



Luminol chemiluminescence induced by silver nanoparticles in the presence of nucleophiles and Cu²⁺

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ABSTRACT

It was found that silver nanoparticles (NPs) in the presence of nucleophiles and Cu²⁺ could induce luminol to produce chemiluminescence (CL). The AgNPs–NaBr–CuSO₄–luminol system was chosen as a model system to study the CL mechanism. UV–vis absorption spectra showed that silver nanoparticles in the presence of NaBr could react with CuSO₄ before injection of luminol. The X-ray diffraction patterns and X-ray photoelectron spectra demonstrated that Cu(I) complex was a key reaction product in AgNPs–NaBr–CuSO₄ system. Besides, it was also found that superoxide dismutase could inhibit the CL, revealing that a superoxide anion was involved in the CL reaction. On this basis, it was suggested that the luminol CL induced by silver nanoparticles in the presence of NaBr and Cu²⁺ derived from Cu(I) complex formed via the reduction of CuSO₄ by AgNPs by the aid of NaBr, which reacted with the dissolved oxygen to generate the superoxide anion; then the superoxide anion reacted with luminol to produce CL. Br[−] as a nucleophile was considered to decrease the oxidation potential of silver nanoparticles so that Cu(II) is readily reduced to Cu(I) and to bind to Cu(I) preventing Cu(I) from dismutation in water. As expected, other nucleophiles such as Cl[−], I[−] and thiosulfate, which were also efficient to decrease the oxidation potential of AgNPs and bind to Cu(I), could also induce the luminol CL.

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1. Introduction

In recent years, nanoparticles (NPs) have been widely studied for their excellent properties [1–3] and their potential applications in microelectronics, optics, electronics, magnetic devices, and catalysis [4–8]. In these investigations, a number of reports focus on the properties of NPs in the presence of nucleophiles [9–11]. Absorption of these nucleophiles on silver NPs can drastically change their optical properties and redox reactivity [12,13]. The silver atoms on the surface are coordinatively unsaturated. One may expect that unoccupied orbitals exist on the surface into which a nucleophilic reagent can donate an electron pair. The consequence is not only a change in the optical absorption of the colloidal particles but also a change in their reactivity. The interaction of surface atoms with nucleophiles leads to a partial oxidation of surface atoms, while the interior of colloidal particles receives a corresponding negative charge which can be picked up by the electron acceptors. Cu²⁺ has been used as a typical electron acceptor to test the enhanced redox capability of the silver NPs in the nucleophiles. Without the nucleophiles, addition of Cu²⁺ could not result in the oxidation of silver particles. The Fermi level of silver NPs modified by nucleophiles was significantly shifted toward a negative potential, and is more

negative than the standard redox potential of the Cu²⁺/Cu⁺ couple. As a result, the reducing ability of silver NPs in the presence of nucleophiles is enhanced so that Cu²⁺ could oxidize silver particles by the aid of the nucleophiles. Besides, other electron acceptors have been investigated to test the enhanced redox capability of the silver particles in the presence of nucleophiles. The fact that the oxidation of metal by oxygen is facilitated by a nucleophilic reagent is well-known [9,10,13]. Cytochrome c was also found to undergo reduction when introduced into a suspension of colloidal silver mixed with aqueous Br[−] and I[−] in micromolar concentration [14].

A class of homogeneous chemical reactions, chemiluminescence (CL) reactions accompanied by light emissions, have been intensively investigated for many years. Recently, metal NPs were employed in the CL study as a catalyst, reductant, luminophor, and energy acceptor [15–27]. However, NPs in the presence of nucleophiles with the enhanced reducing ability were rarely investigated for CL reactions. In our previous work, it was found that in the presence of KI, silver NPs as a reductant could induce the liquid-phase CL of lucigenin [18]. Furthermore, the CL behavior of lucigenin–Ag colloid in the presence of other nucleophiles such as thiourea, sodium thiosulfate, cysteine, mercaptoacetic acid, and mercaptopropionic acid was explored. Instead of AgNPs, Au and Pt were also examined for inducing lucigenin CL in the presence of various nucleophiles. In the present work, luminol CL reaction, another important CL reaction, induced by silver NPs in the presence of nucleophiles was

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explored. It is found that AgNPs in the presence of NaBr and Cu^{2+} could react with luminol, accompanying by a CL emission. The CL mechanism was also studied.

2. Experimental

2.1. Chemicals and solutions

A 1.0×10^{-2} mol/L stock solution of luminol was prepared by dissolving luminol (Sigma, America) in 0.10 mol/L sodium hydroxide solution. Polyvinyl pyrrolidone (PVP, Mw = 36,000), superoxide dismutase (SOD), AgNO_3 , NaBr, NaI, NaCl, thiosulfate, CuSO_4 , and NaBH_4 were obtained from Shanghai Reagent (Shanghai, China). All reagents were of analytical grade, and used as received. Ultrapure water obtained by a Direct-Q 3 UV water purification system (Millipore, USA) was used throughout.

2.2. Preparation of Ag colloid

Ag Colloid was synthesized by chemical reduction method in a solution. In brief, 0.50 g PVP was dissolved in 20.0 mL water. Subsequently, 25 mL NaBH_4 (5.0×10^{-3} mol/L) was mixed with the PVP aqueous solution. Then, 5.0 mL AgNO_3 (5.0×10^{-3} mol/L) were added dropwise to the mixture with vigorous stirring simultaneously. The color of the mixture visibly changed to yellow gradually. The reaction was conducted at room temperature for 30 min and aged for 2 days at 4°C before use. The raw colloid was centrifuged at 12,500 rpm for 30 min (Universal 320, Hettich, Germany). Ag colloid was obtained after the sediment was redissolved in 1% PVP aqueous solution. The resulting yellow silver colloids were characterized by high resolution transmission electron microscope (HRTEM, JEM-2010, Hitachi, Japan). The diameters and size distribution of AgNPs were obtained based on the statistical analysis of HRTEM data as shown in Fig. 1. The image of Fig. 1 showed the AgNPs were well distributed. Statistical analysis of HRTEM data revealed that the average diameter of the NPs was 8.0 ± 4.0 nm.

2.3. CL measurements

The CL was detected by a microplate luminometer (Centro LB 960, Berthold, Germany). In a typical experiment, the mixed solution of $50 \mu\text{L}$ of Ag colloid with $50 \mu\text{L}$ of NaBr was pipetted into

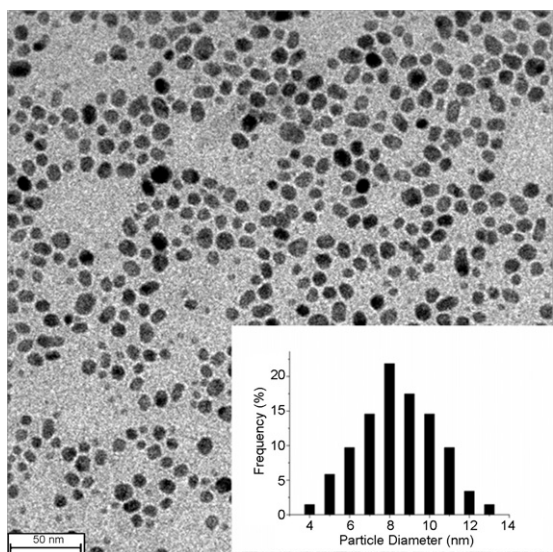


Fig. 1. HRTEM images of AgNPs. The inset is the corresponding size distributions of AgNPs. Calculated diameter is 8.0 ± 4.0 nm by accounting about 100 units.

each well of microtiter plate, and then $50 \mu\text{L}$ of CuSO_4 and $50 \mu\text{L}$ of luminol were injected into the mixture in the well successively. The light emission was measured by the microplate luminometer immediately.

2.4. Optical measurements

The CL spectra were measured on a model FL 5401 spectrofluorometer (Shimadzu, Japan). UV-vis spectra were measured on a model UV-2401 PC spectrophotometer (Shimadzu, Japan). The reaction product of the Ag colloid–NaBr– CuSO_4 system was characterized by X-ray powder diffraction (XRD) and X-ray photoelectron spectrum (XPS). XRD pattern was obtained with a model D/max-rA diffractometer (Rigaku, Japan) and XPS was obtained with a model ESCALAB MK II electron spectrograph (VG, England). The sample was prepared as follows: 4 mL CuSO_4 (0.1 mol/L) was added into 400 mL Ag colloid containing 1.0×10^{-2} mol/L NaBr. The solution was continuously stirred for 60 min. After the reaction finished completely, the reacted system was evaporated and precipitates occurred in the reacted mixture gradually. Then, the obtained precipitates were filtrated by a mixed cellulose membrane with pore size of $0.45 \mu\text{m}$ (XingYa, Shanghai). Subsequently, the precipitates were thoroughly washed by water and ethanol and then dried at room temperature for a night, which was used for the further experiments.

3. Results and discussion

3.1. CL accompanied by reaction of luminol– CuSO_4 –AgNPs in the presence of NaBr

The CL response of AgNPs in the presence of NaBr and CuSO_4 to alkaline luminol solution was studied by static injection. As show in Fig. 2, first, when Ag colloid was mixed with NaBr, no CL emission appeared (the lines before injection). Subsequently, CuSO_4 and luminol were injected to the mixture successively, a reproducible CL was observed (curve a). The maximum CL intensity of the CL system was about one order of magnitude higher than that of a conventional luminol– H_2O_2 CL system (0.001 mol/L H_2O_2) with the same pH value of the CL reaction and the same concentration of luminol. The supernatant of the Ag colloid after centrifugation was used as a control solution for the CL experiments instead of Ag colloid and no considerable CL emission was observed (curve

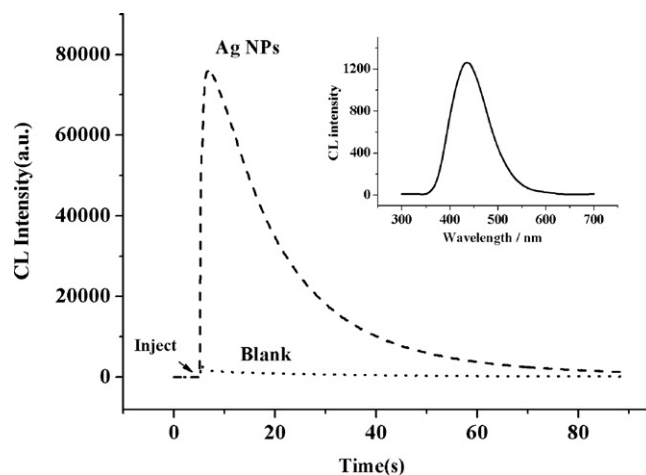


Fig. 2. Chemiluminescence kinetic curves when injecting CuSO_4 and luminol into Ag colloid in the presence of NaBr (a). The supernatant solution after centrifugation of Ag colloid was used as a control solution (b). Reaction conditions: CuSO_4 , 1×10^{-3} mol/L; luminol, 1×10^{-4} mol/L in 0.1 mol/L carbonate buffer (pH 10.0); Ag, 3×10^{-4} mol/L; NaBr, 1×10^{-2} mol/L. The inset is the chemiluminescence spectra.

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