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Permanganate–bromide–silver nanoparticles as a new chemiluminescence system and its application to captopril determination

Mohammad Amjadi *, Jamshid L. Manzoori, Javad Hassanzadeh, Mohammad H. Sorouraddin

Department of Analytical Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz 5166616471, Iran

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ABSTRACT

A novel chemiluminescence (CL) system based on the oxidation of bromide by permanganate in sulfuric acid medium is introduced. The enhancing effect of silver nanoparticles (NPs), synthesized by chemical reduction method, on this reaction was studied. It was demonstrated that spherical silver nanoparticles with average size of 18 nm had a most remarkable catalytic effect on this reaction. CL emission wavelengths and UV–vis spectra were used to characterize the system and propose a possible mechanism. Furthermore, it was found that captopril inhibits the action of NPs and decreases the intensity of CL. Based on this phenomenon, a new CL method was developed for the determination of captopril in the 3.0×10^{-10} to 1.0×10^{-7} mol L^{-1} concentration range with a detection limit (3 s) of 0.12 nmol L^{-1}. The method was successfully applied to the determination of captopril in pharmaceutical formulations, human urine and serum samples.

1. Introduction

Chemiluminescence (CL), which is based on the oxidation of a substrate to produce an electronically-excited species that subsequently emits light, is a powerful tool in many fields of analytical chemistry, especially in pharmaceutical analysis. CL-based analytical methods have many advantages including rapid and simple detection, wide linear dynamic range, good reproducibility, excellent detection limit, high sensitivity and relatively good selectivity. Potassium permanganate in acidic medium, as a versatile oxidizing agent has been extensively used in many CL reactions [1,2]. Although it has been shown that acidic potassium permanganate is able to elicit a CL response from many oxidizable species, direct CL of permanganate–bromide reaction has not yet been reported.

In the last decade, nanoparticles have been introduced in CL reactions mainly as catalysts, reductants, or luminophors [3,4]. Gold and silver nanoparticles (Au NPs and Ag NPs) due to their unique chemical reactivity, surface property and high catalytic activity have been frequently used to improve CL intensity [5–16]. In recent years, catalytic effect of nanoparticles has been demonstrated in permanganate CL reactions. Our group has shown that $KMnO_4$–HCHO CL system can be catalyzed with Au and Ag NPs or their alloys [12]. It has also been found that Au nanorods greatly catalyze $KMnO_4$–rhodamine B CL system [15]. Wang and coworkers [16] have demonstrated the catalyzing effect of Ag NPs on luminal–$KMnO_4$ CL reaction. Based on such CL systems, new analytical methods with relatively good selectivity have been proposed for several organic compounds [5,10,13–15].

Captopril (1-[(2*S*)-3-mercapto-2-methyl propionyl]-l-proline, Fig. 1), an angiotensin converting enzyme (ACE) inhibitor, can decrease systemic vascular resistance without increasing heart rate and promote natriuresis. It is effective in the treatment of hypertension, cardiac conditions such as congestive in heart failure and after myocardial infarction. It also delays the progression of diabetic nephropathy [17]. After a single oral dose of captopril, it is rapidly absorbed from the gastro-intestinal tract with peak blood level of 0.8 μg mL^{-1} in about an hour period. Minimal absorption is approximately 75%. Up to 40% of an oral dose is excreted in the urine as unchanged drug [18]. Despite the captopril therapeutic usefulness, it could also cause some adverse effects including cough, angiodema, agranulocystosis, proteinuria, hyperkalemia, taste alteration, teratogenecity, postural hypotension, acute renal failure and leucopenia [19].

Because of captopril pharmacological importance, a variety of methods have been proposed for its determination in pharmaceutical and biological samples, including chromatography [20–22], atomic absorption spectrophotometry [23] electrochemical methods [24,25], fluorimetry [26–28], resonance light scattering [29],

* Corresponding author. Tel.: +984113393109; fax: +984113340191.
E-mail address: amjadi@tabrizu.ac.ir (M. Amjadi).

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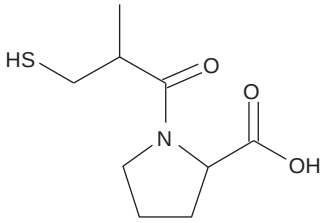

Fig. 1. Chemical structure of captopril.

FT-Raman [30], chemiluminescence [5,20,31–38] and spectrophotometry [39,40]. Tzanavaras et al. [41] have reviewed CL methods proposed for the determination of captopril. Relatively high concentrations of captopril can react with MnO_4^- or Ce(IV) to generate CL emission, which can be sensitized by a proper sensitizer (e.g., rhodamine 6G and quinine) [33,34]. This compound can also change the signals of some CL systems [35–38]. Recently, several nanoparticle-catalyzed CL systems have been reported which exhibit a high sensitivity and good selectivity towards thiols and aminothiols [5,42–44]. Thiol-containing compounds can inhibit the catalyzing effect of NPs by forming NP–S covalent bonds and occupying their active sites, leading to a significant decrease in CL intensity. This decreasing effect is the basis for determination of these compounds [5,42–44]. Such systems have also found application as a detecting tool in high performance liquid chromatography [45,46]. Captopril, as a thiol-containing compound, has been determined by fluorosurfactant-mediated triangular gold NPs-catalyzed luminal CL at nmol L^{-1} levels [5]. The majority of the reported methods for captopril determination suffer from some deficiencies, such as, complex instrumentation, laborious sample preparation and low sensitivity. Thus, developing a sensitive, fast, economical and simple procedure for captopril analysis is still a valuable analytical task.

The present study deals with the reaction of $KMnO_4$ with bromide in an acidic solution which generates a weak CL response. Ag NPs exhibit a remarkable enhancing effect on this CL system. On the other hand, it was found that captopril greatly decreases the CL signal. This inhibiting effect was used to the determination of captopril in pharmaceutical and biological samples. The developed method compared with other NP-based CL methods is quite simpler, more sensitive and has lower detection limit.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (obtained from Ghazi Serum Co. Tabriz, Iran). Sodium citrate, $AgNO_3$, $KMnO_4$, H_2SO_4, KBr, acetonitrile and $HClO_4$ were obtained from Merck (Darmstadt, Germany) and used without further purification. 1.0 mmol L^{-1} stock solution of captopril was freshly prepared by dissolving its commercial powder (Merck) in deionized water and stored at 4 °C until use.

2.2. Apparatus

The chemiluminescence detection was conducted on a LUMAT LB 9507 chemiluminometer (Berthold; www.berthold.com). Ultraviolet–visible (UV–vis) spectra were recorded on a Cary-100 Spectrophotometer (Varian; www.varianinc.com). The size and shape of the NPs were confirmed through transmission electron microscopy (TEM, Philips EM208, operated at 100 kV). Chromatographic analysis was performed by an HPLC system (Smartline 1000 KNAUER) equipped with a C18 column and UV detection.

2.3. Preparation of Ag nanoparticles

Ag NPs (~18 nm) were prepared according to the literature [10]. $NaBH_4$ and trisodium citrate were used as reducing agent and stabilizer, respectively. Briefly, 25 mL of 1.0 mmol L^{-1} $AgNO_3$ solution was added drop wise to 75 mL of 2.0 mmol L^{-1} $NaBH_4$ aqueous solution while stirring vigorously. Ten minutes later, 5.0 mL of 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.

Ag NPs (~4 nm) and triangular Ag NPs were prepared following the literature procedure [47].

2.4. Sample preparation

Pharmaceutical tablets (Capton), with a label amount of 12.5 mg captopril were obtained from Tehran Daru (Iran). Five tablets were weighed and powdered. Two hundred mg of the resulting powder was dissolved in deionized water and filtrated. The filtrate was diluted to 100 mL and stored in dark at 4 °C. A suitable aliquot of this solution was taken for the determination of captopril according to the recommended general procedure.

Human urine sample containing captopril was obtained by adding suitable concentration of standard captopril to drug-free urine. An amount of 1 mL of this sample was gently vortex-mixed with 200 μL of 3.0 mol L^{-1} $HClO_4$ solution, put aside at room temperature for 10 min, and then centrifuged. The clear supernatant was diluted to the appropriate concentration [5].

Human serum sample was spiked by adding suitable concentration of captopril standard solution to drug-free serum. An amount of 1 mL of the spiked serum sample was mixed with 2 mL of acetonitrile and centrifuged at 4000 rpm for 20 min. The resulted supernatant was diluted to 10 mL with deionized water and an appropriate volume was used for analysis under the optimum conditions.

2.5. General procedure for CL detection

Chemiluminescence signals were measured in a 3 mL quartz tube, in the batch condition. Briefly, 100 μL of KBr (0.5 mol L^{-1}), 250 μL of H_2SO_4 (4.0 mol L^{-1}), and 500 μL of Ag NPs (~18 nm) solution were added into the cell. Then an appropriate volume of sample or standard captopril solution was added and the final volume was reached to 2.25 mL with deionized water. After injection of 250 μL $KMnO_4$ (0.005 mol L^{-1}) by an automatic injector, monitoring of CL signal versus time was started automatically. Maximum CL intensity was used as analytical signal.

3. Results and discussion

3.1. CL system

The CL system discussed in this paper is based on the oxidation of Br^- by permanganate in acid medium. To the best of our knowledge, this CL system has not been introduced in the literature up to now. Preliminary experiments were carried out to optimize the reaction conditions (including type of acid and concentrations of acid, permanganate and bromide) in order to obtain the maximum CL intensity. Then at the optimum conditions, the effect of some NPs on emission intensity of this system was examined. Table 1 shows the effect of different NPs

Table 1
Effect of various NPs and preparation reagents on the CL signal.

Added reagents	Relative CL intensity
–	1.0
$AgNO_3$	2.1
Citrate Disodium	2.5
Citrate Disodium+$AgNO_3$	3.1
Ag NPs (~4 nm)	12.3
Ag NPs (~18 nm)	26.2
Triangular Ag NPs	13.4

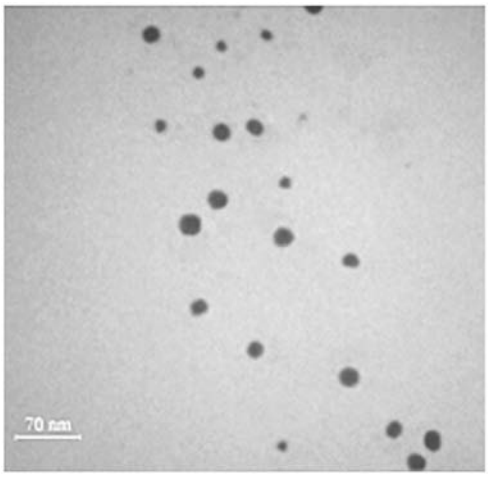

Fig. 2. TEM image of applied Ag nanoparticles.

on permanganate–Br^- CL reaction. As can be seen, enhancing effect of spherical Ag NPs with relatively large size (18 ± 2 nm) is the most remarkable compared with the other examined NPs. Ag NPs were synthesized via a citrate and $NaBH_4$ reduction protocol using $AgNO_3$. Fig. 2 shows TEM image of the synthesized Ag NPs which confirms the proper synthesis and size of NPs. Blank experiments were also carried out in the presence of citrate, $AgNO_3$ and their mixed solution in the concentrations used for the preparation of NPs. Only slight enhancing effects were found for these species (Table 1). These results indicate that the observed enhancing effect is mainly due to the NPs. In the rest of this study, we used Ag NPs with the average size of 18 nm as the best catalysts.

The kinetic profiles for CL reaction in the absence and presence of Ag NPs are shown in Fig. 3. As can be seen, in the absence of NPs, the maximum CL signal is achieved after about 5 s while in the presence of NPs, the CL reaches a maximum approximately 2 s after mixing and also decays more rapidly. Therefore, it can be deduced that the enhancing effect of Ag NPs is, probably, a catalytic effect.

3.2. Possible mechanism for CL reaction

In order to characterize the possible emitting species, the CL emission of KBr–$KMnO_4$ system in the absence and presence of Ag NPs, was measured using a series of filters. According to the results, there was an emission band around 650–750 nm in both cases. This indicates that the emitting species in the CL reaction is probably Mn(II)*, which is known to be the final emitting species in most of the acidic permanganate CL systems and has a broad CL spectrum with a maximum around 700 nm [48,49].

The UV–vis spectra of $KMnO_4$–Br^- and $KMnO_4$–Br^-–Ag NPs in acidic solution (Fig. 4a and b) show that a new peak appears at ca.

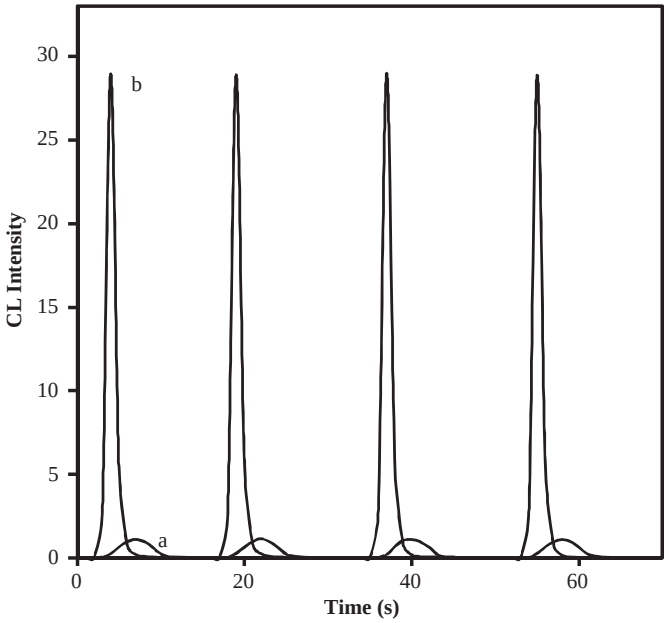

Fig. 3. CL profiles of $KMnO_4$–Br^- (a) and $KMnO_4$–Br^-–Ag NPs (b) systems. The concentrations of Br^-, H_2SO_4 and $KMnO_4$ were 0.02 mol L^{-1}, 0.4 mol L^{-1} and 5×10^{-4} mol L^{-1}, respectively. 500 μL of Ag NPs was used.

380 nm instantly after addition of $KMnO_4$, which is attributed to Br_2 as a product of redox reaction. It was also observed that the absorption peak of Ag NPs at 398 nm disappeared after adding $KMnO_4$, which indicates that $KMnO_4$ can oxidize Ag NPs to Ag^+, as well. Although these Ag^+ ions may have slight enhancing effect on the CL reaction (Table 1), the large enhancement efficiency of NPs cannot solely be attributed to this effect. As mentioned before, it seems that Ag NPs act as catalysts for the reaction. The kinetic profiles of CL reactions (Fig. 3) reveal that in the presence of Ag NPs, the rate of the production of excited species is considerably increased. This may be attributed to the catalysis of the redox reaction by Ag NPs via a particle mediated electron transfer process between reactants [13]. Since the amount of bromide ions is much higher than Ag NPs, it is presumed that NPs react slower than Br^- ions and exert the catalyzing effect before their oxidation. The fact that smaller Ag NPs exhibit lower catalytic activity on this reaction supports this idea. Smaller NPs have higher surface area and surface energy, and so they are oxidized more rapidly than larger NPs. Thus smaller NPs are expected to have lower catalytic effect on the reaction. It should also be mentioned that, halide ions are known to reduce the catalytic activity of Ag NPs as a result of their adsorption on the surfaces of NPs and formation of AgBr layer [10]. However, in the present system, the concentration of Br^- is so high that $AgBr_2^-$ complex ions can be formed instead of AgBr. This prevents the deposition of AgBr layer and subsequent demetalization of NPs surfaces. In summary, the overall mechanism for CL reaction can be suggested as follows:

$$10Br^- + 2MnO_4^- + 16H^+ \xrightarrow{AgNPs} 5Br_2 + 8H_2O + 2Mn(II)^*$$

$$Mn(II)^* \rightarrow Mn(II) + h\nu \ (\sim 700 \text{ nm})$$

$$Ag\ NPs + MnO_4^- \rightarrow Ag^+ + Mn(II)$$

3.3. Optimization of chemical conditions

Type and concentration of acid has a significant influence on permanganate CL emission intensity [1,2]. Thus, to investigate the effect of acidic medium on the CL signal in this system, several

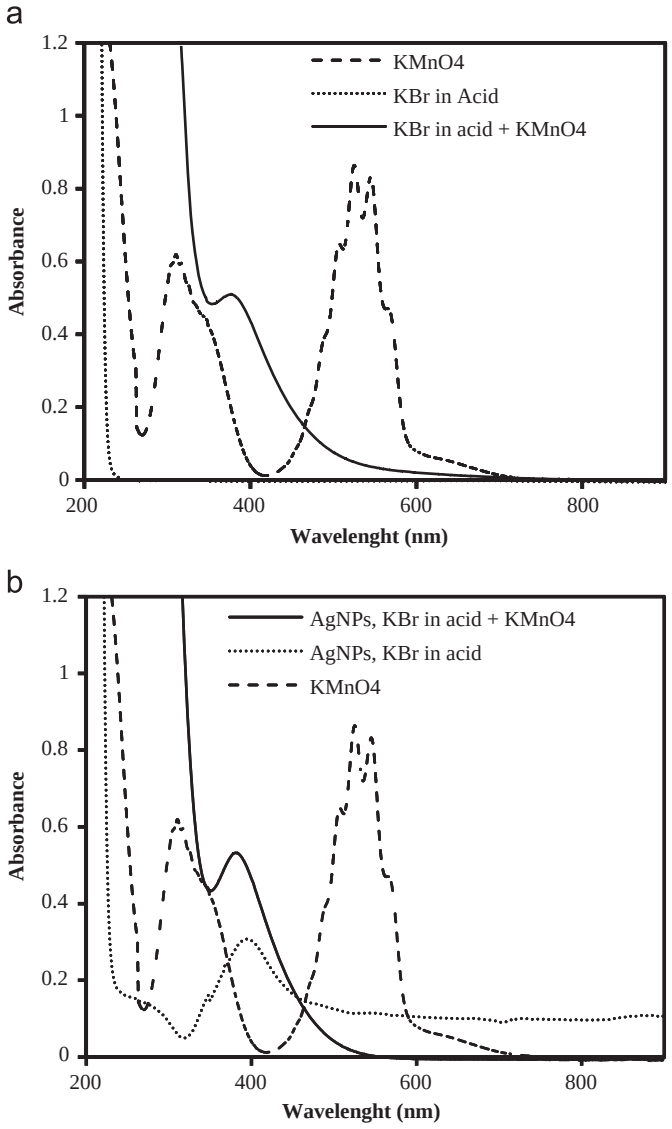

Fig. 4. UV–vis absorption spectra of $KMnO_4$–Br^- (a) and $KMnO_4$–Br^-–AgNPs (b) systems. Experimental conditions are the same as those in Fig. 3.

acids (including HCl, H_2SO_4, HNO_3 and H_3PO_4) with different concentrations were tested. The maximum CL response was achieved at 0.4 mol L^{-1} of H_2SO_4 (Fig. 5a). At lower acid concentrations, the rate of reaction and hence, the CL intensity is decreased. At higher concentrations, the NPs may be demolished and therefore, CL signal is again decreased.

The effect of Br^- concentration over the range of 0.006 mol L^{-1} to 0.04 mol L^{-1} was also examined. According to the results (Fig. 5b) increasing Br^- concentration up to 0.02 mol L^{-1} enhanced the CL intensity because the reaction proceeds to completion and more excited Mn(II) are produced. Excess Br^-, however, decreased the CL emission probably as a result of CL quenching. The maximum CL intensity was obtained at 0.02 mol L^{-1} Br^-; therefore this amount was used as the optimum concentration.

In order to investigate the effect of permanganate concentration, solutions with different concentration of $KMnO_4$ were prepared over the range of 1×10^{-4} to 7×10^{-4} mol L^{-1}. As shown in Fig. 5c, the CL signal increased up to 5×10^{-4} mol L^{-1} and then decreased at higher concentrations. At lower $KMnO_4$ concentrations the number of excited species is decreased and the response is diminished. At higher $KMnO_4$ concentrations the response is again diminished which is probably due to the CL quenching by excess $KMnO_4$ via non-radiative de-excitation pathways [2].

The amount of NPs on the CL response of the assay was examined and the results are shown in Fig. 5d. It can be seen that optimum CL response is achieved with the addition of 500 μL of Ag NPs solution.

3.4. Analytical application of the CL system

It was found that trace amounts of captopril has a considerable diminishing effect on the new CL reaction. Thiol-containing compounds are known to bind onto NPs surfaces via the sulfur atom [16]. The adsorption of such compounds on the NPs active surfaces inhibits their catalytic action and leads to a decrease in the CL signal. Based on this phenomenon, a sensitive method was developed for the determination of captopril. Under the optimum conditions described, the calibration graph was linear in the range of 0.3–100 nmol L^{-1} with a detection limit (3 s) of 0.12 nmol L^{-1}. The equation for regression line was $\Delta I=0.231C+0.05$ ($R^2=0.9997$), where $\Delta I=I_0-I$ is the difference between CL intensity in the absence (I_0) and presence of captopril (I), and C is the concentration of captopril in nmol L^{-1}. The relative standard deviation (RSD) was calculated to be 2.5, 1.1 and 2.9% for five determinations of 1.0, 20 and 70 nmol L^{-1} of captopril, respectively.

The results indicate that this CL system has good linearity, relatively high sensitivity and suitable precision. Furthermore, $KMnO_4$–Br^-–Ag NPs is a new CL system which may have potential applications in the determination of some other compounds. Comparison between the proposed method and some other reported CL methods for captopril quantification is shown in Table 2. As seen, our developed method has much lower limit of detection than most of the previously reported methods [5,19,31–36,38].

3.5. Study of interferences

In order to test the interference effect of some potentially interfering substances, increasing amounts of these species was added into a solution of 1.0 nmol L^{-1} captopril. The tolerable concentration ratios for interferences in relative error of $<5\%$ were over 5000 for Na^+, K^+, Cl^-, NO_3^-, 2000 for SO_4^{2-}, PO_4^{3-}, Mg^{2+}, vitamins B_1, B_2, Fe^{3+}, Ca^{2+}, ethanol, oxalate, 500 for glucose, vitamin C, Zn^{2+}, Cu^{2+}, 80 for cysteine and 70 for glutathione. Thus, the amounts of most of the potentially interfering species in biological fluids are below their tolerable levels or can be decreased with diluting, so there would be no interferences from these species in captopril determination.

3.6. Analysis of real samples

The procedure was easily applied to the determination of captopril in pharmaceutical preparations and human serum and urine samples. Preliminary steps for sample preparation are described in Section 2. Captopril in serum was determined with standard additions method to eliminate the matrix effect. According to the results, with this method, good recoveries were obtained for captopril.

The results for analysis of tablets were also compared with those obtained by an official method (HPLC) [50]. Statistical analysis of these results using Student t-test showed that there is no significant difference between the results of two methods (Table 3). Also, in order to further validate the method, known quantities of captopril were added into the samples before pretreatment step, and then the samples were prepared and analyzed according to the general procedure. The obtained results (Table 3) showed that there are no significant differences between the added and found values.

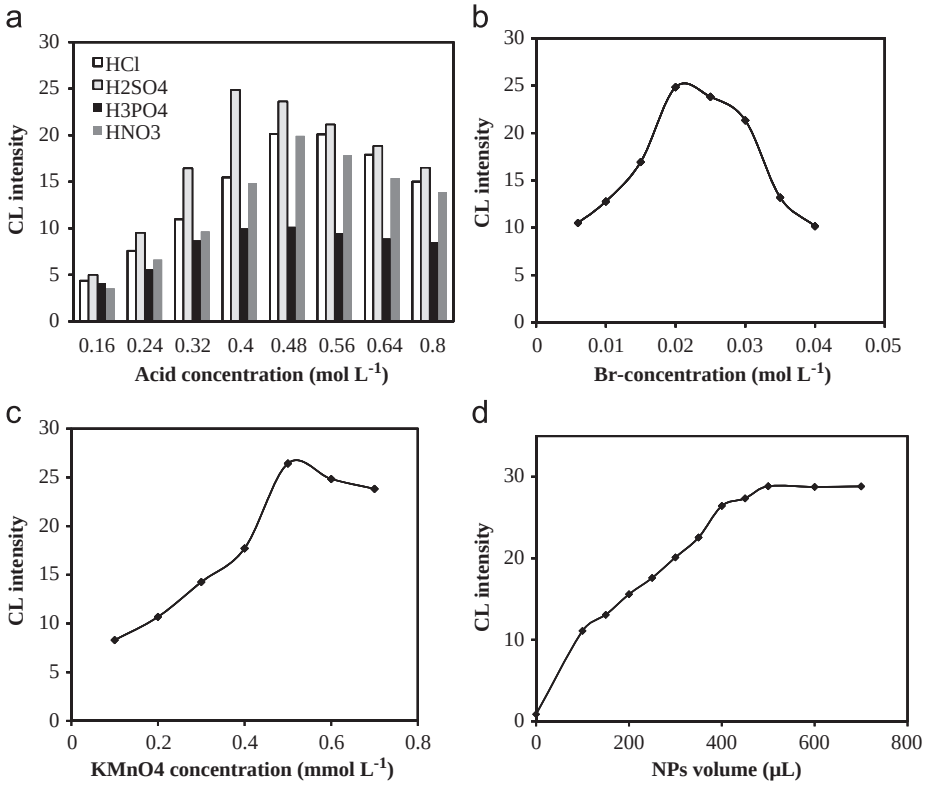

Fig. 5. Effect of (a) type and concentrations of acids (0.02 mol L^{-1} Br^-, 6×10^{-4} mol L^{-1} $KMnO_4$ and 400 μL Ag NPs); (b) concentration of Br^- (0.4 mol L^{-1} H_2SO_4, 6×10^{-4} mol L^{-1} $KMnO_4$ and 400 μL Ag NPs); (c) concentration of $KMnO_4$ (0.02 mol L^{-1} Br^-, 0.4 mol L^{-1} H_2SO_4 and 400 μL Ag NPs) and (d) amount of Ag NPs (0.5 mol L^{-1} Br^-, 0.4 mol L^{-1} H_2SO_4 and 5×10^{-4} mol L^{-1} $KMnO_4$) on the CL intensity.

Table 2
Summary of the published CL methods for determination of captopril.

CL system	LOD (nmol L^{-1})	Linear range (μmol L^{-1})	Sample	Ref.
Tris(2,2-bipyridyl) ruthenium(II)–Ce(IV)	1	2–150	Pharmaceutical formulations	[19]
$KMnO_4$ in acid	50 to120	0.23–9	Pharmaceutical formulations	[31]
Luminol–H_2O_2	9	0.023–23	Pharmaceutical formulations	[35]
Luminol–H_2O_2–triangular AuNPs	4.6	0.023–0.92	Pharmaceutical formulations and human urine	[5]
Rhodamine B- Ce(IV)	37	0.1–6	Pharmaceutical formulations	[33]
Quinine–Permanganate	28	0.09–5	Pharmaceutical formulations	[34]
Ag(II) in acid	28	0.09–46	Pharmaceutical formulations	[32]
Luminal–$Fe(CN)_6^{3-}$	230	0.46–184	Pharmaceutical formulations	[36]
Luminol–dissolved O_2	0.009	0.032–45 (nmol L^{-1})	Human Urine	[38]
$KMnO_4$–Br—AgNPs	0.12	0.3–100 (nmol L^{-1})	Pharmaceutical formulations and human urine and serum	This work

Table 3
Results for the determination of captopril in pharmaceutical and biological samples.

Sample	Added[a]	Found[b]	Recovery %[b]	Found (Official method)	*t*-statistic[c]
Capton tablet (12.5 mg)	–	12.2 ± 0.3	–	12.3 ± 0.2	0.64
	2.5	14.8 ± 0.1	103.0 ± 2.8	–	1.98
	5.0	17.3 ± 0.2	103.0 ± 3.9	–	1.30
	7.5	19.6 ± 0.2	99.2 ± 2.7	–	0.49
Urine	0.40	0.40 ± 0.01	99.6 ± 3.2	–	0.24
	2.0	1.98 ± 0.06	99.0 ± 2.8	–	0.60
	4.0	4.04 ± 0.08	100.9 ± 2.0	–	0.77
Serum	0.05	0.048 ± 0.01	97.0 ± 2.6	–	2.03
	0.50	0.51 ± 0.02	102.4 ± 4.0	–	1.03
	1.0	0.98 ± 0.04	98.0 ± 4.4	–	0.79

[a] The unit for added and found amounts is mg for tablet and μmol L^{-1} for urine and serum samples.
[b] Mean of three determinations ± standard deviation.
[c] *t*-critical = 4.3 for $n=2$ and $P=0.05$.

4. Conclusion

$KMnO_4$–Br^- system as a new reaction that leads to CL generation has been described. It has been shown that CL intensity of this system is considerably enhanced in the presence of spherical Ag NPs (~18 nm) due to their catalytic effect on the reaction. Possible mechanism has been discussed for this CL reaction. In addition, a method has been developed for the determination of captopril, based on its inhibiting effect on the catalytic action of Ag NPs. The method has good linearity, high sensitivity and good precision, and is suitable for the determination of captopril in pharmaceutical samples and biological fluids.

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