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Ag nanoparticle-catalyzed chemiluminescent reaction between luminol and hydrogen peroxide

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Abstract

Ag colloid was found to enhance intensely the chemiluminescence (CL) from the reaction between luminol and hydrogen peroxide. Ag nanoparticles exhibited the better CL catalysis activity than gold and platinum nanoparticles. The superoxide anion scavenger nitro blue tetrazolium and superoxide dismutase was added to the hydrogen peroxide–Ag colloid and the luminol–hydrogen peroxide–Ag colloid systems, respectively, showing that the decomposition of hydrogen peroxide by catalysis of silver nanoparticles formed superoxide anion and superoxide anion was involved in luminol–hydrogen peroxide–Ag colloid CL reaction. The Ag nanoparticle-enhanced CL was ascribed to that Ag nanoparticles could catalyze the decomposition of H_2O_2 to produce some reactive intermediates such as hydroxyl radical, superoxide anion. Hydroxyl radical reacted with luminol to form luminol radical and diazaquinone, followed by the reaction with superoxide anion or monodissociated hydrogen peroxide, giving rising to light emission. Halide ions (X^-) were found to quench the CL in the following order: $I^- > Br^- > Cl^-$, due to the formation of AgX shell on Ag nanoparticles surface which poisoned the Ag catalyst. An obvious turning point was observed in the curve of CL intensity versus iodine ion concentration, which corresponded to the I^- concentration needed for mono-layer saturation adsorption on the Ag nanoparticles. A chemical adsorption model for iodine ions on the surface of Ag colloids has been proposed. Among 20 natural amino acids, cysteine, histidine, methionine, tyrosine and tryptophan were found to inhibit the CL due to their adsorption on the Ag nanoparticles and their competitive consumption for the reactive intermediates. The most intense inhibition of cysteine may be of potential for selective determination of cysteine.

Keywords: Ag colloid; Catalyst; Luminol; Hydrogen peroxide; Chemiluminescence

1. Introduction

As chemiluminescence (CL) analysis promises high sensitivity with simple instruments and rapidity in signal detection, lots of CL systems such as luminol, lucigenin, 1,10-phenanthroline and peroxyoxalate have been explored [1]. Among of them, the chemiluminescent reaction between luminol and H_2O_2 is most intensively studied and widely used. The oxidization of luminol by H_2O_2 is catalyzed by transition metal ions such as Co(II), Cu(II), Fe(III), etc., or by peroxidases [2–4]. Other catalysts, such as *p*-idophenol, 2-(3-methylthioureido) thiazole and phenylboronic acid for luminol CL have also been reported [5–7]. Based on their catalysis on luminol CL reaction, a great number of analytical methods have been developed, which has been successfully applied in bioanalysis and immunoassay [8,9], or as sensitive detectors for liquid chromatography [10,11] and capillary electrophoresis [12–14].

Nanocatalysis has recently been a rapidly growing field which involves the use of nanoparticles as catalysts for a variety of organic and inorganic reactions [15–17]. Our group has found that gold nanoparticles and platinum nanoparticles could catalyze luminol–H_2O_2 CL [18,19]. The catalysis ability of gold nanoparticles varied from their sizes and the synthesis method, and the protecting agent played important roles in platinum nanoparticles catalyzed luminol–H_2O_2 CL [18]. The results demonstrated that metal nanoparticles-catalyzed CL is of great application potential in analytical chemistry. However, the CL catalytic behavior of other metal nanoparticles than gold and platinum nanoparticles still remains unknown. For fundamental interests and practical analytical applications, it is necessary to carry out a systematic investigation about the effect

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of various metal nanoparticles on the luminol–H_2O_2 CL. Ag nanoparticles show excellent catalytic and electrocatalytic activities [20,21]. In our previous work, Ag nanoparticles-assembled gold electrode exhibited better electrogenerated chemiluminescence property for the luminol system than Au nanoparticle assembled gold electrode [22]. In this basis, it is deduced that Ag nanoparticles may be a sufficient catalyst for the luminol–H_2O_2 CL reaction. Therefore, in the present work, the effect of Ag nanoparticles on the luminol–H_2O_2 CL was studied. Ag nanoparticles were found to enhance intensely the CL from the reaction between luminol and H_2O_2. Ag nanoparticles exhibited a better CL catalysis ability than gold and platinum nanoparticles. The effects of the reaction conditions such as pH and reagents concentration on the CL intensity were examined. The CL spectra were analyzed and the intermediate radicals of the CL reaction were investigated. The CL mechanism has been proposed. Moreover, the effects of halide ions and 20 natural amino acids on the CL system were also explored.

2. Experimental

2.1. Chemicals

A 1.0×10^{-2} mol/L stock solution of luminol (3-aminophthalhydrazide) was prepared by dissolving luminol (Sigma, America) in 0.10 mol/L sodium hydroxide solution.

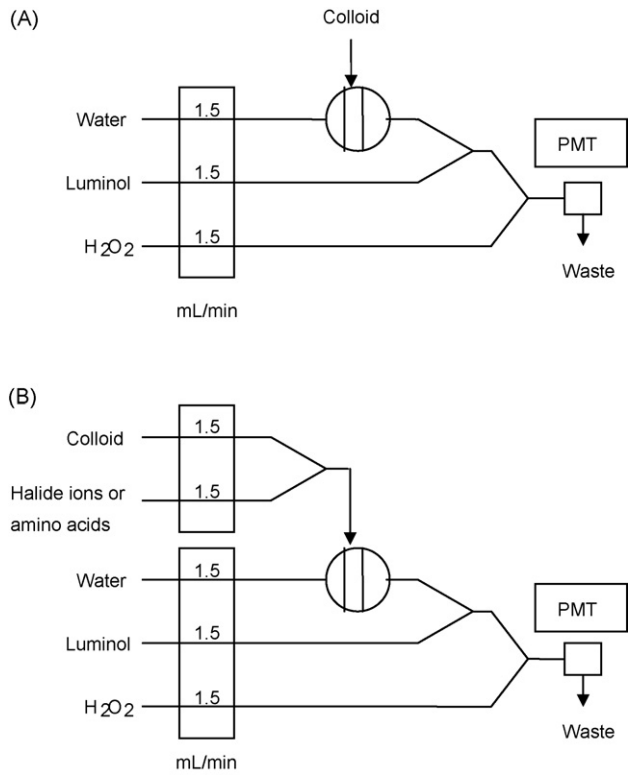


Fig. 1. Schematic diagram of flow-injection chemiluminescence detection systems for experiments: (A) investigating Ag colloid catalyzed CL; (B) investigating the effects of halide ions and amino acids on luminol–H_2O_2–Ag colloid CL.

$AgNO_3$, $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ (48%, w/w) were obtained from Shanghai Reagent (Shanghai, China). A 1.0 g/L $HAuCl_4$ stock solution was prepared by dissolving 1.0 g of $HAuCl_4$ in 1 L of redistilled water and stored at 4 °C. Working solutions of luminol were prepared by diluting the stock solution with 0.02 mol/L carbonate buffer solution. Working solutions of H_2O_2 were freshly prepared everyday from 30% (v/v) H_2O_2 (Xinke Electrochemical Reagent Factory, Bengbu, China). All the reagents were of analytical grade, and double-distilled water was used throughout.

2.2. Preparation of Ag, Au and Pt colloids

Silver colloid was prepared according the literature [23] with some modifications. Briefly, a 25 mL 1×10^{-3} mol/L $AgNO_3$ aqueous solution was added dropwise to 75 mL 2×10^{-3} mol/L $NaBH_4$ aqueous solution with vigorous stirring simultaneously. Ten minutes later, a 5 mL 1% (w/w) sodium citrate aqueous solution was added to stabilize the colloid. The colloid was stirred for another 20 min and aged for 2 days at 4 °C before use. The resulting yellow silver colloids were characterized by transmission electron microscopy (TEM) (Hitachi H-800, Japan). Statistical analysis of TEM data revealed that the average diameter of the silver particles was 20 ± 2 nm. Thirty eight nanometers of Au and 2.5 nm Pt colloids were prepared according the method used in references [18,19].

2.3. Chemiluminescence measurements

The chemiluminescence detection was conducted on a flow injection chemiluminescence system (Ruimai Electronic Science Co., China), including a model IFFM-D flow injection system, a model IFFS-A luminometer and a computer. Double distilled water was used as a carrier of the Ag colloid to mix with luminol and then with H_2O_2, as described in Fig. 1(A). When the system was used to investigate the effects of halide ions and amino acids, the Ag colloid was firstly mixed with halide ion or amino acids, the mixture was met with luminol and then with H_2O_2, as shown in Fig. 1(B). To study the effect of superoxide dismutase (SOD), a static CL experiment was done by injecting H_2O_2 into a homemade cell in front of a photomultiplier tube (PMT).

2.4. Optical measurements

The CL spectra of this system were measured on a model FL 5401 spectrofluorometer (Shimadzu, Japan). UV–vis spectrum and X-ray photoelectron spectrum were measured on a model UV-2401 PC spectrophotometer (Shimadzu, Japan) and a model ESCALAB MK II electron spectrograph (VG, England), respectively. The XPS sample was prepared as follows: KNO_3 was added to a 100 mL Ag colloid containing 1×10^{-4} mol/L KI to precipitate the particles, then, the mixture was centrifuged and the precipitation obtained was thoroughly washed by water.

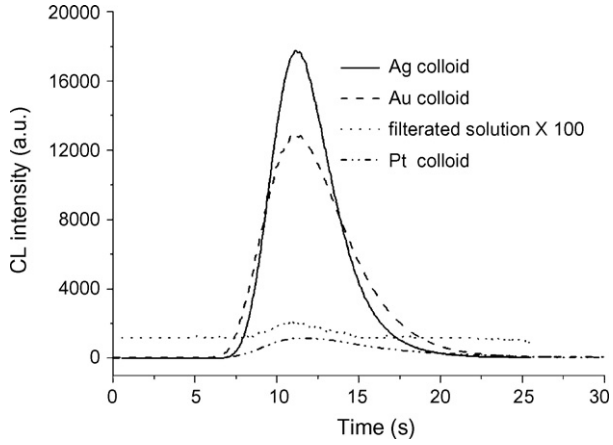


Fig. 2. Effect of Ag colloid (solid line), 38 nm Au colloid (dashed line), Pt colloid (dash-dot-dot line) and filtrated solution of precipitated Ag colloid (dotted line) on luminol–H_2O_2 CL. The blank (filtrated solution of precipitated Ag colloid) signal was amplified by 100 times. *Conditions*: luminol, 1×10^{-4} mol/L; H_2O_2, 0.15 mol/L; pH 9.32 carbonate buffer for Ag, pH 12.0 NaOH for Au, pH 10.3 carbonate buffer for Pt.

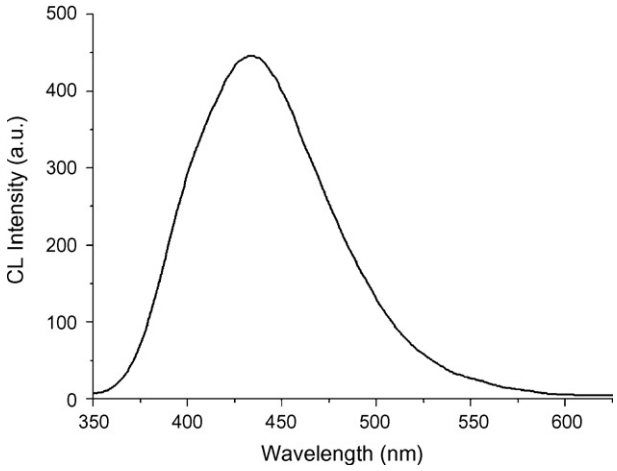


Fig. 3. Spectra of Ag catalyzed luminol–H_2O_2 CL. *Conditions*: luminol, 1×10^{-4} mol/L in 0.02 mol/L carbonate buffer (pH 9.32); H_2O_2, 0.15 mol/L, Ag colloid as prepared.

3. Results and discussion

3.1. Catalysis of Ag colloid for luminol–H_2O_2 CL

As shown in Fig. 2, when the Ag colloid was injected, CL emission from the luminol–H_2O_2 system was greatly enhanced. Under the optimized conditions, the CL intensity was enhanced by a factor of about 2000 by Ag colloid. This value is greater than that of Au nanoparticles and Pt nanoparticles at the optimal pH 12.0 and 10.3, respectively, as reported [18,19]. To exclude the effect of the concomitants, the colloid was precipitated by a 0.1 mol/L KNO_3, and filtered by a filter paper in order to remove Ag nanoparticles. The filtered solution also reacted with the luminol–H_2O_2 system and only weak enhanced CL was observed, indicating that the CL led by the concomitants in the solution could be ignored. Accordingly, the enhancement of Ag colloid on the CL did not arise from the concomitants in the colloid but from Ag nanoparticles.

Fig. 3 is the CL spectra of luminol–H_2O_2–Ag colloid system. The maximal emission was at 425 nm, indicating that the luminophor was still the excited state 3-aminophthalate anions.

3.2. Optimization of the reaction conditions

The reaction conditions were optimized for luminol–H_2O_2–Ag colloid CL system as shown in Fig. 4. The effect of the pH of luminol solution on the CL was studied in carbonate buffer. The strong CL emission was observed in the pH range from 9.00 to 10.00, and the maximal emission was at pH 9.32, whereas the background emission of luminol–H_2O_2 monotonously increased with the pH value over the whole tested range. The effect of the luminol concentration on the CL intensity was examined in the range of 4×10^{-6}–4×10^{-4} mol/L. It was found that the CL intensity increased linearly with the luminol concentration from 4×10^{-6} to 2×10^{-4} mol/L. The effect of H_2O_2 concentration on the CL was studied in the range of 2×10^{-3}–0.30 mol/L, the CL intensity increased with H_2O_2 concentration in the range of 2×10^{-3}–0.20 mol/L and decreased when the concentration of H_2O_2 was higher than 0.2 mol/L. The effects of the concentration of Ag nanoparticles were also investigated, as shown in Fig. 4(A). The CL intensity increased exponentially with the concentration of Ag nanoparticles. Considering the CL intensity and the consumption of the reagents, the selected conditions were as follows: 1×10^{-4} mol/L luminol in pH 9.32 carbonate buffer, 0.15 mol/L H_2O_2, and the Ag colloid as prepared.

3.3. Mechanism discussion

It is well-known that bulk metals and metal ions can catalyze the decomposition of H_2O_2 to oxygen. Metal ion catalyzed luminol–H_2O_2 CL systems have been widely studied, and the catalysis attributes to that some strong oxidizing species are generated during the catalysis decomposition, which is essential for luminol CL [24,25]. As for Ag colloid, when it mixed with a basic hydrogen peroxide solution, violent reaction occurred as a large amount of bubbles was observed, indicating that Ag colloid could also efficiently catalyze the H_2O_2 decomposition.

It was reported that the H_2O_2 decomposition on supported metal catalysts such as Ag, Au and Pt involved the formation of superoxide anion [26]. It was deduced that the H_2O_2 decomposition by virtue of Ag colloid may also involved the formation of superoxide anion. When a superoxide anion scavenger nitro blue tetrazolium (NBT) was added to the mixture of H_2O_2 and Ag colloid, the solution turned to purple rapidly. The UV–vis spectra of resulted solution (Fig. 5) had an absorption peak at 530 nm, which corresponded to the absorption of diformazan, a reduction product of NBT [27]. The results demonstrated that H_2O_2 interacted with Ag colloid to produce superoxide anion. Furthermore, the mechanism of luminol–H_2O_2 CL system was suggested due to the reaction of luminol radical with

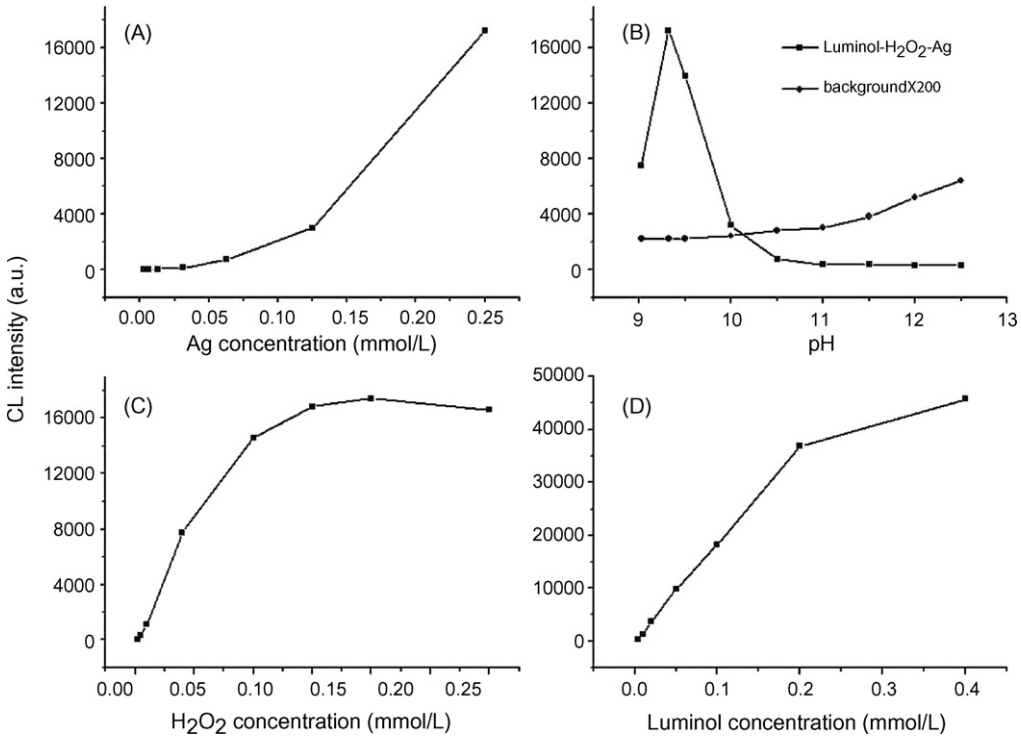


Fig. 4. Effects of reaction conditions on the CL intensity. (A) Ag nanoparticles concentration, *conditions*: luminol, 1×10^{-4} mol/L in 0.02 mol/L carbonate buffer (pH 9.32); H_2O_2, 0.15 mol/L. (B) pH, *conditions*: luminol, 1×10^{-4} mol/L in 0.02 mol/L carbonate buffer; H_2O_2, 0.15 mol/L, Ag colloid as prepared. (C) H_2O_2 concentration, conditions: luminol, 1×10^{-4} mol/L in 0.02 mol/L carbonate buffer (pH 9.32); Ag colloid as prepared. (D) Luminol concentration, *conditions*: luminol in 0.02 mol/L carbonate buffer (pH 9.32); H_2O_2, 0.15 mol/L, Ag colloid as prepared.

superoxide anion ($O_2^{\bullet -}$) [28,29]. When SOD was added to the luminol–H_2O_2–Ag colloid CL system in a static CL experiment, the CL intensity decreased compared with that from the luminol–H_2O_2–Ag colloid system as shown in Fig. 6. The experiments further confirmed that the reaction of H_2O_2 with Ag colloid indeed produced superoxide anion that was a crucial species participating in the CL reaction. According to Ono et al. [26], the reaction of H_2O_2 with Ag colloid may follow Eqs. (1), (4), (5) and (6). H_2O_2 decomposed by Ag colloid to $^{\bullet}OH$, which followed by the reactions of H_2O_2 and luminol anion to generate superoxide anion and luminol radical. The key intermediate of light emission was generated through two pathways (7) and (8) [30]. The CL reaction, similar to the luminol–H_2O_2–Au colloid CL reaction [18], may proceed in the following pathways:

$$Ag_n + H_2O_2 \rightarrow Ag_n^{+} + {}^{\bullet}OH + OH^{-} \quad (1)$$

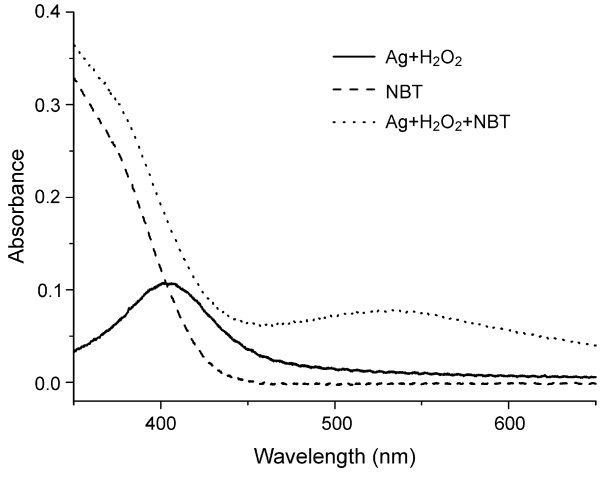


Fig. 5. Absorption spectra of Ag colloid + H_2O_2 (solid line), NBT (dashed line) and Ag colloid + H_2O_2 + NBT (dotted line). The final concentration of each reagent: 2 mmol/L NaOH, 4 mmol/L H_2O_2, 0.3 mmol/L NBT, 10 μmol/L Ag.

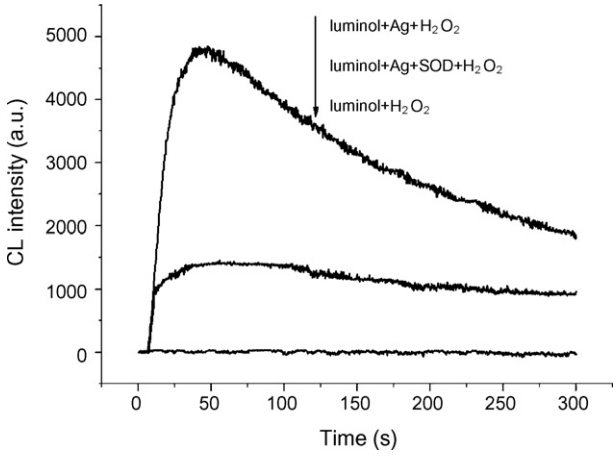
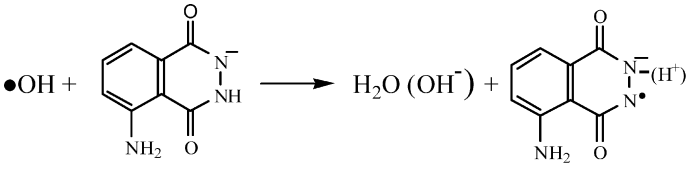
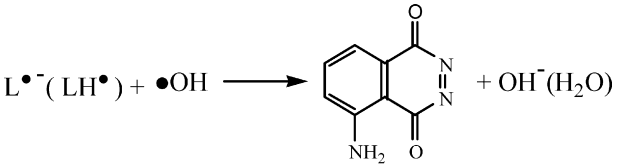


Fig. 6. Effect of SOD on luminol–H_2O_2–Ag colloid CL. From top to bottom: luminol + Ag colloid + H_2O_2, luminol + Ag + SOD + H_2O_2, luminol + H_2O_2. *Conditions*: luminol, 2.5×10^{-5} mol/L; pH 9.32; Ag colloid, 6.25×10^{-5} mol/L; SOD, 75 U/mL; H_2O_2, 2.5 mmol/L.



(2)

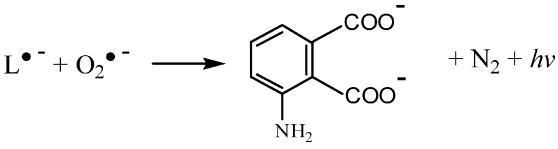


(3)

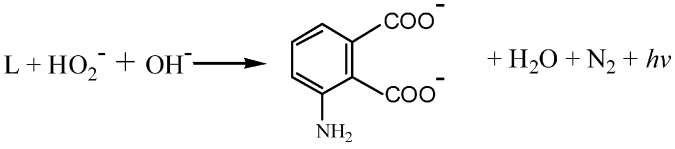
$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$$HO_2^{\bullet} + OH^- \rightarrow O_2^{\bullet -} + H_2O \quad (5)$$

$$Ag_n{}^{+} + O_2^{\bullet -} \rightarrow Ag_n + O_2 \quad (6)$$



(7)



(8)

In this mechanism, the electron transfer reaction between the metal nanoparticles and H_2O_2 is an initiating step for the subsequent chemiluminescent process. The redox potential of metal nanoparticles should be important for its catalysis ability in luminol–H_2O_2 CL system. Silver can be oxidized by H_2O_2 more easily than gold, producing hydroxyl radicals, since its oxidation potential is lower than that of gold [31]. Therefore, the CL catalytic ability of silver nanoparticles was stronger than that of gold nanoparticles.

3.4. Effect of halide ions

Since Ag nanoparticles played a heterogeneous catalyst in the luminol–H_2O_2 CL system, the enhanced CL should be affected by the surface adsorption. Halide ions were readily adsorbed on the surface of Ag nanoparticles [32]. It is deduced that halide ions may change the catalytic activity of the Ag nanoparticles due to the adsorption. Therefore, the effect of halide ions on the luminol–H_2O_2–Ag nanoparticles CL system was examined. The effect of potassium iodide (KI) on the CL and surface plasmon resonance (SPR) absorption is shown in Fig. 7(A) and (B), respectively. Both CL intensity and SPR absorption decreased rapidly with increasing iodine ion concentration, had a same turning concentration, and then got to a plateau. The sharp decrease of the CL could be utilized for accurate determination of I^- from 1.0×10^{-6} to 1.0×10^{-5} mol/L with a regression equation $I = 7325 - 6.7 \times 10^8$ [I^-]. X-ray photoelectron spectra (XPS) showed that the addition of KI to Ag colloid formed AgI on the particles surface (Fig. 8). The formed AgI layer could induce the demetalization of several atomic layers of Ag nanoparticles, which resulted in the damping of SPR absorption [32]. The AgI shell isolated Ag nanoparticles and changed their surface electron states, and as a result, the Ag nanoparticles as the CL catalyst were poisoned. The effects of KBr and KCl are shown in Fig. 7(C) and (D). The concentration of the curve turning point for I^-, Br^- and Cl^- was 1.03×10^{-5}, 2.28×10^{-5}, 1.7×10^{-3} mol/L, respectively, which increased with a decrease in diameter of halide ions. On the other hand, if considering the Ag nanoparticle as a 20 nm sphere, the halide ion concentrations required for mono-layer saturation adsorption on the Ag nanoparticles could be calculated according to that the ion diameter for I^-, Br^- and Cl^- was 220, 196, 181 pm, respectively. The value for I^- was 0.87×10^{-5} mol/L, similar to the turning point, while 1.1×10^{-5} mol/L for Br^- and 1.28×10^{-5} mol/L for Cl^-, far smaller than the turning point. For low degree of specific adsorption of Cl^- and Br^- [33], higher concentrations were required than the calculated values to complete the surface cover, since the on-line mixing of halide ions and Ag colloid was performed for only tens of seconds.

To simulate the effect of I^- adsorption, a static analysis was performed. For each concentration, we assumed the I^- adsorption process reached its balance and a Langmuir adsorption model was applied as Eq. (9),

$$\theta = \frac{AC}{1 + AC} \quad (9)$$

where θ is the fraction of covered Ag particles surface, A is the ratio of adsorption rate constant to desorption rate constant, and C is the equilibrium concentration of free I^- in the solution. Because a total amount of I^- was limited, C should accord with Eq. (10),

$$B\theta = C_0 - C \quad (10)$$

where B is the concentration of the total adsorption sites of the prepared Ag colloid, C_0 is the total I^- concentration before adsorption. From Eqs. (9) and (10), the relation of θ and C_0 can be described by Eq. (11),

$$C_0 = \frac{\theta}{A - A\theta} + B\theta \quad (11)$$

On the other hand, the catalyzed CL intensity is proportional to fraction of uncovered surface of the catalyst, Ag particles

$(1-\theta)$,

$$\frac{I}{I_0} = 1-\theta \tag{12}$$

where I and I_0 are the CL intensity in the presence and absence of I^-, respectively. Replacing θ in Eq. (10) by $(I_0-I)/I_0$ gives the following equation,

$$C_0 = \frac{I_0-I}{AI} + B\left(1-\frac{I}{I_0}\right) \tag{13}$$

Based on the experiment data and Eq. (13), the most fitted curve was obtained when $A = 4.8\times10^7$ L/mol and $B = 1.1\times10^{-5}$ mol/L, as seen from Fig. 7(A). The B is quite close to the mono-layer saturation adsorption concentration (0.87×10^{-5} mol/L). Therefore, the inhibition of halide ions for the luminol–H_2O_2–Ag colloid CL should be ascribed to the chemical adsorption on the Ag particles catalyst.

3.5. Effects of 20 natural amino acids

Some amino acids were found to inhibit the CL from the luminol–H_2O_2–Au colloid system [18]. The effects of 20 natural amino acids on the luminol–H_2O_2–Ag colloid CL were also investigated as listed in Table 1. For 1×10^{-4} mol/L amino acids, the CL was obviously inhibited by cysteine, histidine, methionine, tyrosine and tryptophan. Among them, cysteine exhibited the strongest inhibition and even the inhibition of 1×10^{-5} mol/L cysteine was stronger than 1×10^{-4} mol/L other amino acids. Furthermore, as seen from Fig. 9, the effects of cysteine concentration on CL intensity also had a similar

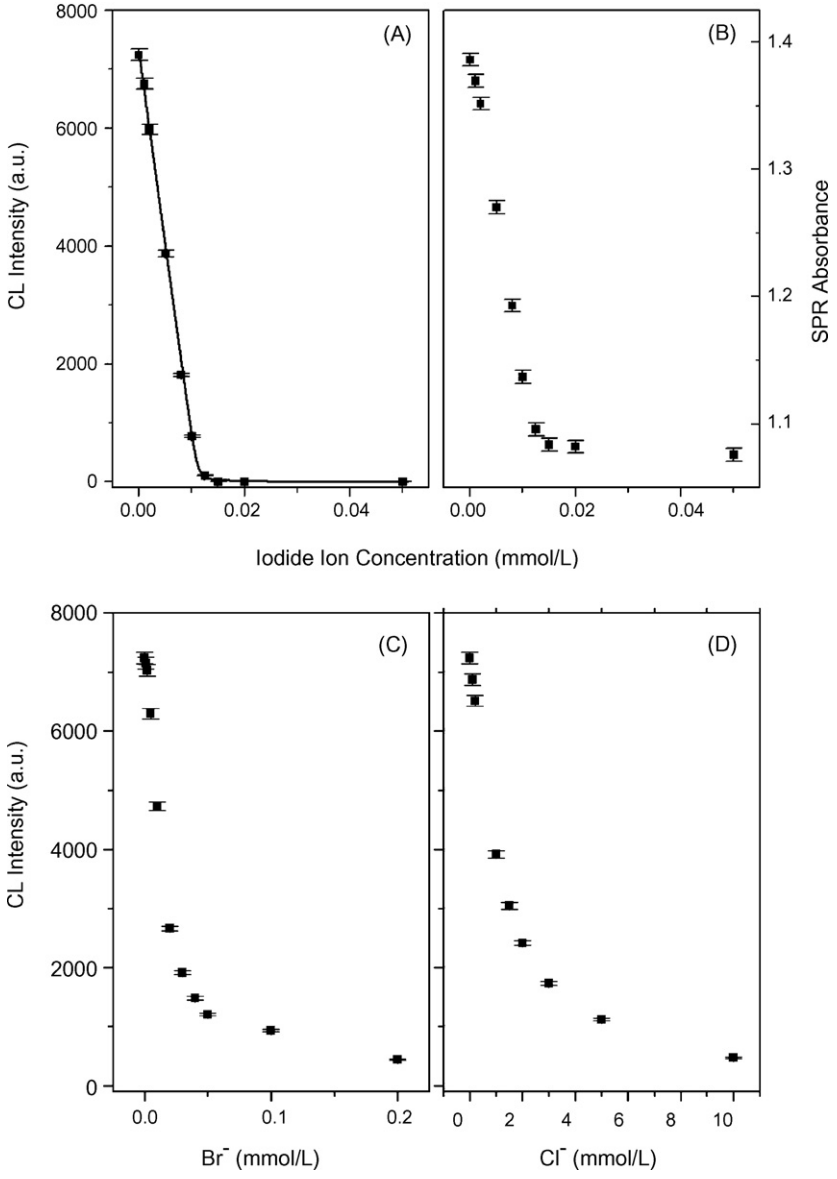


Fig. 7. (A) Effect of iodide ion on the luminol–H_2O_2–Ag colloid CL (■) and the fitted curve (solid line) by Eq. (13), (B) effects of iodine ion on the SPR absorption of Ag colloid. (C) Effect of bromide ion and (D) effect of chloride ion on luminol–H_2O_2–Ag colloid CL.

Table 1
Effects of 1×10^{-4} mol/L 20 natural amino acids on the luminol–H_2O_2–Ag colloid CL

Amino acids	CL intensity (I)	I/I_0	Amino acids	CL intensity (I)	I/I_0	Amino acids	CL intensity (I)	I/I_0
Blank[a] (I_0)	6662	1.000	Glycine	6662	1.000	Glutamine	6920	1.039
Alanine	6707	1.007	Histidine	2310	0.347	Proline	6837	1.026
Arginine	6926	1.040	Isoleucine	6854	1.029	Serine	6592	0.989
Asparagine	6710	1.007	Leucine	6627	0.995	Threonine	6740	1.012
Aspartic acid	6688	1.004	Lysine	6446	0.968	Tyrosine	5112	0.767
Cysteine	30	0.005	Methionine	4365	0.655	Tryptophan	5572	0.836
Glutamic acid	6803	1.021	Phenylalinine	6226	0.935	Valine	6753	1.014

[a] The blank CL signal I_0 of luminol–H_2O_2–Ag colloid system without amino acids was 6662.

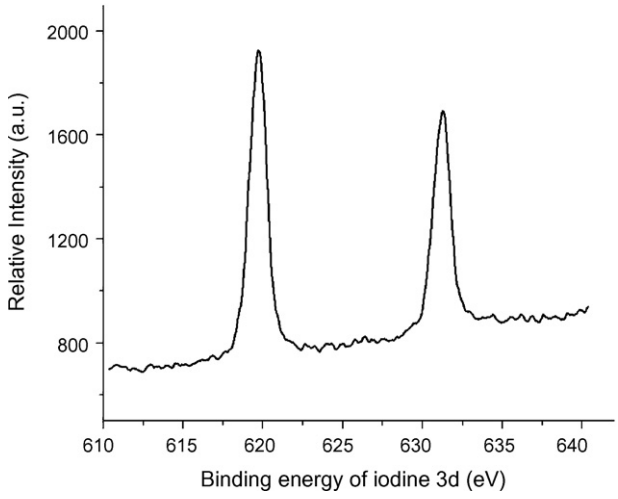


Fig. 8. XPS of Ag nanoparticles after addition of 1×10^{-4} mol/L KI to the Ag colloid.

profile as I^-, indicating that the adsorption of cysteine on Ag nanoparticles may play an important role in the CL inhibition. Amino acids such as glycine, praline, cysteine, can be adsorbed on the Ag nanoparticles through their $–NH_2$, –NH–, $–COO^-$, –S– groups [34,35], and the cover of amino acids could form a space hinder, declining the catalysis ability of nanoparticles. However, the amino acids such as alanine, glycine, serine and glutamic acid did not show obvious effects on the CL, indicating that another factor might also play an important role in the CL inhibition. Amino acids with strong CL inhibition such as cysteine, histidine, methionine, tyrosine and tryptophan were all redox-active [36]. During the CL reaction, H_2O_2 decomposed by Ag colloid to form some active radicals such as hydroxyl radical and superoxide anion. The reducing amino acids might compete with luminol for the radicals, leading to a decrease in CL intensity. To sum up, the adsorption and reductivity of amino acids may lead to their inhibition on the luminol–H_2O_2–Ag colloid CL. Cysteine can be far more easily adsorbed on Ag nanoparticles than other amino acids, and thus has a strongest inhibition on the luminol–H_2O_2–Ag colloid CL.

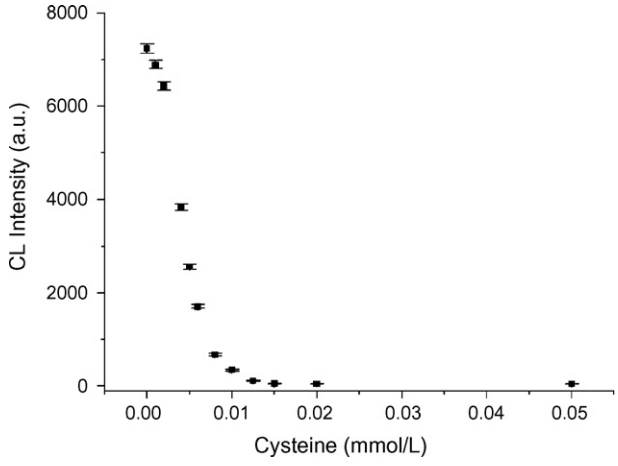


Fig. 9. Effect of cysteine on luminol–H_2O_2–Ag colloid CL. *Conditions*: luminol, 1×10^{-4} mol/L; pH 9.32; H_2O_2, 0.15 mol/L.

4. Conclusions

In this paper, Ag colloid was found to catalyze the chemiluminescence from luminol–hydrogen peroxide system. The catalytic activity is better than Au and Pt colloid. The experiments showed the evidence that the decomposition of hydrogen peroxide by catalysis of silver nanoparticles formed superoxide anion and superoxide anion was involved in luminol–hydrogen peroxide–Ag colloid CL reaction. The CL mechanism has been proposed to be due to that luminol radicals and diazaquinone generated by the reaction with intermediate $^{\bullet}OH$ decomposed by H_2O_2 interacted with superoxide anion or monodissociated hydrogen peroxide to give rise to luminescence. The heterogenous catalysis by Ag colloid was strongly inhibited by halide ions. A chemical adsorption model has been proposed for the inhibition mechanism of iodine ions. The amino acids such as cysteine, histidine, methionine, tyrosine and tryptophan could inhibit the catalyzed CL due to their adsorption on the Ag nanoparticles and their competitive consumption for the reactive intermediates. Among them, cysteine exhibited the strongest inhibition of the CL, which may be of potential for selective determination of cysteine.

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