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Nanoparticle coated paper-based chemiluminescence device for the determination of L-cysteine

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ABSTRACT

A laminated paper-based analytical device (LPAD) combined with gold nanoparticles (AuNPs) catalyzed luminol chemiluminescence (CL) system for the determination of L-cysteine (L-cys) was presented here. It is based on the principle that L-cys can greatly inhibit CL signal of AuNPs–luminol–H_2O_2 system. The paper-based device was fabricated by a low-cost cutting method, followed by lamination with two polyester films. This approach of cutting/lamination to fabricate LPAD is very similar to making a lamination picture. A good linear relationship was obtained between the CL intensity and the concentrations of L-cys in the range from 1.0×10^{-8} M to 1.0×10^{-6} M with a detection limit at 8.2×10^{-10} M ($S/N=3$). This study shows the successful integration of the LPAD and the CL method. It will be of interest for use in areas such as disease diagnosis in the future.

1. Introduction

The paper-based analytical devices (PADs), which have the advantages of low-cost, high abundance, elevated porosity, biodegradability and excellent chemical compatibility [1–3], have made fast progress in the last few years. Inspired by these attractive features, many groups have put great efforts to the development of PADs including the fabrication method [4–7], functionalizations or modifications on PADs [8–11], and detection methods on PADs [12–15]. The first paper published on PADs was reported by Whitesides' and co-workers [16] which used a patterning paper to create hydrophilic channels on it for simultaneous detection of glucose and protein in urine sample. Because the liquids can be transported just by capillary forces without the assistance of external forces, PADs have stood out as a new class of point-of-care (POC) diagnostic devices for molecular analysis, environmental detection, and health monitoring field in developing countries, resource-limited area and remote regions.

PADs have gained more interests than before because paper has the superiority that high speed coating and printing techniques can be available on it. So, one main fabrication method was to define hydrophobic zones by impregnating SU-8 into paper and then photo-patterning [17,18], or printing wax and then melting it into paper [19–21]. But in these devices, the paper always has low mechanical strength and it is a little bit fragile being folded. The hydrophilic channels cannot always have a clear edge with the hydrophobic parts because the hydrophobic substances cannot penetrate into the paper fiber with the uniform depth and length. The other fabrication method was creating the hydrophilic channel by the cutting method to form physical boundaries using a laser, cutter or knife plotter [22,23]. Here, we used a simple fabrication method which has been reported recently for producing devices by craft-cutting and lamination [24]. The method used a craft cutter to generate boundaries of paper according to the design of device, followed by a roll laminator to produce laminated paper-based analytical device (LPAD). The LPAD has the advantage of simplicity, durability and flexibility. It is best suited for fabricating large numbers (>100) of LPAD in a single batch to create low-cost devices.

Recently, the mainly reported detection methods which have been established on PADs were colorimetry [25], electrochemical methods [26,27] and electrochemiluminescence [28]. Nowadays, chemiluminescence (CL) has been proven to be a powerful analytical method which can be used on PADs due to its high sensitivity and wide dynamic range. Yu's group has published several papers on CL PADs in these 3 years which were mainly on immunoassay with very lower detection limits [29–32]. As we know, metal nanoparticles have been used on the PADs [33] for colorimetric detection. While, metal nanoparticles such as gold or silver nanoparticles can also be used as catalysts to enhance the inherent sensitivity in CL system which has been investigated in CL field for many years [34]. The catalysis of gold nanoparticles (AuNPs) for luminol CL is now an expanding area [35,36]. Cui and his co-workers systematically investigated the catalytic action of AuNPs in luminol–H_2O_2 CL reactions [35].

In this work, L-cysteine (L-cys) was detected by CL on the paper-based chip with AuNPs for the first time. Different detection

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methods including colorimetry [39,40] fluorimetry [41,42] have been reported for the determination of L-cys. But CL detection with nanoparticles [35,43–45] for L-cys detection can have low detection limit and high sensitivity. Here, the CL of the luminol and H_2O_2 system could be inhibited by L-cys with AuNPs involved. With AuNPs firstly coated on the paper surface, L-cys can be detected on the paper-based device with higher sensitivity. Based on this, a LPAD based on the inhibit effect of L-cys on the luminol–H_2O_2–AuNPs CL system was established to detect L-cys sensitively and cost-effective. The device is designed as a single use, inexpensive and can process one sample at a time. It has the advantages of low cost and portable device without expert requirement and suitable for analysis of the routine screening of large scale samples. This work could make a contribution to further expand analytical protocol on PADs.

2. Experimental

2.1. Reagents and materials

L-cysteine (L-cys) monohydrochloride and Chloroauric acid ($HAuCl_4$) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Whatman chromatography paper 3 mm CHR (20.0 cm × 20.0 cm) was obtained from Fisher Scientific (Pittsburgh, PA). Sodium citrate and H_2O_2 were purchased from Xi′an Chemical Reagent Company (Xi′an, China). The L-cys stock solution (0.01 M) was prepared by dissolving L-cys (0.0121 g) in 10 mL deionized water. Working standard solutions of L-cys were freshly diluted with deionized water. Luminol was obtained from Sigma and the stock solution (25 mM) was prepared by dissolving luminol (4.43 g) in 0.10 M NaOH (20 mL) and then diluted to 1 L with water. The luminol solution was stored in the dark for one week prior to use to ensure that the reagent had stabilized. Working solution of H_2O_2 was prepared freshly daily from 30% (w/w) H_2O_2. Unless other indicated, all reagents and solvents were purchased in their highest available purity and used without further purification. Millipore Milli-Q water (18 MΩ cm^{-1}) was used in all experiments.

2.2. Apparatus

The chemiluminescence (CL) intensity was measured and recorded with a model IFFS-A Chemiluminescence Analyzer (Xi′an Remex Electronic Sci. Tech. Co. Ltd., Xi′an, China). CL data acquisition and treatment were performed using RFL-1 software running under Windows XP (Xi′an Remax, China). The results of UV were obtained using Shimadzu UV-1800 recording spectrophotometer (Beijing Purkinje, China). The transmission electron microscopy (TEM) images of gold nanoparticles (AuNPs) were taken using a Hitachi H-600 TEM (Tokyo, Japan). The CL emission spectrum of the luminol–H_2O_2–AuNPs was obtained using the modified FL-4600 spectrofluorimeter (Hitachi, Japan).

2.3. Preparation and characterization of AuNPs

All glassware used in the following procedure was cleaned in a bath of freshly prepared 3:1 HNO_3–HCl, rinsed thoroughly in water and dried in air prior to use. AuNPs were prepared according to the literature method with some modifications [37]. Briefly, a sodium citrate solution (0.1 M, 1.94 mL) was rapidly added to a boiled $HAuCl_4$ solution (50 mL H_2O, 0.167 mL 10% $HAuCl_4$) under vigorous stirring. The mixed solution was boiled for 10 min and further stirred for 15 min. The resulting wine-red solution was cooled to room temperature, which was stored in the 4 °C refrigerator before use. The UV–vis absorption spectra of the AuNPs solution was recorded and shown in Fig. 1A. The size and shape of the AuNPs was characterized by TEM (Fig. 1B). From Fig. 1A, we can see a sharp absorbance peak centered 520 nm. Statistical analysis of TEM data revealed that the average diameter of the AuNPs was about 13 nm and its dispersion was very good. The concentration of the AuNPs solution was 1.7×10^{-8} M, which was estimated by using the absorption spectra, based on an extinction coefficient of 2.7×10^8 M^{-1} cm^{-1} at $\lambda = 520$ nm (Fig. 1A) for 13 nm particles [38].

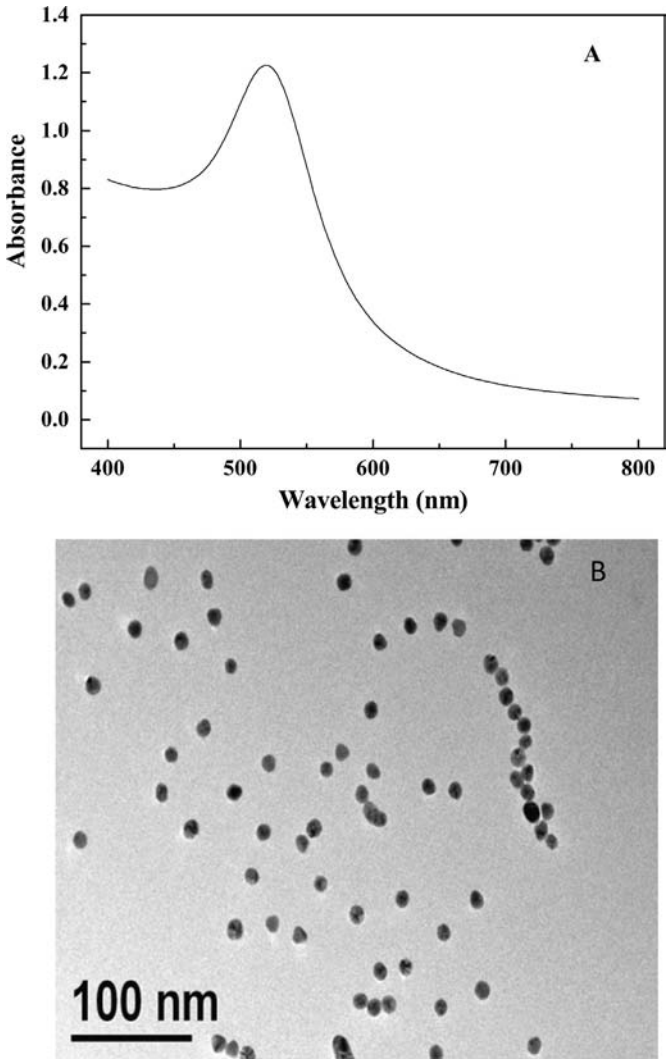

Fig. 1. (A) UV–vis absorption spectrum of AuNPs and (B) TEM image of AuNPs.

2.4. The fabrication of the laminated paper-based analytical device (LPAD)

The fabrication procedure was according to the reported method previously [24]. As illustrated in Fig. 2, the pattern of the device was firstly designed using CorelDraw X6. The design was then exported as a DXF file into the controller software of a craft cutter, ROBO Master-Pro (Graphtec Corporation). Using a carrier sheet, circle shape of paper with the diameter of 6 mm was cut by using the cutting plotter (Graphtec Craft Robo-S, Graphtec Corporation) and the unwanted edges were removed. Then two polyester films which served as the backing and cover for the paper strips were cut. For the sample deposition was required on the strip, the cover film was left open and it was cut with the same size and shape of the paper test strip. The paper

strip was then laminated (LTS-450T, Buytem, Korea) with a cover film and a bottom film as shown in Fig. 2.

2.5. CL assay procedure of this LPAD

As shown in Fig. 3, the CL signal was measured using a computerized ultraweak luminescence analyzer. After lamination, 10 μL of AuNPs was firstly dropped on the detection area of LPAD and dried for 20 min. Then 10 μL of L-cys of different concentration was dropped on the same area and dried. The LPAD was put on the bottom of the device holder which was fixed on the bottom of the cassette. When detecting the CL intensity by photomultiplier tube (PMT), the cassette can be shut with a black metallic cover. 15 μL mixture solutions of luminol and H_2O_2 were dropped onto the detection area through the injection hole on top of the cassette by an injector (Fig. 3). The CL intensity was detected by the PMT. Data acquisition and treatment was performed with RFL software running under Windows XP. The concentration of sample was quantified by the peak height of the CL signal.

3. Results and discussion

3.1. CL behavior of this AuNPs catalyzed luminol system

The CL behavior of L-cys in the luminol system which was catalyzed by AuNPs on the LPAD was studied first. AuNPs can enhance the luminol–H_2O_2 CL system greatly which can be seen from Fig. 4A. But after L-cys was dropped on the detection area, the CL signal of AuNPs–luminol–H_2O_2 can be decreased greatly. Results revealed that the extent of inhibition is related to the concentration of L-cys which can be seen from Fig. 4B.

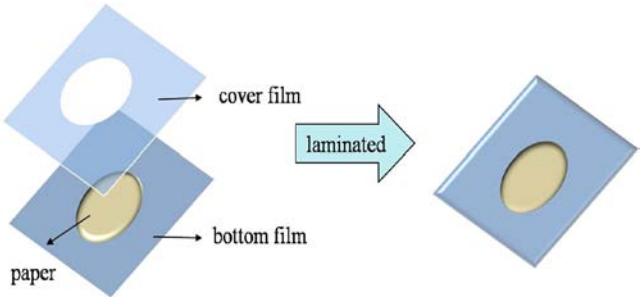

Fig. 2. Fabrication procedure of the LPAD.

3.2. Possible reaction mechanism of L-cys involved luminol–H_2O_2–AuNPs CL system

In order to obtain the possible mechanism of the CL reaction, the CL emission spectrum of the luminol–H_2O_2–AuNPs was obtained using the modified FL-4600 spectrofluorimeter. The results showed that the maximum wavelengths of CL emission enhanced by AuNPs were 425 nm. The maximum wavelengths of CL emission did not change when L-cys was added into the above system. So 3-aminophthalate (3-APA*) is the luminophor of this system.

Cui [35] has reported the major CL-generating mechanism for luminol–H_2O_2–AuNPs system. Firstly, luminol and H_2O_2 were changed to be luminol anion and HO_2^- in alkaline solution. Then AuNPs can catalyst the decomposition of H_2O_2 and the O–O bond of H_2O_2 might be broken up into double $HO^\bullet$ radicals. The generated hydroxyl radicals might be stabilized by AuNPs via partial electron exchange interactions [46,47]; $HO^\bullet$ radicals reacted with luminol anion and HO_2^- to facilitate the formation of luminol radical anion ($L^{\bullet -}$) and superoxide radical anion ($O_2^{\bullet -}$); At last, further electron-transfer processes between $L^{\bullet -}$ and $O_2^{\bullet -}$ radicals anions on the surface of AuNPs would take place to produce the key intermediate hydroxyl hydroperoxide [48] which can lead to the enhancement of the CL. With some other metal nanoparticles such as AgNPs, there was the same phenomenon as in this system we used. We have done some experiments about it and the results revealed that L-cys can also inhibit the CL of luminol–H_2O_2–AgNPs.

In the luminol–H_2O_2–AuNPs system, some intermediate radicals such as $HO^\bullet$ and $O_2^{\bullet -}$ were formed during the reaction. The reducing groups of $-SH$ and $-NH_2$ are likely to compete with luminol for active oxygen intermediates, leading to a decrease in CL intensity [35]. On the other hand, organic compounds containing $-OH$, $-NH_2$, or $-SH$ groups have been reported to interact readily with AuNPs [49]. Therefore, these compounds may interact with AuNPs to interrupt the formation of luminol radicals anion ($L^{\bullet -}$) and superoxide radical anion ($O_2^{\bullet -}$) which can take place on the surface of AuNPs. So the CL intensity decreased according to the above reason. The CL with any other organic compounds

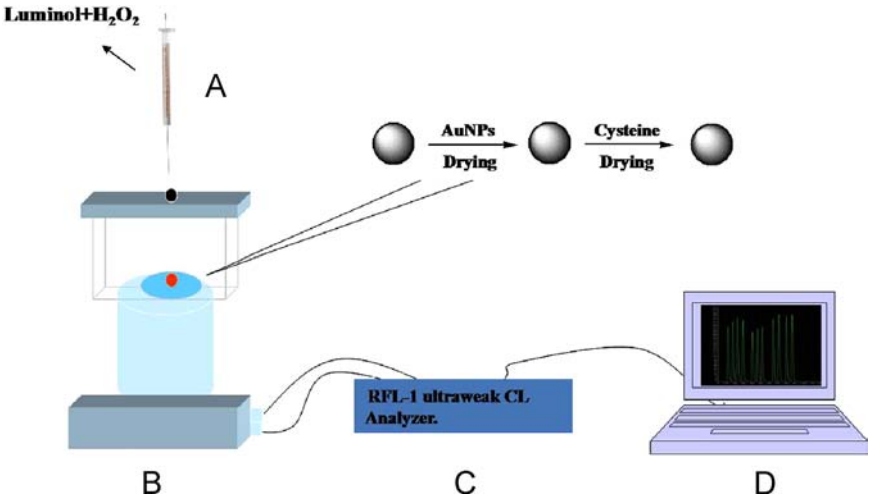

Fig. 3. Schematic diagram and assay procedure of this LPAD biosensor. (A) sample injector; (B) CL detector; (C) ultraweak luminescence analyzer; and (D) data acquisition with the computer.

containing $-OH$, $-NH_2$ or $-SH$ groups such as phenol, pyrogallol, p-phenylenediamine, aminopyrine, propranolol and glutathione were tired to testify the above mechanism. As we expected, with the concentration of 10^{-4} M, all these six compounds can inhibit the CL signal of luminol–H_2O_2–AuNPs system.

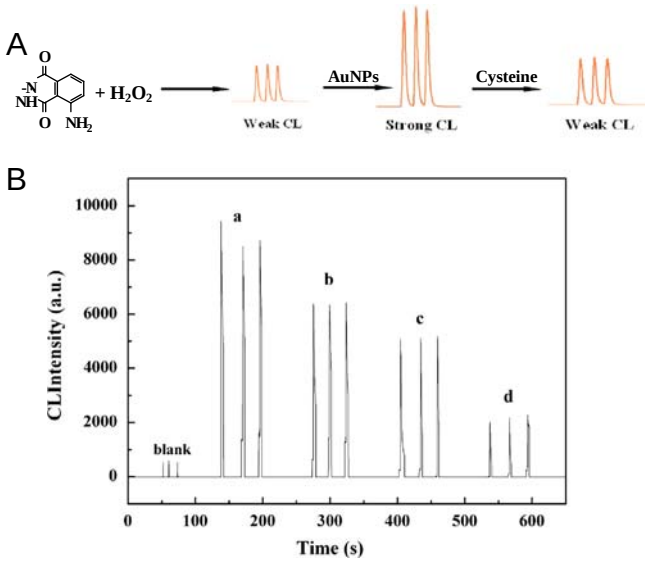

Fig. 4. (A) Schematic diagram of the CL behavior of L-cys; (B) Chemiluminescence profiles of luminol–H_2O_2 mixed with AuNPs and different concentration of L-cys. Blank, signal of luminol–H_2O_2. (a) Signal of luminol-H_2O_2-AuNPs. (b)–(d) Signals of luminol-H_2O_2-AuNPs with different concentration of L-cys. (b) 2.0×10^{-8} M, (c) 6.0×10^{-8} M, (d) 1.0×10^{-7} M.

3.3. Optimization of the LPAD

In order to achieve the highest sensitivity, different kind of paper was tried here first. They are quantitative filter paper, qualitative filter paper and Whatman chromatographic paper. From Fig. 5A we can see that Whatman chromatographic paper has the higher signal/noise ratio. For the quantitative filter paper and qualitative filter paper, the thickness was not always the same which can be fluctuated in the range of 10–250 μm. Whatman 3 mm chromatography paper has the advantage of the high quality, purity and consistency. So it can get the better signal/noise ratio and reproducibility than the other kinds of paper.

In addition to the optimization of the paper's type, the concentration of H_2O_2, luminol and pH of the solution also had to be optimized to obtain sensitive and precise detection of L-cys in the CL system.

The effect of H_2O_2 concentration on the CL system was studied in the range of 1.0–90 mM. As shown in Fig. 5B, the CL intensity increased with H_2O_2 concentration in the range of 1.0–50 mM. When the H_2O_2 concentration was higher than 50 mM, the CL intensity decreased. The reason for this is the decomposition of H_2O_2 increased with a higher concentration and this can affect the CL signal directly. So, 50 mM H_2O_2 was selected as the optimal concentration for further experiments.

Using a fixed concentration of H_2O_2 (50.0 mM) and solution pH (12.0), the luminol concentration was varied in the range 0.5–5.0 mM (Fig. 5C). It was found that the CL intensity increased with the luminol concentration from 0.5–1.0 mM. When the luminol concentration was higher than 1.0 mM, the CL intensity began to decrease. Hence, 1.0 mM of luminol concentration was chosen for further experiments.

In luminol CL system, the pH value was very important since it can directly affect the CL signal. When fixed the concentration of luminol (1.0 mM) and H_2O_2 (50 mM), the effect of pH on the CL intensity was examined in the range of 9.5–12.5 (Fig. 5D). The

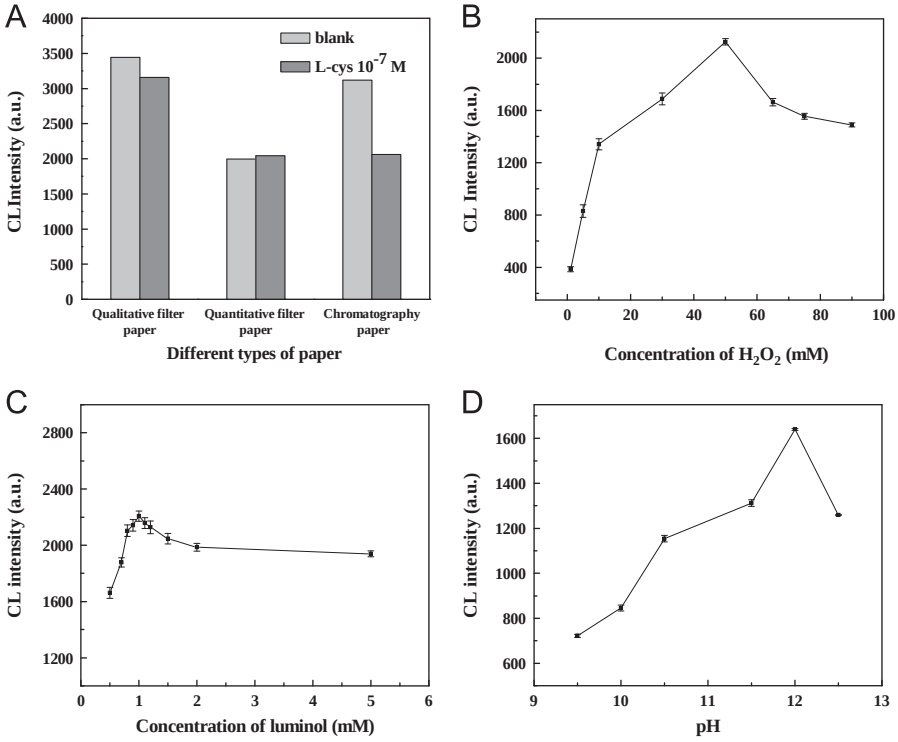

Fig. 5. Parameter optimization for chemiluminescence on LPAD. (A) Influence of the different types of paper on the LPAD. (B) Influence of the H_2O_2 concentration on the LPAD (1.0 mM luminol, pH: 12.0). (C) Influence of luminol concentration on the LPAD (50.0 mM H_2O_2, pH: 12.0). (D) Influence of the pH value on the LPAD (1.0 mM luminol, 50 mM H_2O_2).

CL intensity began to decline after pH of 12.0. So pH of 12.0 was chosen as the best condition for this work.

3.4. Analytical performance of this LPAD for L-cys measurement

Under the above optimum conditions, the analytical parameters of the present method for L-cys detection were investigated. As shown in Fig. 6, the CL intensity decreased with the increasing L-cys concentration, revealed a linear relationship in the L-cys concentration range from 1.0×10^{-8} M to 1.0×10^{-6} M. In order to obtain a better linearity, we adopted a piecewise linear. The regression equation was $I=2176.9-2627.7\times10^{7}C$ (Fig. 6A) and $I=401.2-37.1\times10^{7}C$ (Fig. 6B) respectively for the range of 1.0×10^{-8}–7.0×10^{-8} M and the range of 1.0×10^{-7}–1.0×10^{-6} M. The detection limit (taken to be 3 times the standard deviation in the blank solution) was 8.2×10^{-10} M, which is comparable with most previous assay techniques (shown in Table 1). The results indicate that the relative CL intensity (I) is proportional to the L-cys concentration.

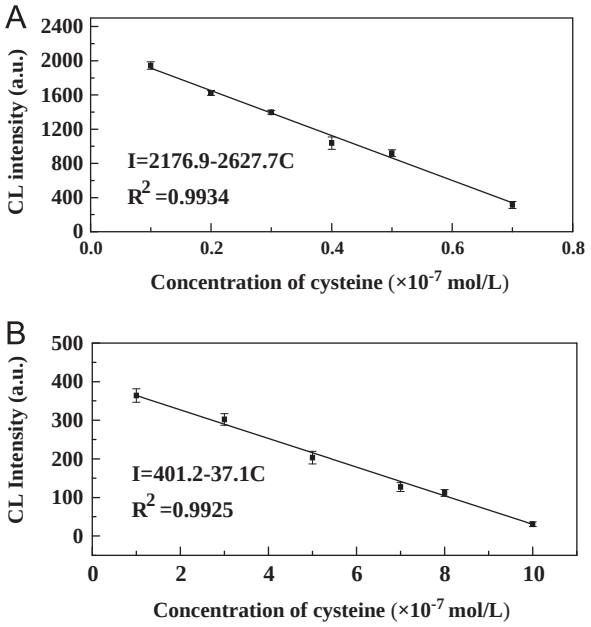

Fig. 6. Representative recorder outputs of the LPAD system in the presence of different concentration of L-cys under the optimized experiment conditions. (A) Linear relationship between the CL intensity (I) and L-cys concentration (C) from 1.0×10^{-8} M to 7.0×10^{-8} M. (B) Linear relationship between the CL intensity (I) and L-cys concentration (C) from 1.0×10^{-7} M to 1.0×10^{-6} M. Error bars represent the standard deviations of three independent measurements.

3.5. Effect of interferences

In order to assess the possible analytical application of the proposed method to the analysis of L-cys in injection sample solution, the effect of some common metal ions and some other amino acids on the detection of L-cys was investigated. They were carried out by mixing each 1.0×10^{-7} M L-cys standard solution with different concentration of interference ion or amino acid. The maximum tolerable concentration for every interference substance is shown in Table 2. A substance was considered not to interfere if it caused a relative error of less than 5% for 1.0×10^{-7} M L-cys. It can be seen that all interferences had no serious effect on the determination of L-cys even though they are present at a 500–1000 times concentration ratio to L-cys.

3.6. Determination of L-cys in injection sample

The proposed method was applied to the determination of L-cys in injection sample. Suitable aliquots from this solution were taken for the determination of L-cys. To examine the reliability of the method, certain amounts of standard L-cys solution were added to the sample solutions. The data in Table 3 showed the recoveries obtained before and after adding of standard L-cys solutions in the sample solutions. There was no significant difference between the label content and the result obtained by

Table 2
Maximum tolerable concentration for the determination of 1.0×10^{-7} M L-cys

Interferences	Tolerance (1.0×10^{-7} M)
SO_4^{2-}	1000
PO_3^{3-}	1000
Mn^{2+}	500
Ca^{2+}	500
Mg^{2+}	500
BSA	1000
L-leucine	1000
L-isoleucine	1000
L-threonine	1000
L-valine	1000
L-aspartic	1000

Table 3
Determination of L-cys in pharmaceutical sample by the proposed method ($n=3$).

Sample	Sample taken (mol L^{-1})	Added (mol L^{-1})	Found (mol L^{-1})	Recovery (%)	RSD (%, $n=3$)
1	0.0	2.0×10^{-8}	2.1×10^{-8}	106	1.94
2	2.0×10^{-8}	5.0×10^{-8}	7.2×10^{-8}	104	1.95
3	2.0×10^{-8}	6.0×10^{-8}	7.5×10^{-8}	92	4.00

Table 1
Different technique for determination of L-cys.

Methods used	Concentration linear range	Detection limit (nM)	System	Ref.
Chemiluminescence	5.0 nM to 1.0 μM	2.5	Ce(IV) ion and sulfite ion	[43]
	2.0 nM to 2.0 μM	0.64	luminol	[35]
	50 nM to 2.0 μM	0.5	luminol	[44]
	1.0 nM to 7.0 μM	0.29	luminol	[45]
Colorimetry	100 nM to 10 μM	100	–	[39]
	10 nM to 100 μM	10	–	[40]
Fluorescence detection	25 nM to 6.0 μM	20	Silver clusters	[41]
	60 to 500 nM	44	FAM	[42]
Our work	10 nM to 1.0 μM	0.82	luminol	

the analysis of the sample. Relative standard deviation was found to be 1.94%, 1.95% and 4.00%. The results showed that the proposed method was suitable for analysis of L-cys in injection.

4. Conclusions

A laminated paper-based analytical device (LPAD) with gold nanoparticle catalyzed luminol CL system for the determination of L-cys was established in this paper. To our knowledge, this is the first report to use the AuNPs on paper-based CL device for L-cysteine detection. Using a craft-cutter and lamination method, the device fabrication process is simple and the cost of manufacturing a large quantity of devices is low. This kind of paper-based device has the advantage of simplicity, durability and flexibility. With the principle that L-cys can greatly inhibit CL signal of AuNPs–luminol–H_2O_2 system, the L-cys can be detected with higher sensitivity on paper-based device with the detection limit of 8.2×10^{-10} M. The LPAD platform is especially useful for point of care, environmental testing, and medical diagnostics in remote regions and developed countries.

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