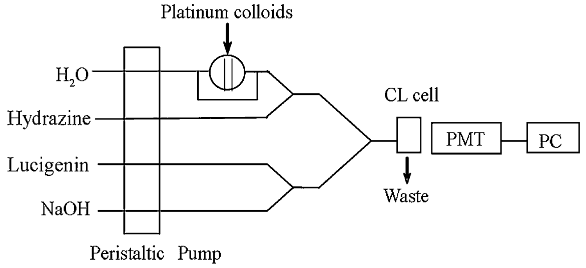

Fig. 1. Schematic diagram of flow-injection CL detection system.

2.4. Optical measurements

CL spectra and fluorescence spectra were conducted on a model F-7000 Fluorescence Spectrophotometer (Hitachi, Japan). UV–visible spectra and X-ray photoelectron spectra were carried out on a model UV-8453 UV–visible spectrometer (Agilent, USA) and on a model ESCALAB MK II electron spectrometer (VG, England). The XPS sample was prepared as follows: NaCl was added to a 100 mL Pt NPs to precipitate the particles, then, the mixture was centrifuged and the precipitates obtained were thoroughly washed by water.

3. Results and discussion

3.1. Platinum colloids-involved lucigenin CL

When water carrying the colloidal solution of Pt NPs protected by citrate was mixed with hydrazine and then with NaOH–lucigenin solution, a strong CL emission was observed as shown in Fig. 2, curve a. The CL intensity was even comparable with that of well-known lucigenin–H_2O_2 system. In the absence of colloidal Pt nanoparticles, only a weak CL was observed from the baseline of curve a. To exclude the effect of the concomitants in the experiment, Pt colloids were centrifuged at 12,000 rpm for 30 min, the obtained supernatant instead of Pt colloids was injected into the CL system and no obvious CL signal was observed as shown in Fig. 2, curve c. Therefore, the CL was related to the Pt NPs.

The effects of platinum colloids protected by different reagents on the lucigenin–hydrazine CL system were also investigated. As shown in Fig. 2, curves b and c, the CL intensity with platinum colloids protected by citrate (Fig. 2, curve a) was stronger than that with platinum colloids protected by PVP (Fig. 2, curve b).

The CL spectra for the platinum colloids–lucigenin–hydrazine system were studied as shown in Fig. 2, inset. The result demonstrated that the maximum emission wavelength was at 480 nm, which was in good agreement with the emission of the typical lucigenin system, revealing that the luminophor was still the excited state N-methylacridone (NMA) [12]. Therefore, the addition of platinum colloids did not lead to the generation of new luminophor.

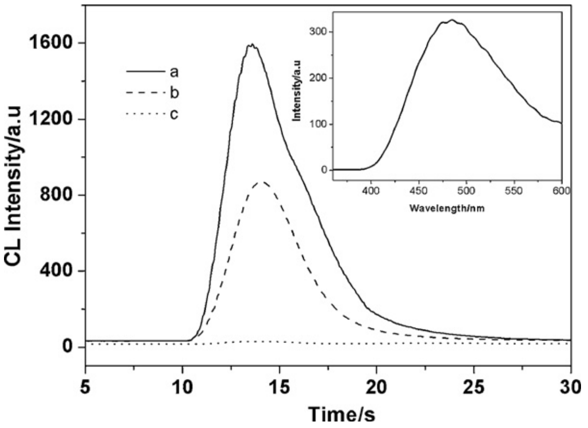

Fig. 2. CL profiles when Pt NPs were injected into hydrazine, then combined with the mixture of lucigenin and NaOH. (a) citrate-protected Pt; (b) PVP-protected Pt; (c) blank (the supernatant of the citrate-protected Pt NPs after centrifugation). Conditions: lucigenin, 5×10^{-6} mol/L; NaOH, 0.1 mol/L; hydrazine, 0.01 mol/L; Pt NPs, 1.5 μmol/L. The inset is the CL spectra.