



Luminol chemiluminescence induced by silver nanoparticles in the presence of nucleophiles and Cu^{2+}

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ABSTRACT

It was found that silver nanoparticles (NPs) in the presence of nucleophiles and Cu^{2+} could induce luminol to produce chemiluminescence (CL). The AgNPs–NaBr– CuSO_4 –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 CuSO_4 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– CuSO_4 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 Cu^{2+} derived from Cu(I) complex formed via the reduction of CuSO_4 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. Cu^{2+} 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 Cu^{2+} 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 $\text{Cu}^{2+}/\text{Cu}^+$ couple. As a result, the reducing ability of silver NPs in the presence of nucleophiles is enhanced so that Cu^{2+} 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

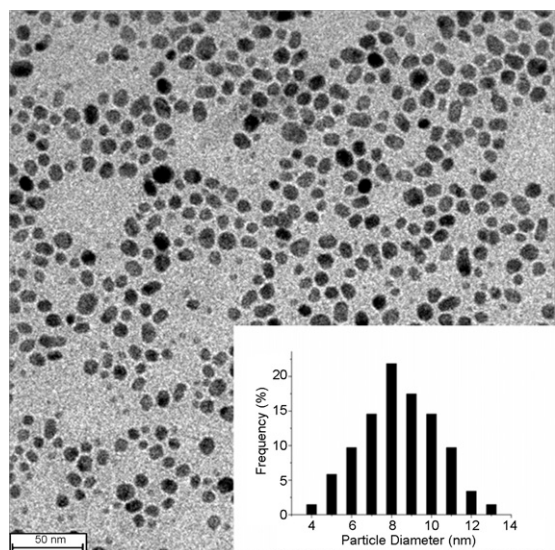


Fig. 1. HRTEM images of AgNPs. The inset is the corresponding size distributions of AgNPs. Calculated diameter is 8.0 ± 4.0 nm by accounting about 100 units.

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

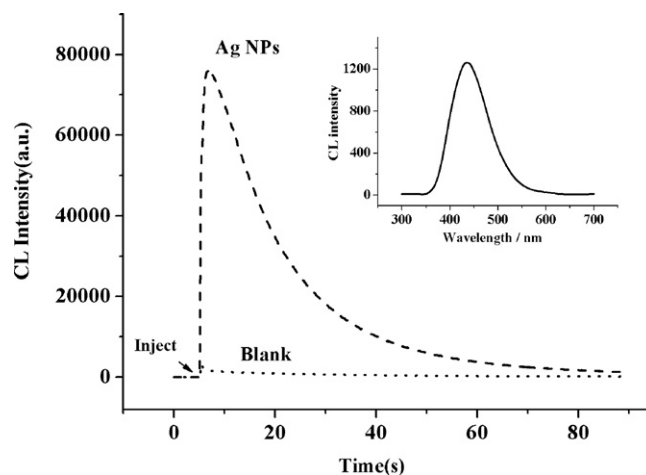


Fig. 2. Chemiluminescence kinetic curves when injecting CuSO_4 and luminol into Ag colloid in the presence of NaBr (a). The supernatant solution after centrifugation of Ag colloid was used as a control solution (b). Reaction conditions: CuSO_4 , 1×10^{-3} mol/L; luminol, 1×10^{-4} mol/L in 0.1 mol/L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

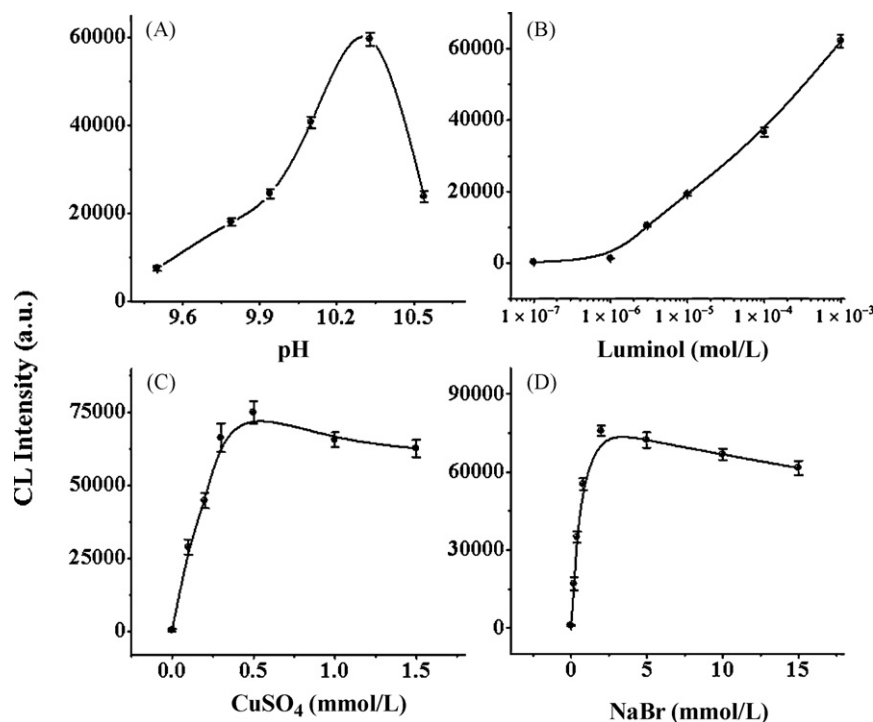


Fig. 3. Effects of the reaction conditions on the CL intensity. (A) Effect of the pH, reaction conditions: 1×10^{-3} mol/L CuSO_4 , 0.01 mol/L NaBr, 1×10^{-4} mol/L luminol in 0.1 mol/L carbonate buffers with varying pH values. (B) Effect of the luminol concentration, reaction conditions: pH 10.0, 1×10^{-3} mol/L CuSO_4 , 0.01 mol/L NaBr, luminol with different concentrations in 0.1 mol/L carbonate buffers. (C) Effect of the CuSO_4 concentration, reaction conditions: pH 10.3, 0.01 mol/L NaBr, 1×10^{-4} mol/L luminol in 0.1 mol/L carbonate buffers. (D) Effect of the NaBr concentration, reaction conditions: pH 10.3, 1×10^{-3} mol/L CuSO_4 , 1×10^{-4} mol/L luminol in 0.1 mol/L carbonate buffers.

b). Therefore, the CL accompanying the luminol– CuSO_4 –Ag colloid reaction in the presence of NaBr was related to the AgNPs rather than associated species present in the synthesis. The CL spectra showed that the maximum emission wavelength was ca. 425 nm, indicating that the luminophor was 3-aminophthalate, an oxidation product of luminol [28].

The effects of the reaction conditions on the CL intensity were investigated. As shown in Fig. 3, the CL intensity was largely dependent on the pH of the reaction and the reactant concentrations, including CuSO_4 , NaBr, and luminol. The CL intensity increased with the pH from 9.5 to 10.3, which was similar to other luminol systems, but it decreased when the pH was higher than 10.3 (Fig. 3(A)). It may be due to that CuSO_4 with high concentrations under ultra-basic condition would form $\text{Cu}(\text{OH})_2$ precipitates before the CL reactions. Increasing the concentration of the hydroxide ion causes more $\text{Cu}(\text{OH})_2$ to precipitate, which decrease concentration of Cu^{2+} from the solution. Based on the results in Fig. 3(C), the decrease of Cu^{2+} concentration (0.5–0 mmol/L) leads to the decrease of the CL intensity. Accordingly, the decrease of the Cu^{2+} concentration in the reaction might be the reason for the decrease of the CL intensity during the high pH range. As shown in Fig. 3(B), the CL intensity increased with the luminol concentration over the range of 1.0×10^{-7} to 1.0×10^{-3} mol/L. As shown in Fig. 3(C), the CL intensity increased obviously with the CuSO_4 concentration over 0–0.5 mmol/L, but it decreased slightly when the CuSO_4 concentration was higher than 0.5 mmol/L. The effect of the NaBr concentration on the CL intensity was similar as the effect of the CuSO_4 concentration as shown in 3(D). With the NaBr concentration over 0–2.0 mmol/L, the CL intensity increased. However, when the concentration was higher than 2 mmol/L, the CL intensity decreased gradually. It is reasonable that the increase of CL intensity followed by the initial increase of the concentration of CuSO_4 or NaBr because they are reactants in the CL reaction. However, further increase of the concentration of CuSO_4 or NaBr also led to an increase in ionic strength. It was reported that the increase of

ionic strength could cause the CL decrease [29]. As a result, the CL intensity decreased slightly or remained intact beyond a particular concentration of CuSO_4 or NaBr.

3.2. Mechanism of the CL reaction

It reported that Cu^{2+} could oxidize Ag colloid in the presence of nucleophiles [12]. Therefore, it was deduced that CuSO_4 might react with AgNPs by the aid of NaBr at the beginning; then, luminol might react with the intermediate products of AgNPs–NaBr– CuSO_4 to yield a CL emission when luminol was injected in the mixture. To validate this hypothesis, supporting experiments were carried out as follows.

First of all, UV–vis absorption spectra were utilized to monitor the reaction between CuSO_4 and AgNPs in the presence of NaBr. AgNPs exhibited SPR absorption bands in the visible region (ca. 410 nm) before the reaction, in good agreement with reported results [30]. When NaBr and CuSO_4 were added to the yellow Ag colloid, the time-dependent SPR absorption spectra of the mixture are shown in Fig. 4. The SPR absorption spectra were measured at a time interval of 0.5 s. Although 121 spectra were obtained in 60 s, only 5 typical ones at different moments are shown in Fig. 4. The insets show the temporal absorbance of ca. 410 nm (λ_{max}) at a time interval of 0.5 s. Clearly, with the increase of reaction time, the SPR absorbance decreased gradually. After the reaction, the yellow color of the mixture disappeared. These results indicated AgNPs could react with CuSO_4 in the presence of NaBr and the concentration of AgNPs decreased during the reaction.

Subsequently, to ascertain the reaction product of AgNPs–NaBr– CuSO_4 , the reaction system was evaporated and precipitates occurred in the reacted mixture. The brown powders derived from the precipitates were involved into XRD and XPS analysis. In Fig. 5, XRD pattern of the precipitate from the AgNPs–NaBr– CuSO_4 system is in good agreement with XRD pattern of pure CuBr and AgBr [31,32]. The peaks at 30.9° , 44.4° ,

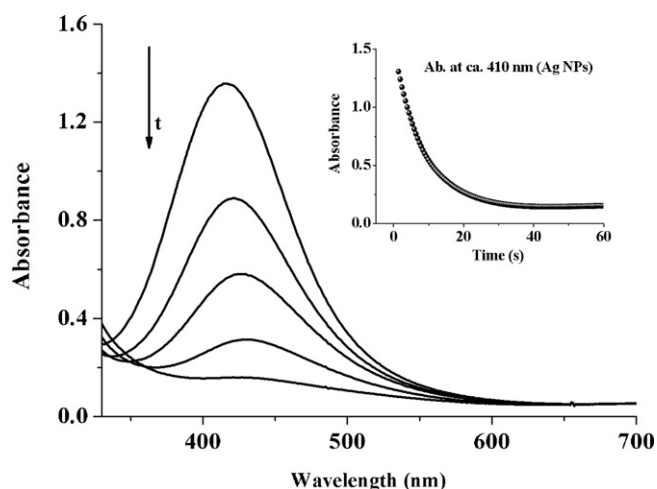


Fig. 4. Time-dependent UV-vis absorption spectra during the reaction between CuSO_4 and AgNPs in the presence of NaBr. 5 selected spectra were recorded at 2.5, 5.0, 10.0, 18.0 and 32.0 s after the addition of CuSO_4 in the mixing solution of the Ag colloid with NaBr. The insets display the corresponding temporal SPR absorption at ca. 410 nm (SPR absorption maximum wavelength) at a time interval of 0.5 second. Conditions: 1×10^{-3} mol/L of CuSO_4 , 0.01 mol/L of NaBr, 3×10^{-4} mol/L of Ag.

55.2° , 73.3° exactly corresponded to the peaks of (200), (220), (222), (420) of AgBr, respectively. Other peaks at 27.3° , 45.1° , 53.5° exactly corresponded to the peaks of (111), (220), (311) of CuBr, respectively. The results indicated that CuBr and AgBr were a reduction product and an oxidation product, respectively. It strongly supported that AgNPs could be oxidized by CuSO_4 by the aid of NaBr. Besides, Cu(I) compounds were one of main products in the reaction.

Furthermore, Cu 2p X-ray photoelectron spectra of the reaction product, the brown powders, derived from the precipitates, are shown in Fig. 6(B). All binding energies (BE) were calibrated with respect to the C 1s BE at 284.6 eV. As can be seen from Fig. 6, the Cu 2p spectrum of the precipitates was curve-fitted into four components at 932.0, 934.4, 951.8, and 954.3 eV. The components at 932.0 and 951.8 eV were attributed to the Cu(I), which is in good agreement with Cu(I) 2p XPS of pure CuBr as shown in Fig. 6(A). The components at 934.4 and 954.3 eV were attributed to Cu(II), being in good agreement with Cu(II) 2p XPS of Cu(II) in reported results [33]. Additionally, the components at 941.8 and 943.7 eV in Fig. 6(B) belong to the Cu(II) 3p spectrum. The data of XPS demonstrated that the average atomic ratio (Cu(I)/Cu(II)) was 1.6:1 on

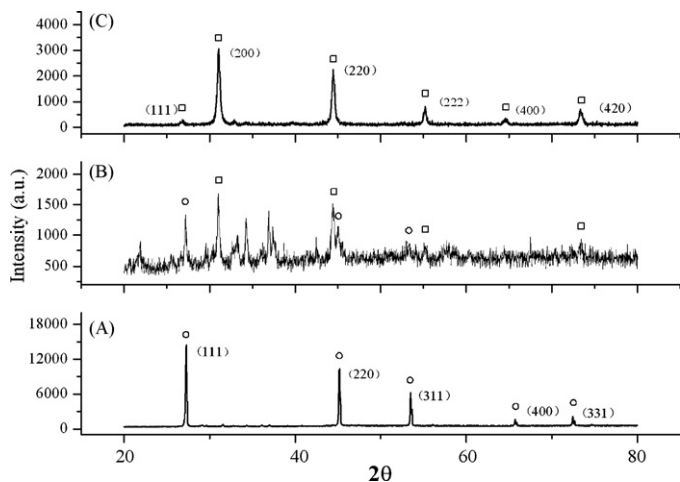


Fig. 5. (A) Typical XRD pattern of CuBr. (B) XRD pattern of the precipitate from the CuSO_4 -AgNPs-NaBr reaction system. (C) Typical XRD pattern of AgBr.

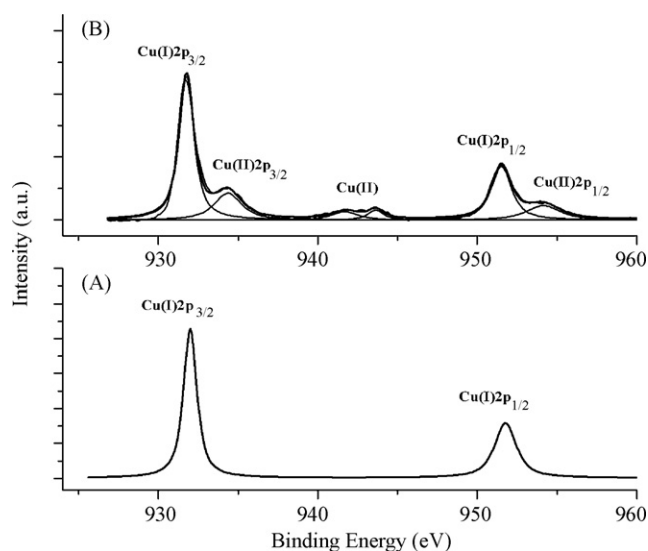


Fig. 6. X-ray photoelectron spectra of (A) Cu 2p of pure CuBr and (B) Cu 2p of the precipitate from the CuSO_4 -AgNPs-NaBr reaction system.

the surface of precipitates, indicating that Cu(I) was main form of Cu.

Therefore, the reaction between CuSO_4 and AgNPs in the presence of NaBr produced Cu(I) complex in its final products. It has been reported that Cu(I) can react with the dissolved oxygen to produce superoxide [34,35]. The CL of the luminol/superoxide system, which was one of the common CL systems, has been studied deeply in the past [36–38]. It is reasonable to suggest that the injection of luminol to the Cu(I) solution could yield CL emission. Subsequently, the CL reaction of CuBr with the luminol was examined. CuBr was dissolved into a NaBr and HCl solution. As shown in Fig. 7, the mixture of other cocomitants (AgNPs-AgNO₃-NaBr) was employed in CL test and no considerable CL signal appeared with the injection of luminol. However, when luminol was injected into the CuBr solution, a considerable CL emission was observed. Considering AgNPs or Ag(I) complex might coexist with Cu(I) complex, AgNPs or AgNO₃ was also added into the CuBr solution for the CL tests. In the presence of AgNO₃ or AgNPs, a visible increase in the

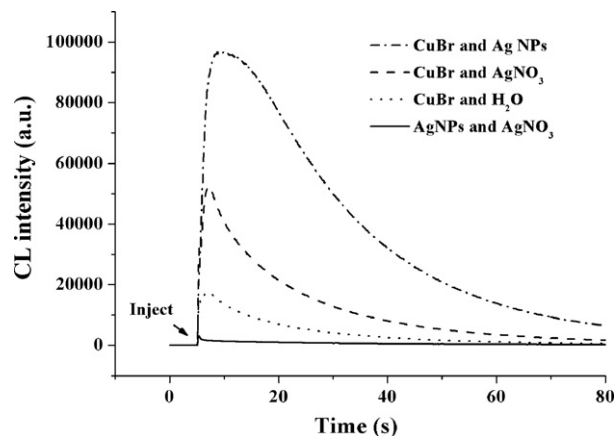
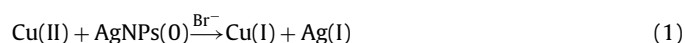


Fig. 7. Chemiluminescence kinetic curves. (a) Control solution: the mixture of AgNPs-AgNO₃-NaBr. (b) CL of the Cu(I) complex solution with luminol (dot line). Coexist reagents, AgNO₃ (c) (shot line) or AgNPs (d) (shot dot line) were added into the CuBr solution for CL tests. The insets displays the inhibition effect of SOD on the Cu(I)-luminol CL. Conditions: 1×10^{-4} mol/L CuBr in 0.01 mol/L NaBr and 0.1 mol/L HCl solution, 3×10^{-4} mol/L Ag, 1×10^{-5} mol/L AgNO₃, 1×10^{-4} mol/L luminol in 0.1 mol/L carbonate buffers (pH 10.0). Control solution: 3×10^{-4} mol/L Ag, 1×10^{-5} mol/L AgNO₃, 0.01 mol/L NaBr.

CL intensity appeared after injecting luminol into the CuBr solution. It is supported that the Cu(I) complex solution could react with luminol to generate CL emission and the coexisted AgNO₃ or AgNPs could enhance the CL intensity. Then, SOD was used to determine whether a superoxide anion was involved in the CL reaction of the Cu(I) complex solution and luminol. SOD was added into the CuBr solution before injection of luminol and the CL was decreased with the increase of the SOD concentration. These results revealed that a superoxide anion was involved in the CL reaction. On this basis, it was suggested that the luminol CL induced by AgNPs in the presence of NaBr derived from Cu(I) complex, one of products in the reaction of AgNPs–NaBr–CuSO₄, which reacted with the dissolved oxygen to generate the superoxide anion; then the superoxide anion reacted with luminol to produce CL. The CL process may proceed as follows:



Based on the proposed mechanism, Cu(I) complex is a key intermediate product in the CL reaction. Br⁻ is considered as a nucleophile and there are two important functions in the luminol CL.

The one function of Br⁻ is to enhance redox capability of AgNPs, which reduces Cu(II) to generate Cu(I) complex. Increasing the concentration of the Br⁻ could cause more AgBr to precipitate. Based on Nernst's equation, precipitation of Ag⁺ with halides could decrease the reduction potential of Ag(0). Therefore, the tendency of the oxidation of AgNPs by Cu(II) and the generation of Cu(I) increase with the NaBr concentration.

The dismutation of Cu(I) to Cu(0) and Cu(II) in water is well-known. Without nucleophiles, Cu(I) was consumed in the dismutation reaction before reacted with oxygen so that the CL of Cu(I) with luminol would be terminated. Fortunately, Br⁻ in the CL reaction was efficient ligands to bind to Cu(I) and to prevent Cu(I) from dismutation:



$$K_c = \frac{[\text{CuBr}_2^-]}{[\text{Cu}^+][\text{Br}^-]^2} = 10^{5.89} \quad (6)$$

$$\frac{[\text{CuBr}_2^-]}{[\text{Cu}^+]} = 10^{5.89} \times [\text{Br}^-]^2 = 10^{5.89} \times 10^{-4} = 10^{1.89} = 77.6 \quad (7)$$

where K_c is the steady constant of CuBr₂⁻. With 0.01 mol/L Br⁻ in a solution, the concentration ratio [CuBr₂⁻]/[Cu⁺] is about 78. Accordingly, Cu(I) might be in the form of CuBr₂⁻ in the CL reaction system by the virtue of Br⁻. Br⁻ in the luminol CL is efficient ligands for Cu(I) so that Cu(I) could be accumulated in the solution for the CL reaction, which is another function of Br⁻.

3.3. The respond of other nucleophiles to the CL

Since other nucleophiles, such as Cl⁻, I⁻, and thiosulfate are also efficient ligands for Cu(I), it is reasonable to deduce that the similar reactions could generate the CL in the presence of these nucleophiles. However, when NaCl substituted for NaBr, AgNPs could not induce the luminol CL under the same reaction conditions. It is known that the solubility products of AgCl ($K_{sp,AgCl} = 1.8 \times 10^{-10}$) are much larger than that of AgBr ($K_{sp,AgBr} = 5.0 \times 10^{-13}$). Accordingly, the reducing ability of AgNPs in the presence of NaCl is weaker than that in the presence of NaBr at the same concentration. During the experiments, when CuSO₄ was added into Ag colloid in the

presence of NaBr, the color of Ag colloid faded quickly and obviously. But in the presence of NaCl, there was no visible bleaching when CuSO₄ was added into the yellow Ag colloid in a short time. We deduced the inefficient of Cl⁻ was relative to the unproductive reaction so that the CL was too weak to be detected. In order to accumulate enough Cu(I) in the reaction between CuSO₄ and AgNPs in the presence of NaCl for the CL reaction, luminol was injected into the mixture after waiting a quite longer time. The waiting time was investigated. More than 600 s after CuSO₄ mixed with AgNPs in the presence of NaCl, a considerable CL appeared when injecting luminol into the mixture. Furthermore, NaI was also investigated in the CL reaction instead of NaBr and the CL emission could be observed. As a matter of fact, I⁻ is more efficient ligand for Cu(I) than Br⁻. However, I⁻ could react with Cu²⁺ to yield CuI and I₂. Although CuI could lead to the CL emission of luminol, I₂–luminol system is another well-known CL system. In other words, Cu²⁺–I⁻–luminol–Ag system with a different mechanism from other systems could not be taken as an example for discussion. Accordingly, Br⁻ was chosen as the main nucleophile in this work. Besides, thiosulfate, a good ligand for Cu(I) in the aqueous solution, was used as a nucleophile to be tested in the CL reaction. The results with thiosulfate were similar to NaBr. Ag colloid faded when mixing with thiosulfate and CuSO₄ and a considerable CL emission was generated by further injecting luminol.

4. Conclusions

In the presence of nucleophiles and Cu²⁺, AgNPs could initiate luminol CL. The AgNPs–NaBr–CuSO₄–luminol reaction was chosen as a model system to study the CL process. The CL mechanism is likely due to the fact that AgNPs by the aid of NaBr could be oxidized by CuSO₄ to produce Cu(I) complex; Cu(I) complex reacted with the dissolved oxygen to generate the superoxide anion; then the superoxide anion reacted with luminol to produce CL. Cu(I) complex is a key intermediate product in the CL reaction. In the presence of other nucleophiles, such as Cl⁻, I⁻ and thiosulfate, AgNPs could also react with Cu(II) to produce Cu(I) and nucleophiles could also bind to Cu(I) preventing them from dismutation, which could induce the luminol CL.

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