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The new approach for captopril detection employing triangular gold nanoparticles-catalyzed luminol chemiluminescence

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ABSTRACT

In this work, we utilize the triangular gold nanoparticles (AuNPs) prepared by trisodium citrate reduction of $HAuCl_4$ in presence of nonionic fluorosurfactant (FSN) as a novel chemiluminescence (CL) probe for the determination of captopril. Captopril can induce a sharp decrease in CL intensity from the triangular AuNPs-catalyzed luminol system. Under the selected experimental conditions, a linear relationship was obtained between the logarithm of CL intensity and the logarithm of concentration of captopril in the range of 23.0–920 nM, and the detection limit at a signal-to-noise ratio of 3 for captopril was 4.6 nM. The as-prepared triangular AuNPs were easier to synthesize, stable at a wider pH range and high ionic strength, and exhibited a high selectivity and an excellent sensitivity toward captopril. The applicability of the proposed method has been validated by determining captopril in commercial pharmaceutical formulations and human urine samples with satisfactory results. The recoveries for captopril in spiked samples were found to be between 95.0% and 103.5%. The method shows promise for routine control analysis of pharmaceutical preparations and human urine samples. Moreover, based on the CL spectra, UV–vis spectra and transmission electron microscope (TEM) measurements, a possible CL mechanism was proposed. The mechanism of high selectivity toward captopril is supposed to originate from the tight binding of the sulphydryl groups of captopril to the active site of the as-prepared triangular AuNPs, leading to oxygen-related radicals cannot easily be generated from H_2O_2 on the surface of triangular AuNPs.

1. Introduction

Captopril (Scheme 1) is an angiotensin converting enzyme (ACE) inhibitor used for treating hypertension, heart failure, and for preventing kidney failure and some types of congestive heart failure. As the first ACE inhibitor, captopril is considered a great breakthrough because of its novel mechanism of action and the revolutionary development process [1–3]. The molecular formula of captopril is $C_9H_{15}NO_3S$, and it is readily converted into its disulfide dimer as a result of poor thiol stability [4,5]. In Table 1, the characteristics of the proposed method were compared with those of others published methods. Captopril exhibits no native fluorescence with weak absorbance at short wavelengths, and, it requires precolumn or postcolumn derivatization of the sulphydryl groups with high extinction coefficients or high fluorescence yields. Therefore, spectrometric or fluorimetric methods after chemical derivatization are most commonly used for the precise determination of captopril [6–12]. However, chemical derivatization techniques exhibit some drawbacks, such as complex derivatization procedures, cross-reactivity and unstable captopril adducts. Moreover, electroanalytical methods have been reported for the determination of captopril, which suffers from the complicated preparation process of the electrodes and low sensitivity [13–15].

Chemiluminescence (CL) has become an attractive detection method in pharmaceutical analysis for its high sensitivity, simple instrumentation, wide dynamic range and good reproducibility [16,17]. In recent years, CL has been applied to the determination of captopril [18–29]. In 2011, Tzanavaras et al. reviewed various CL methods for the determination of captopril. In brief, captopril can react with a lot of oxidants, such as potassium permanganate and Ce(IV) to produce light, which is sensitized by a suitable sensitizer (*e.g.*, rhodamine 6G and quinine) [19–25]. In another model, captopril or captopril–cobalt complex can enhance the luminol CL, including luminol–H_2O_2 system, luminol–O_2 system, luminol–$KMnO_4$ system and luminol–$K_4Fe(CN)_6$ system [26–29]. Almost all reported CL methods [18–28] have been used for the determination of captopril in pharmaceutical preparations, and thus they concluded that some excipients, such as lactose, starch, dextrin, gelatine, sorbitol, glucose, fructose, sucrose and maltose have no effect on the detection of captopril. However, some common substance in human urine samples (*e.g.*, inorganic anions and

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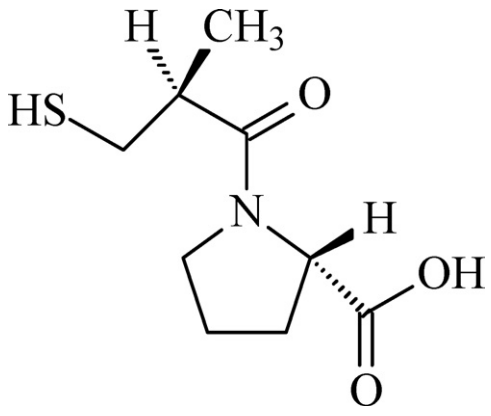
Table 1
Comparison of this method with others published methods.

Methods	Characteristics	Ref.
Spectrometric or fluorimetric methods	(a) Complex derivatization procedures (b) Cross-reactivity (c) Unstable captopril adducts	[6–12]
Electroanalytical methods	(a) Complicated preparation process of the electrodes (b) Low sensitivity	[13–15]
CL methods	(a) Inadequate selectivity (b) Simple instrumentation (c) Wide dynamic range and good reproducibility	[16–47]
This method	(a) Highly selectivity and sensitivity (b) Simple instrumentation (c) Wide dynamic range and good reproducibility	–

cations, urea, thiourea, amino acids) were not investigated in the reported CL methods [18–28].

In recent years, a variety of nanoparticles including gold, platinum, silver, bimetallic, semiconductor and magnetic nanoparticles have been utilized to amplify CL signals due to their unique physical and chemical properties, and they have exhibited great potential in analytical application [30,31]. Gold nanoparticles (AuNPs) have been extensively studied as a catalyst for the luminol–H_2O_2 CL system, and many organic compounds containing OH, NH_2 or SH groups were observed to inhibit the CL intensity from the AuNPs-catalyzed lumino–H_2O_2 reaction, indicating its inadequate selectivity toward target molecules [32]. Therefore, there are few available reports concerning direct determination for analytes by using AuNPs-catalyzed luminol–H_2O_2 CL system [33–36]. Nowadays, its most prominent analytical applications are achieved by employing separation techniques [37–39], or by coupling with immunoassay and hybridization assay [40–47]. Recently, we demonstrated that cetyltrimethylammonium bromide (CTAB)-stabilized gold nanorods-catalyzed luminol–H_2O_2 CL can exhibit a higher selectivity toward aminothiols, and thus glutathione in the cell extracts of *Saccharomyces cerevisiae* can be determined selectively [48]. This success encourages us to extend analytical applications of AuNPs-catalyzed luminol–H_2O_2 CL by surface functionalization and morphological changes of AuNPs.

In our recent paper [49], we synthesized the triangular AuNPs by trisodium citrate reduction of $HAuCl_4$ in presence of nonionic fluorosurfactant (FSN). The as-prepared triangular AuNPs exhibited higher catalytic activity toward luminol–H_2O_2 CL than spherical AuNPs because of their high surface-to-volume ratio, electron density and low activation energy. Furthermore, only thiol-containing compounds can interrupt the formation of the active oxygen intermediates on the surface of triangular AuNPs by forming Au–S covalent bonds, leading to a significant decrease in CL intensity. Herein, we employed the triangular AuNPs-catalyzed luminol–H_2O_2 CL system to investigate its interaction with captopril. Interestingly, it was found that a decrease in the logarithm of CL intensity was proportional to the logarithm of concentration of captopril; while other excipients in pharmaceutical formulations and various potential interference compounds in human urine samples had no effect on the triangular AuNPs-catalyzed luminol–H_2O_2 CL. Under the optimum experimental conditions, this proposed method was successfully used for the determination of captopril in commercial pharmaceutical formulations and human urine samples. Compared with the reported CL methods for the determination of captopril, where captopril acts as a reducing agent or sensitizer [18–29], captopril in the present system takes effect by interrupting the formation of the active oxygen intermediates on the surface of triangular AuNPs as a result of the formation of Au–S covalent bonds. Therefore, the proposed method showed a higher selectivity toward captopril.



Scheme 1. Chemical structure of captopril.

2. Experimental

2.1. Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (Milli Q, Millipore, Barnstead, CA, USA). Zonyl FSN-100 ($F(CF_2CF_2)_{1-7}CH_2CH_2O(CH_2CH_2O)_{0-15}H$) were purchased from Sigma–Aldrich (St. Louis, USA). Hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4{\cdot}3H_2O$) were purchased from Acros (Geel, Belgium). Trisodium citrate, lactose, starch, dextrin, gelatine, sorbitol, glucose, fructose sucrose and maltose were purchased from Beijing Chemical Reagent Company (Beijing, China). Captopril standard was purchased from National Institute for the Control of Pharmaceutical and Biological Products (Beijing, China). Captopril tablets were supplied by Beijing Jingfeng Pharmaceutical Co., Ltd. (12.5 mg captopril per tablet) and Beijing Shuguang Pharmaceutical Co. Ltd. (25 mg captopril per tablet). 4.6 μM stock solution of captopril was freshly prepared by dissolving its commercial crystal in deionized water and stored at 4 °C until analysis. A 0.01 M stock solution of luminol (3-aminophthalhydrazide) was prepared by dissolving luminol (Acros, Geel, Belgium) in 0.1 M sodium hydroxide solution without purification. The storage of luminol leads to a stabilization of the luminol reactivity, and thus it is used after several weeks. Working solutions of luminol were prepared by diluting the stock solution with deionized water. Working solutions of H_2O_2 were prepared daily from 30% (*v*/*v*) H_2O_2 (Beijing Chemical Reagent Company, Beijing, China). The triangular AuNPs with average diameters of 32-nm were prepared following the literature procedure

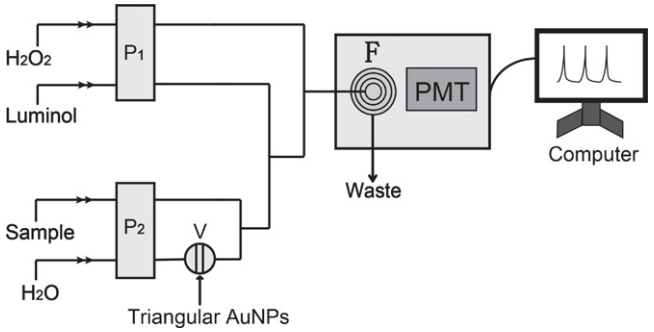


Fig. 1. Schematic diagram of CL detection by flow injection system. P_1 and P_2, peristaltic pumps; V, a six-channel injection valve (100-μL); F, flow cell (0.5 mm i.d. × 40.0 cm length); PMT, photomutiplier tube. In the flow system, PTEF tube (0.5 mm i.d.) is used, keeping the tubing lengths as short as possible for the rapid reaction rate of the present CL system. Experimental conditions: the flow rates of P_1 and P_2 were 2.0 mL/min and 1.5 mL/min, respectively; the concentrations of triangular AuNPs, luminol, NaOH and H_2O_2 were 1.06 nM, 0.1 mM, 4.0 mM, and 0.5 mM, respectively.

[49]. The as-prepared triangular AuNPs remain stable in aqueous solution for several months.

2.2. Apparatus

UV–visible spectra of triangular AuNPs were measured on a USB 4000 miniature fiber optic spectrometer in absorbance mode with a DH-2000 deuterium and tungsten halogen light source (Ocean Optics, Dunedin, FL). The sizes, shape and their distribution of as-prepared triangular AuNPs were confirmed through transmission electron microscope (TEM) measurements using a Hitachi-800 TEM (Tokyo, Japan). The TEM specimens were prepared by depositing an appropriate amount of AuNPs onto the carbon-coated copper grids and micro-grid respectively, and excess solution was wicked away by a filter paper. The grid was subsequently dried in air before measure. The CL spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan) at a slit of 10 nm and at a scanning rate of 1200 nm/min. The excitation lamp was off and the emission slit width was opened maximally to 10 nm during the CL spectra recording. The CL detection was conducted on an Ultra-Weak Luminescence Analyzer, which was purchased from institute of Biophysics, Chinese Academy of Science, Beijing, China (Biophysics Chemiluminescence, BPCL).

2.3. Procedures for CL detection

The schematic diagram of the flow system was shown in Fig. 1. It consisted of two peristaltic pumps (BT-100M, Baoding, China), a 100 μL loop injector, a six-way injection valve (Shimadzu, Tokyo, Japan), a CL flow cell (PTEF: 40 cm in length and 0.5 mm i.d.), and an Ultra-Weak Luminescence Analyzer, which was purchased from institute of Biophysics, Chinese Academy of Science, Beijing, China (Biophysics Chemiluminescence, BPCL). In the flow system, PTEF tube (0.5 mm i.d.) is used, keeping the tubing lengths as short as possible for the rapid reaction rate of the present CL system. The flow rate for the carrier stream/captopril, luminol/H_2O_2 was 1.5 mL/min, or 2.0 mL/min, respectively. The as-prepared triangular gold colloidal solution was injected into the carrier stream (ultrapure water) through a 100 μL loop-valve injector, mixed sequentially with ultrapure water or captopril solution, 0.1 mM luminol in 4.0 mM NaOH, and 0.5 mM H_2O_2 through three-way pieces. Finally, the mixed solution flowed into the spiral flow CL cell, which was placed in front of the photomultiplier (PMT) operating at −950 V. The PMT signals were imported to the computer for data acquisition. The inhibition ratio in CL intensity can be described

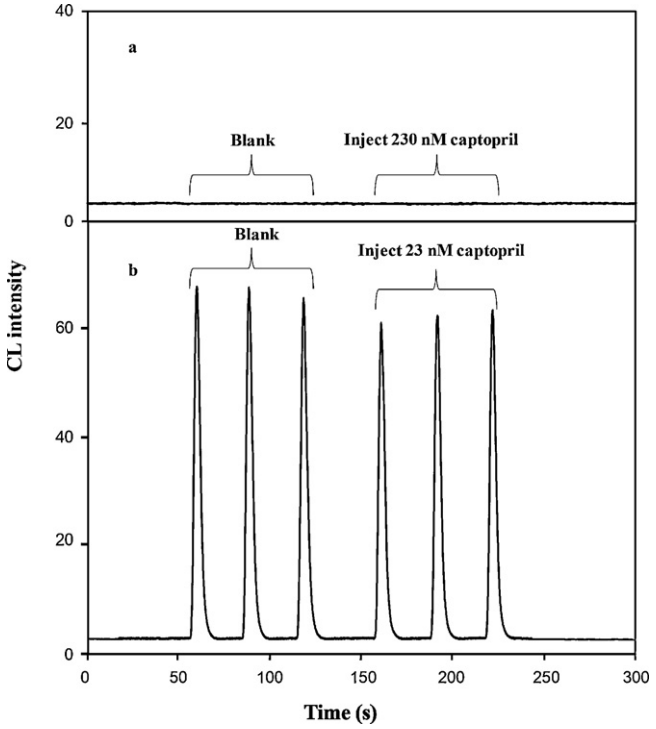


Fig. 2. CL intensity of luminol–H_2O_2 system by adding 230 nM captopril (a), and CL intensity of the triangular AuNPs-catalyzed luminol–H_2O_2 system by adding 23 nM captopril (b).

as $CL_{IR} = (I_0 - I)/I_0$, where I_0 was the CL intensity in the absence of captopril and I was the CL intensity in the presence of captopril.

2.4. Procedure for pharmaceutical formulations and human urine samples

Two types of pharmaceutical tablets, labeled 12.5 and 25 mg captopril per tablet were used for analysis. Six tablets of each formulation were powdered in a mortar and dissolved in deionized water to form a solution of 4.6 μM, the mixture was filtered with 0.22 μm membrane filters. The filtrate was stored in dark at 4 °C for further use. The calibration curve in pharmaceutical tablets after the appropriate dilution of the filtrate (ensuring the signal fell within the linear range) was obtained and used for the determination of captopril. All measurements for pharmaceutical tablets repeated three times.

Human urine samples were collected from a male volunteer and a female volunteer, and stored in dark at 4 °C for further use. Human urine sample containing with captopril was obtained by following procedure: 8 nM standard captopril was added into 1.0 mL of urine sample, then the solution was gently vortex-mixed with 200 μL of 3.0 M $HClO_4$ solution, put aside at room temperature for 10 min, and then centrifuged at 13,000 rpm for 10 min. The clear supernate was filtered with 0.22 μm membrane filters and diluted to appropriate concentration.

3. Result and discussion

3.1. Advantages of triangular AuNPs-catalyzed luminol CL for the determination of captopril

Early studies [26,50] demonstrated that some sulphur-containing compounds (*e.g.*, cysteine and glutathione) may enhance or inhibit the luminol–H_2O_2 CL, depending on the specific chemical conditions, such as the concentrations of H_2O_2

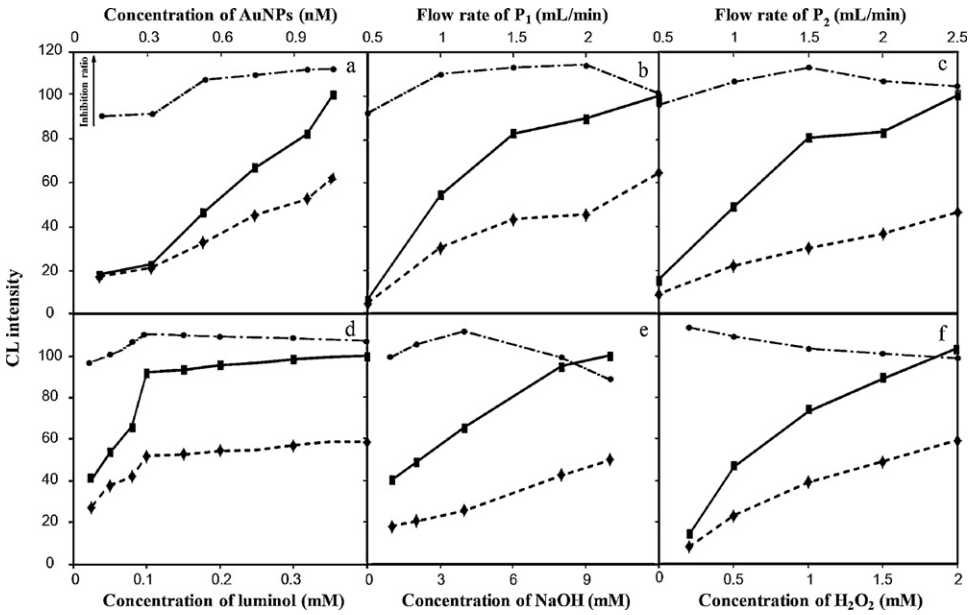


Fig. 3. Effect of the reaction conditions on the triangular AuNPs-catalyzed luminol CL in the absence (solid line) and the presence (dashed line) of 230 nM captopril (dash dot lines mean the inhibition ratio in CL intensity): (a) Concentration of the triangular AuNPs: the flow rates of P_1 and P_2 were 2.0 mL/min and 1.5 mL/min, respectively; the concentrations of luminol, NaOH and H_2O_2 were 0.1 mM, 4.0 mM, and 0.5 mM, respectively. (b) Flow rate of P_1: the flow rate of P_2 was 1.5 mL/min; the concentrations of triangular AuNPs, luminol, NaOH and H_2O_2 were 1.06 nM, 0.1 mM, 4.0 mM, and 0.5 mM, respectively. (c) Flow rate of P_2: the flow rate of P_1 was 2.0 mL/min; the concentrations of triangular AuNPs, luminol, NaOH and H_2O_2 were 1.06 nM, 0.1 mM, 4.0 mM, and 0.5 mM, respectively. (d) Concentration of luminol: the flow rates of P_1 and P_2 were 2.0 mL/min and 1.5 mL/min, respectively; the concentrations of triangular AuNPs, NaOH and H_2O_2 were 1.06 nM, 4.0 mM, and 0.5 mM, respectively. (e) Concentration of NaOH: the flow rates of P_1 and P_2 were 2.0 mL/min and 1.5 mL/min, respectively; the concentrations of triangular AuNPs, luminol, and H_2O_2 were 1.06 nM, 0.1 mM, and 0.5 mM, respectively. (f) Concentration of H_2O_2: the flow rates of P_1 and P_2 were 2.0 mL/min and 1.5 mL/min, respectively; the concentrations of triangular AuNPs, luminol, and NaOH were 1.06 nM, 0.1 mM, and 4.0 mM, respectively.

and sulphur-containing compounds. Therefore, sulphur-containing compounds have a complex effect on the luminol–H_2O_2 CL. Herein, in a flow-injection CL setup, the sensitivity of this assay was compared to a previously described one based on a conventional luminol–H_2O_2 system [26]. As shown in Fig. 2, the results indicated that the CL intensity of the triangular AuNPs-catalyzed luminol–H_2O_2 system significantly decreased upon the addition of 23 nM captopril, and the inhibition ratio in CL intensity was 8% (Fig. 2b); however, in the absence of the triangular AuNPs no enhancement or inhibition of the luminol–H_2O_2 CL was detected in the presence of 230 nM captopril (Fig. 2a).

3.2. Optimization conditions for the CL detection of captopril

A series of experiments were conducted in order to establish the optimum analytical conditions. The optimized parameters included the pH of the solution, the concentrations and the flow rates of the reagents.

3.2.1. Concentration of the triangular AuNPs

The CL intensity depends on the concentration of triangular AuNPs. Therefore, the concentration of the triangular AuNPs was investigated by diluting the as-prepared 1.06 nM triangular gold colloidal solution. It can be seen from Fig. 3a that the inhibition ratio in CL intensity increased steadily with increasing the concentration of the triangular AuNPs. Note that the concentration of the as-prepared 32-nm triangular AuNPs was calculated to be ~1.06 nM [49], and thus a concentration of 1.06 nM particle concentration was chosen throughout this study in view of the CL intensity and the operation simplification (no need to dilute or concentrate the as-prepared triangular AuNPs).

3.2.2. Flow rates of the reagents

The flow rates for pump 1 (P_1, for luminol and H_2O_2 solutions) and pump 2 (P_2, for the carrier water and captopril solution), were optimized in the range of 0.5–2.5 mL/min. The inhibition ratio in CL intensity was the strongest when the flow rate of the P_1 was 2.0 mL/min (Fig. 3b). When the flow rate of the P_2 was larger than 1.5 mL/min, the inhibition ratio in CL intensity decreased slowly (Fig. 3c). Therefore, the optimal flow rates of P_1 and P_2 were selected as 2.0 and 1.5 mL/min, respectively.

3.2.3. Concentration of luminol

The concentration of luminol was optimized in the range of 0.02–0.4 mM (Fig. 3d). It was shown that the maximum inhibition ratio in CL intensity was obtained at a luminol concentration of 0.1 mM, and then the inhibition ratio in CL intensity remained constant up to 0.4 mM concentration of luminol. Therefore, this system was operated at 0.1 mM luminol throughout this study.

3.2.4. Concentration of sodium hydroxide

In this study, luminol solution was adjusted to the appropriate pH with aqueous NaOH solution. As shown in Fig. 3e, the maximum inhibition ratio in CL intensity was found at a NaOH concentration of 4.0 mM. Note that the pH of the working solution of 0.1 mM luminol in 4.0 mM NaOH solution was 11.3. Therefore, 4.0 mM NaOH was chosen as the reaction medium in further experiments.

3.2.5. Concentration of H_2O_2

The concentration of H_2O_2 was examined in the range of 0.2–2.0 mM. As shown in Fig. 3f, the catalytic activity of the triangular AuNPs was increased with increasing the concentration of H_2O_2, the inhibition ratio in CL intensity was decreased with increasing the concentration of H_2O_2. Considering the catalytic activity of the triangular AuNPs and the inhibition ratio in CL intensity, 0.5 mM H_2O_2 was chosen in this study.

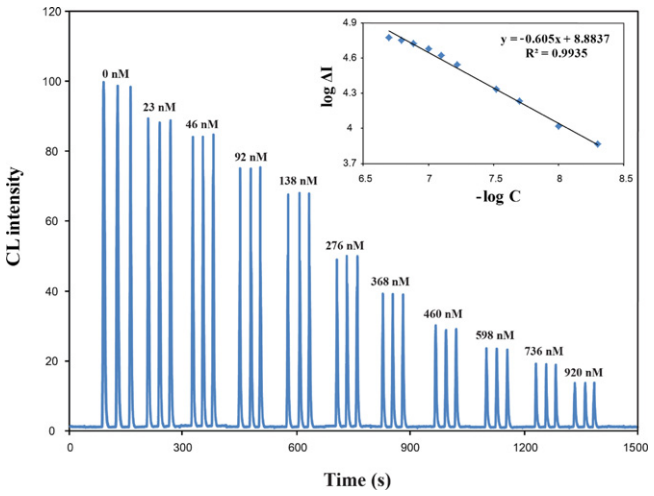


Fig. 4. The CL inhibition of the triangular AuNPs-catalyzed luminol CL by adding different concentrations of captopril; inset, calibration curve for standard captopril, $\Delta I = I_0 - I$, showed the effect of captopril on the CL intensity of the system, where I_0 stands for the signal in the absence of captopril and I stands for the signal in the presence of captopril.

3.3. Analytical performances

Under the optimum conditions described above and using the flow system depicted in Fig. 1, a series of captopril concentrations were used to construct the calibration curve. A logarithmic calibration graph of CL intensity versus logarithmic captopril concentration was presented in Fig. 4. The calibration curve was linear in the range 23.0–920 nM. The detection limit of captopril through this approach (S/N = 3) was 4.6 nM, and the relative standard deviation for eight repeated measurements of 230 nM captopril was 2.7%.

3.4. Interference study

In order to apply the developed methodology to the determination of captopril in pharmaceutical formulations and human urine samples, the effects of some compounds commonly used as excipients in pharmaceutical formulations, and various potential interference compounds in human urine samples were assessed. A sample solution containing a fixed amount of captopril (230 nM) and different concentrations of the interference compounds under evaluation were analyzed by the present method. A compound was considered as non-interfering if the analytical CL signal variation was ±5% when compared to the analytical signal obtained in the absence of the referred compound.

The results revealed 100-fold gelatine, Fe^{2+}, Fe^{3+}, Mn^{3+}, 500-fold Ca^{2+}, Mg^{2+}, NH_4^+, Al^{3+}, CO_3^{2-}, threonine, tryptophane, 1000-fold starch, glucose, maltose, sucrose, sorbitol, fructose, starch, dextrin, methionine, alanine, thiourea and urea, and 2000-fold K^+, NO_3^-, SO_4^{2-}, ClO_4^-, Cl^-, Br^-, F^- at a relative mass ratio regarding captopril did not interfere. Therefore, it can be concluded that the proposed method shows very high selectivity for the determination of captopril in commercial pharmaceutical formulations and human urine samples.

3.5. Analysis of pharmaceutical formulations and human urine samples

In order to evaluate the applicability and reliability of the proposed methodology, it was applied for the determination of captopril in commercial pharmaceutical formulations and human urine samples. The analytical merits of the present method were evaluated by comparing the captopril contents obtained between the present method and the officially taken method [51]. As shown in Table 2, the results obtained were in good agreement for the determination of captopril in commercial pharmaceutical formulations. Also, the recoveries for captopril in spiked samples were found to be between 95.0% and 103.5%. The method shows promise for routine control analysis of pharmaceutical preparations and human urine samples.

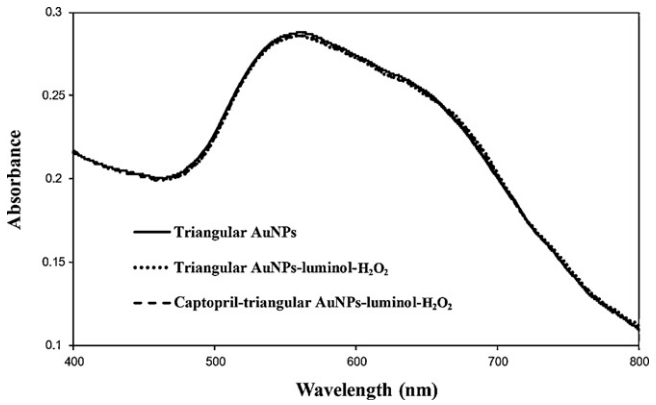


Fig. 5. UV–visible absorption spectra for the triangular AuNPs-catalyzed luminol system before and after the CL reaction with captopril. Experimental conditions were the same with those in Fig. 1.

3.6. A discussion about a reaction scheme

To clarify the CL mechanism of the present system, the UV–vis absorption spectra of the triangular AuNPs, captopril and their mixture were carried out. From Fig. 5, it can be seen that the spectrum of the triangular AuNPs revealed a wide absorbance peak with dark blue color. The wavelength of maximum absorption of AuNPs dark blue solution is about 555 nm. The reaction of the triangular AuNPs with captopril did not cause the change of UV–visible spectra of the triangular AuNPs. TEM studies also revealed that the shape and size of the triangular AuNPs did not change before and after the reaction (data not shown).

The CL spectrum of the triangular AuNPs-luminol–H_2O_2 system in the absence of captopril was acquired using a FL-7000 model spectrofluorimeter combined with a flow-injection system.

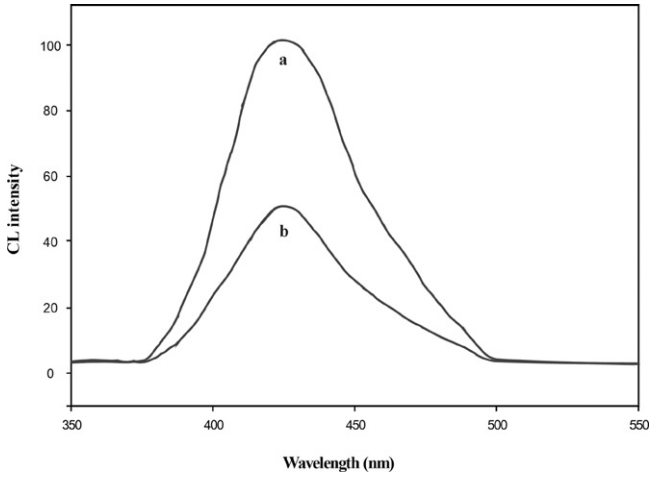
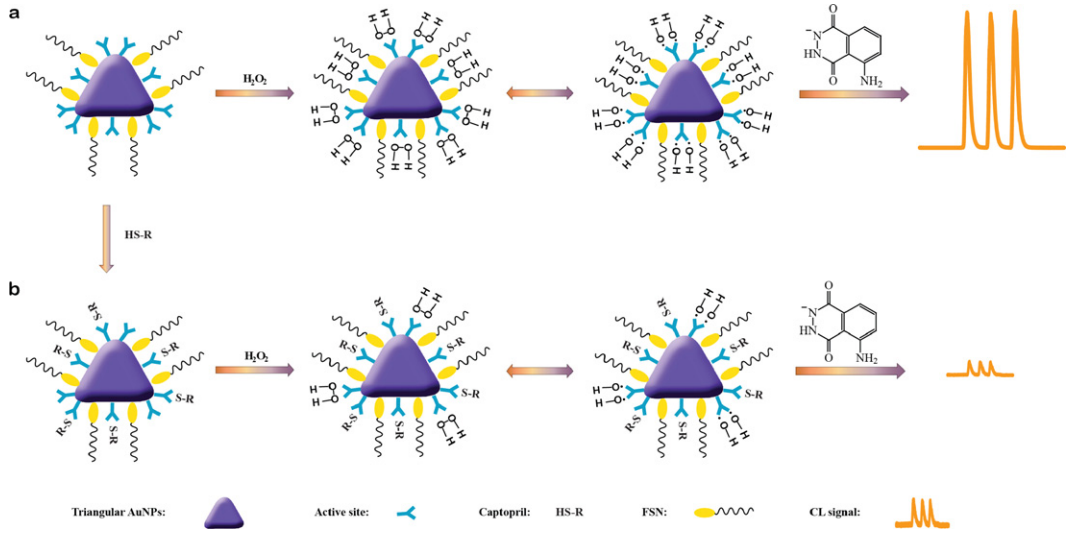


Fig. 6. CL spectra of the triangular AuNPs-catalyzed luminol system in the absence of captopril (a) and in the presence of captopril (b). Luminol, 0.25 mM; H_2O_2, 1.25 mM; NaOH, 3.0 mM; triangular AuNPs, 1.06 nM; captopril, 460 nM; other conditions were the same with those in Fig. 1.

Table 2
Determination of captopril in pharmaceutical tablets and urine samples.

Sample	Official method (μM)	This method (μM)	Added (μM)	Found (μM)	Recovery (%)
Tablet	22.8 ± 0.20	22.9 ± 0.33	11.5	11.6 ± 0.22	100.9 ± 1.91
	–	–	34.5	35.7 ± 0.13	103.5 ± 0.38
Tablet	22.7 ± 0.17	22.8 ± 0.36	11.5	11.4 ± 0.32	99.1 ± 2.78
	–	–	34.5	34.5 ± 0.44	100.0 ± 1.27
Urine	–	–	0	–	–
	–	–	4.0	3.9 ± 0.07	97.5 ± 1.75
	–	–	8.0	7.8 ± 0.10	97.2 ± 1.25
	–	–	16.0	15.7 ± 0.12	98.1 ± 0.75
Urine	–	–	0	–	–
	–	–	4.0	3.8 ± 0.06	95.0 ± 1.50
	–	–	8.0	7.7 ± 0.10	96.2 ± 1.25
	–	–	16.0	15.8 ± 0.11	98.8 ± 0.69

All results are mean and standard deviation of three measurements. Human urine samples were made from a male volunteer and a female volunteer.



Scheme 2. Schematic illustration of (a) the catalytic activity of the triangular AuNPs on luminol CL; (b) the inhibition of captopril on the triangular AuNPs-luminol CL.

As shown in Fig. 6a, the maximum emission for the triangular AuNPs-luminol–H_2O_2 system in the absence of captopril were about 425 nm, indicating that the luminophor for the present CL system was still the excited-state 3-aminophthalate anions. The CL spectrum of the triangular AuNPs-luminol–H_2O_2 system in the presence of captopril was also performed as shown in Fig. 6b, indicating that the CL intensity decreased and the peak of the CL spectrum was also at about 425 nm. These results demonstrated that the addition of the triangular AuNPs and captopril into the luminol–H_2O_2 system cannot generate a new luminophor.

Based on the above results, the CL mechanism can be summarized in Scheme 2. The stronger CL enhancement on the luminol–H_2O_2 system by the triangular AuNPs was supposed to originate from a higher catalytic activity of the triangular AuNPs, which facilitated the radical generation and electron-transfer processes taking place on the surface of the AuNPs [49]. When captopril was injected into the triangular AuNPs-luminol–H_2O_2 system, the sulphydryl groups of captopril can bind tightly at the active site of the as-prepared triangular AuNPs, leading to oxygen-related radicals cannot easily be generated from H_2O_2 on the surface of triangular AuNPs. Therefore, captopril can greatly inhibit the triangular AuNPs-catalyzed luminol CL signals.

4. Conclusions

Most reports of the CL determination of captopril in the literature were based on the reaction of captopril with various oxidants, and thus they exhibited low selectivity toward captopril. This work explored a novel route for highly selective and sensitive determination of captopril by using high-affinity binding of the sulphydryl groups of captopril onto the surface of the as-prepared triangular AuNPs, leading to greatly inhibition of the triangular AuNPs-catalyzed luminol CL. To the best of our knowledge, this is the first work to use the triangular AuNPs-based CL sensors for the determination of analytes in pharmaceutical formulations and human urine samples.

Acknowledgements

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