



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Hydrogen bonding recognition and colorimetric detection of isoprenaline using 2-amino-5-mercapto-1,3,4-thiadiazol functionalized gold nanoparticles

Somayeh Khezri, Morteza Bahram*, Naser Samadi

Department of analytical Chemistry, Faculty of chemistry, Urmia University, Iran

ARTICLE INFO

Article history:

Received 8 March 2017

Received in revised form 29 May 2017

Accepted 30 June 2017

Available online 5 July 2017

Keywords:

2-Amino-5-mercapto-1,3,4-thiadiazol

Hydrogen bonding interaction

Colorimetric detection

Isoprenaline

Gold nanoparticles

ABSTRACT

In this paper, we describe a rapid, low-cost and highly sensitive colorimetric method for the detection of isoprenaline, based on 2-amino-5-mercapto-1,3,4-thiadiazol (AMTD) functionalized gold nanoparticles (AMTD-AuNPs) as a sensing element. Hydrogen bonding interaction between isoprenaline and AMTD resulted in the aggregation of AuNPs and a consequent color change of AuNPs from red to blue. The concentration of isoprenaline could be detected with the naked eye or a UV-visible spectrometer. Results showed that the absorbance ratio (A_{650}/A_{524}) was linear with isoprenaline concentrations in the range of 0.2 to 2.6 μM ($R = 0.997$). The detection limit of this method was 0.08 μM . The proposed method is simple, without using complicated instruments and adding salts for enhancing sensitivity. This probe could be successfully applied to the determination of isoprenaline in human serum samples and urine samples after deproteinization.

© 2017 Published by Elsevier B.V.

1. Introduction

Isoprenaline or isoproterenol (4-[1-hydroxy-2-[(1-methylethyl)-amino]ethyl]-1,2-benzenediol) is a catecholamine drug which has been used for the therapy of allergic emergencies, bronchial asthma, status asthmatic, glaucoma, heart block, cardiac arrest, and ventricular bradycardia [1]. The cardiovascular effects of isoprenaline are compared with epinephrine and norepinephrine, which can relax nearly every type of smooth musculature that contains adrenergic nervous system, but this effect is pronounced in the musculature of bronchus and also in the gastrointestinal tract. The isoprenaline is better absorbed when dispensed by inhalation [2,3]. A variety of methods have been reported for the quantitative determination of isoprenaline, such as chemiluminescence [4–6], electrochemical procedures [7–9], spectrofluorimetry [10,11] and chromatography [12,13]. However, most of these methods are expensive, require time-consuming and complex instruments. Therefore, it is important to develop a simple, inexpensive, sensitive and rapid method for the determination of isoprenaline. Colorimetric methods can be considered as simple, rapid and convenient approaches due to their ability to detect the analyte with the naked eye rather than using sophisticated equipment. Gold nanoparticles (AuNPs) are commonly used as the colorimetric probes, due to their high extinction coefficient and distance-dependent optical properties [14–16]. The well-dispersed AuNPs solution shows red color, while the color will change

from red to blue or purple once AuNPs aggregate [17]. The reason for color change is possibly due to the inter-particle surface plasmon coupling caused by the aggregation of AuNPs [18]. This optical phenomenon has been applied to determine many substances such as protein [19], DNA [20], metal ions [21,22], drugs [23,24] and small molecules [25,26]. To the best of our knowledge, there has been no report on the colorimetric assay of isoprenaline using AuNPs. Herein, in this paper, a simple, rapid and sensitive colorimetric sensor was developed for isoprenaline detection based on 2-amino-5-mercapto-1,3,4-thiadiazol (AMTD) functionalized AuNPs. AMTD is used as a recognition element and the AuNPs are used as indicators. The AMTD-coated AuNPs are stable in aqueous solution and protect the AuNPs from aggregation, due to the electrostatic repulsion of the positive capping agent against van der Waals attraction between AuNPs. However, in the presence of isoprenaline, the strong hydrogen bonding between AMTD and isoprenaline results in the aggregation of AuNPs. The aggregated AMTD-AuNPs caused color change that can be used for the determination of isoprenaline in human and serum samples.

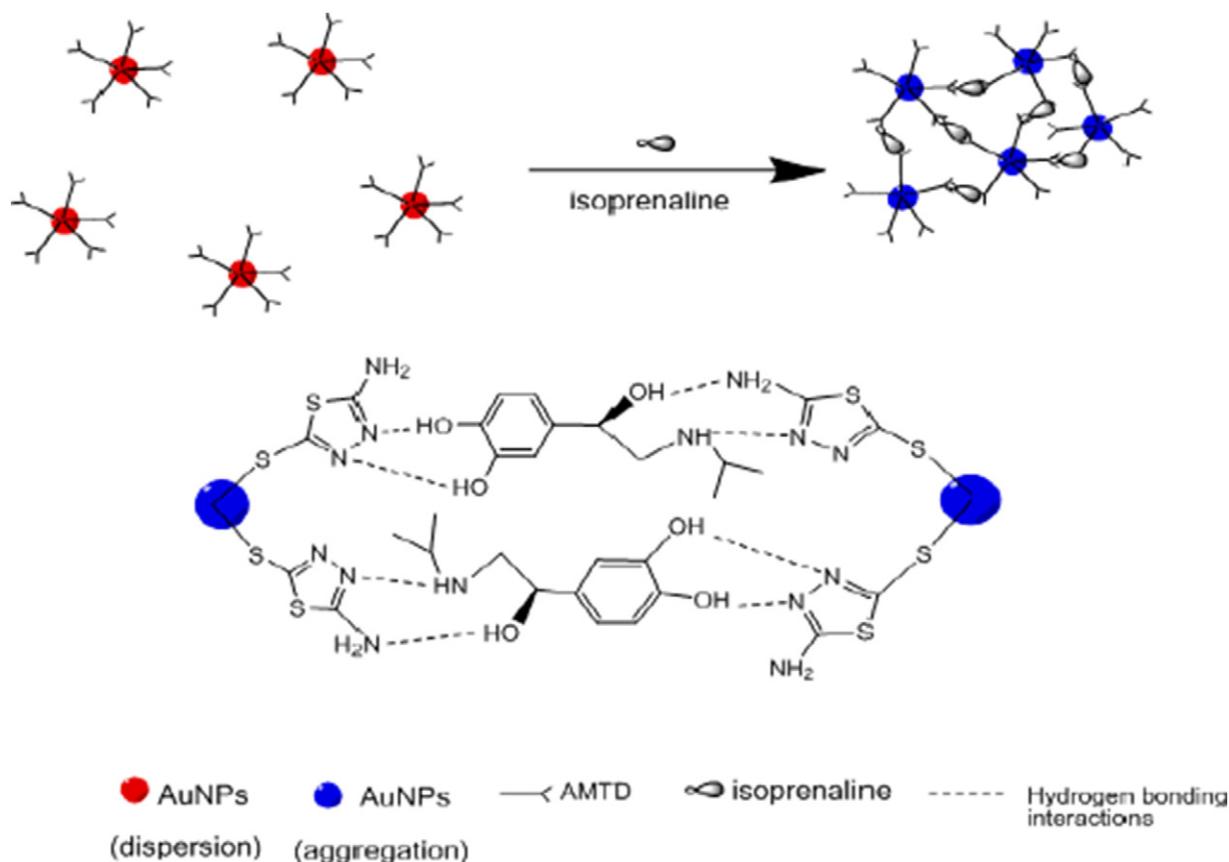
2. Experimental

2.1. Reagents and Apparatus

All chemicals used in the experiments were of analytical grade and were used without further purification. Tetrachloroauric (III) trihydrate, trisodium citrate dehydrate and isoprenaline were obtained from Merck (Darmstadt, Germany). 2-Amino-5-mercapto-1,3,4-thiadiazol (AMTD)

* Corresponding author.

E-mail address: m.bahram@urmia.ac.ir (M. Bahram).



Scheme 1. Schematic illustration of the aggregation mechanism for AMTD-AuNPs in the presence of isoprenaline.

was purchased from Sigma-Aldrich. All solutions were prepared using deionized water.

Ultraviolet-visible (UV–vis) absorption spectra were recorded on an Agilent 8453 UV–visible Spectrophotometer. Transmission electron microscopy (TEM) images were recorded by a Philips (CM 100 BioTwin, The Netherlands) microscope operated at 75 kV. The IR spectra were recorded on Thermo-Nicolet Nexus FTIR using KBR pellets.

2.2. Preparation of AHMT-functionalized AuNPs

The AuNPs were prepared by citrate-mediated reduction of HAuCl_4 according to literature [27]. Briefly, 300 mL of 0.3 mM HAuCl_4 aqueous

solution was heated to vigorous boiling, and then 15 mL of 1% sodium citrate was quickly added into the solution under stirring. The solution changed from pale yellow to deep red within 10 min, and then cooled to room temperature under continuous stirring. The final product was stored at 4 °C. The concentrations of the AuNPs were measured by UV–vis absorption spectroscopy using the molar extinction coefficients at the maximum absorption band of the colloidal gold solution [28].

The AMTD-functionalized AuNPs were prepared by putting 0.1 mM AMTD into the colloidal AuNPs solution (10 nM, 300 mL). The mixture was reacted in dark for 2 h under stirring at room temperature to ensure self-assembly of AMTD onto the surface of the AuNPs. After the ligand exchange reaction, the AMTD-AuNPs were purified by centrifugation

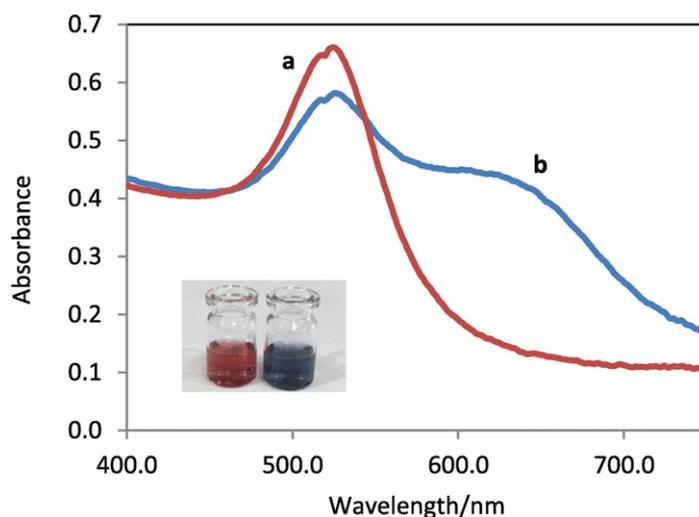


Fig. 1. UV–vis spectra and photo images of AMTD-AuNPs without isoprenaline (a) and with 1.5 μM isoprenaline (b).

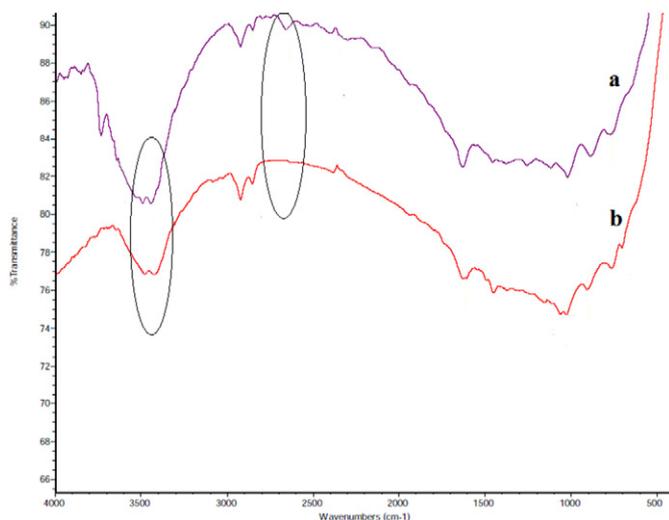


Fig. 2. IR spectra of (a) AMTD (b) AMTD-AuNPs.

and the deposition was washed several times by deionized water to remove free AMTD molecules in solution. The AMTD-AuNPs colloid was diluted to original volume with 10 mM HEPES buffer.

2.3. Preparation of Real Samples

Human serum samples and urine samples were collected from healthy adult volunteers. Acetonitrile removes proteins more effectively. After addition of acetonitrile to urine sample and mixing, the mixture was then centrifuged for 15 min at 1000g to separate urine protein residues and the supernatant was taken carefully. The supernatant was diluted (dilution ratio 1:100) and used for further analysis under optimum conditions. For determination of isoprenaline in human serum, certain amounts of isoprenaline were independently spiked into the fresh human serum. In order to deproteinization, serum samples were mixed with acetonitrile followed by centrifugation at 1000g for 15 min. The resulted clear supernatant was diluted (dilution ratio 1:100) and analyzed according to the proposed method under optimum conditions.

2.4. General Procedure of Colorimetric Detection of Isoprenaline

For isoprenaline detection, different concentrations of isoprenaline were added into 2 mL AMTD-AuNPs solution. The mixture was then incubated at room temperature for 20 min. UV/vis absorption spectra of the mixture were recorded immediately. The calibration curve for this assay was made by measuring the ratio of the absorbance value at

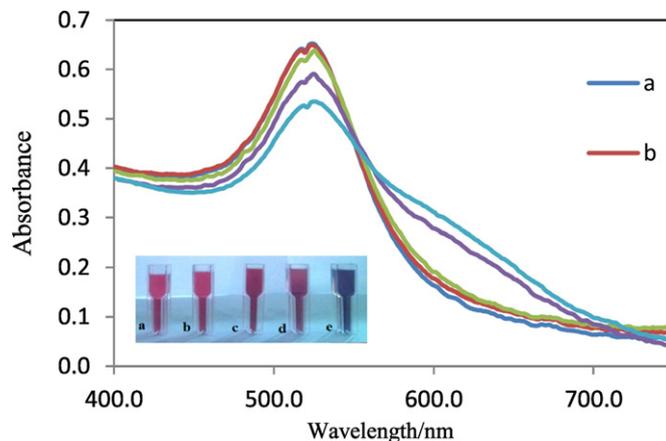


Fig. 4. UV-vis spectra and colorimetric visualization of AuNPs solution modified with different concentrations of AMTD (a: 0, b: 0.05 mM, c: 0.1 mM, d: 0.16 mM, e: 0.2 mM).

650 nm and at 524 nm (A_{650}/A_{524}) versus the different concentrations of isoprenaline.

3. Results and Discussion

3.1. Principle of Isoprenaline Detection Using the AMTD-AuNPs

The surface attachment of mercapto group and electron-rich nitrogen-containing ligands on AuNPs has been well developed [29,30]. On one hand, AMTD contains one mercapto group, which can strongly coordinate to the surface of AuNPs. In addition, AMTD has one exocyclic amino group and a two nitrogen hybrid ring in its molecule, which means good hydrogen-bonding ability. On the other hand, isoprenaline has one amine group and three hydroxyl groups which may combine with the AMTD through hydrogen-bonding interaction. It can form $\text{NH}\cdots\text{N}$ and $\text{OH}\cdots\text{N}$ hydrogen bonds. Scheme 1 shows the concept for this proposed method based on aggregation of AuNPs. Initially, the AMTD capped AuNPs were well dispersed in the colloidal solution due to the electrostatic repulsion of AMTD molecules as capping agent against van der Waals attraction between AuNPs, and the color of the uniform colloid was wine red. Upon exposure of the AMTD-AuNPs to isoprenaline, hydrogen-bonding recognition between isoprenaline and AMTD resulted in the aggregation of gold nanoparticles, and the wine red color of the gold colloid was accordingly changed to a blue color. Thus, the adjacent AMTD-AuNPs can be cross-linked together by hydrogen bonds between isoprenaline and AMTD molecules, leading to the aggregation of the AMTD-AuNPs. We performed two control experiments with catechol and *p*-Aminophenol to further elucidate the principle of isoprenaline detection. The addition of 2 μM catechol into AMTD-

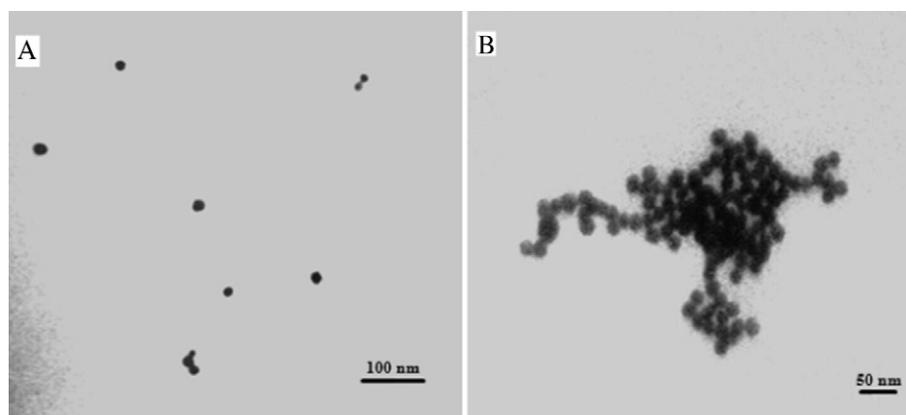


Fig. 3. TEM images of (A) AMTD-AuNPs (B) after addition of isoprenaline to AMTD-AuNPs solution.

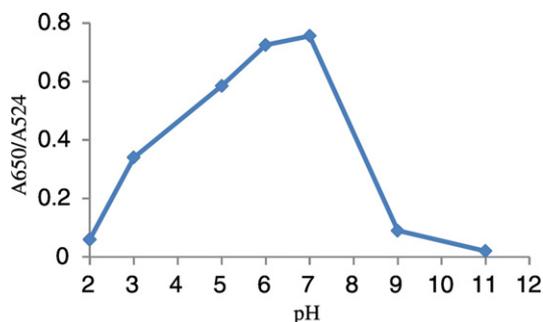


Fig. 5. The effect of pH on the absorbance ratio (A_{650}/A_{524}) of AMTD-AuNPs.

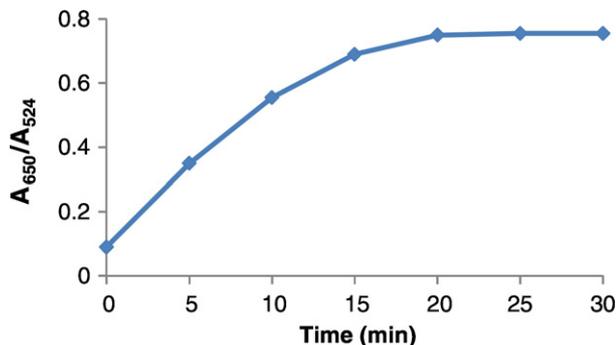


Fig. 6. The effect of the incubation time on the absorbance ratio (A_{650}/A_{524}) of AMTD-AuNPs in the presence of $1.7 \mu\text{M}$ isoprenaline.

AuNPs solution did not induce any changes in color of AMTD-AuNPs solution or the absorbance ratio (A_{650}/A_{524}). It is due to that each catechol molecule contains two hydroxyl groups in ortho position. Thus, this molecule has only two sites to form hydrogen bonds on one side of phenyl ring and cannot induce the inter-particle crosslinking of AMTD-AuNPs. The addition of $2 \mu\text{M}$ *p*-Aminophenol into AMTD-AuNPs induced the color changes in the colloidal solution of AuNPs, but lower sensitivity was obtained for *p*-Aminophenol in comparison with isoprenaline. The absorbance ratio (A_{650}/A_{524}) of *p*-Aminophenol is less than half of the one produced by isoprenaline. This is due to the fact that each *p*-Aminophenol molecule has one amino group in para position of the phenyl ring and one hydroxyl group on the other side of the phenyl ring of *p*-Aminophenol. Thus this molecule has only two sites to form hydrogen bonds, while isoprenaline molecule has four sites for hydrogen bonding interactions. These sites include two hydroxyl groups in ortho position at the phenyl ring of isoprenalina at one side and one amino group and one hydroxyl group in other side of phenyl ring, as shown in Scheme 1. The results of the absorbance ratio (A_{650}/A_{524}) of

the AMTD-AuNPs in the presence of $2 \mu\text{M}$ *p*-Aminophenol and $2 \mu\text{M}$ catechol are shown in Fig. 8.

3.2. Characterization

Fig. 1 shows the surface plasmon resonance and photo images of AMTD-AuNPs without (a) and with (b) isoprenaline. In the absence of isoprenaline, AMTD-AuNPs were wine red and displayed an intense surface Plasmon resonance absorption at about 524 nm . While in the presence of isoprenaline, the absorbance of AuNPs at 524 nm decreased and a new peak appeared at about 650 nm and the color of AuNPs changed from wine red (a) to blue (b), indicating considerable aggregation of the modified nanoparticles in the presence of the analyte.

To elucidate the modification of AMTD-AuNPs, FT-IR measurements were carried out. As shown in Fig. 2a, the characteristic skeleton peaks of AMTD were 3436 cm^{-1} (N—H), 3480 cm^{-1} (N—H), 2646 cm^{-1} (S—H). In Fig. 2b, the peak that was originally at 2646 cm^{-1} (S—H) disappeared, indicating that SH group coordinate with the gold atoms on the surface of AuNPs, conforming the successful modification of AMTD onto the surface of AuNPs via the SH group.

In order to provide a direct evidence for isoprenaline induced aggregation of AMTD-AuNPs, the morphology of the nanoparticles was evaluated by TEM technique. Fig. 3 shows the TEM images of AMTD-AuNPs in the absence and presence of $1.5 \mu\text{M}$ isoprenaline. In the absence of isoprenaline, AuNPs were well dispersed in solution (Fig. 3A). On the other hand, apparent aggregation occurs when isoprenaline was added into the AMTD-AuNPs solution (Fig. 3B).

3.3. Optimization of Experimental Conditions

Based on the proposed method, a series of experiments was conducted to establish the optimum analytical conditions for the detection of isoprenaline.

3.3.1. The Concentration of AMTD

To achieve better assay results, the absorption spectra of AMTD-AuNPs at different AMTD concentration were investigated (Fig. 4). AuNPs should be modified by an appropriate concentration of AMTD to a critical state, at with the presence of AMTD was more than enough and could not induce AuNPs to aggregate. As shown in Fig. 4, when the concentration of AMTD increased over 0.1 mM , the color of the solution changed from wine red to light purple and a significant change in the UV–vis spectrum of AuNPs was observed. But it was different with the isoprenaline-AMTD-AuNPs system, which showed another peak at 650 nm . It is because that the mercapto group of AMTD can bind with the AuNPs on the surface. Furthermore, the exocyclic amino group and two nitrogen hybrid ring of AMTD lead to the combination of AMTD and AuNPs either, so the color changed from red-to-purple and self-assembly of the AMTD-AuNPs was observed and the AMTD-AuNPs also became unstable. But the N—Au bond is not so stronger than the

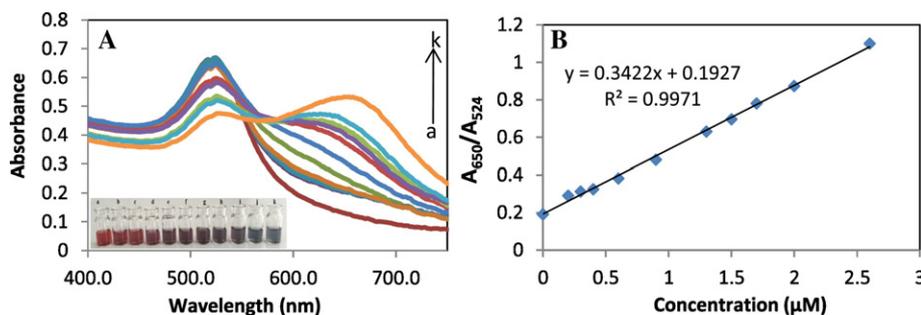


Fig. 7. (A) The UV–vis absorbance spectra of the AMTD-AuNPs with various concentrations of isoprenaline. Inset: the photographic images of AMTD-AuNPs with various concentrations of isoprenaline. (B) Plot of the absorbance ratio (A_{650}/A_{524}) vs. isoprenaline concentrations. The concentration of isoprenaline (curves a–k): $0, 0.2, 0.3, 0.4, 0.6, 0.9, 1.3, 1.5, 1.7, 2$ and $2.6 \mu\text{M}$, respectively.

Table 1
Comparison between the proposed colorimetric method and other techniques for isoprenaline detection.

Method	Linear range	Detection limit	References
Flow injection spectrophotometric method by using a solid-phase reactor containing MnO ₂	1.0×10^{-5} – 2.0×10^{-4} M	1.7 μ M	[33]
Voltammetric determination using a copper(II) hexacyanoferrate(III) modified carbon paste electrode	1.96×10^{-4} – 1.07×10^{-3} M	8.0×10^{-5} M	[34]
Electrocatalytic determination using multiwalled carbon nanotubes/ferrocen nanocomposite paste electrode	5.0–50.0 μ M	0.1 μ M	[35]
Voltammetric and electrochemical impedance spectroscopic techniques using a multiwall carbon nanotubes paste electrode modified with ferrocenemonocarboxylic acid as a mediator	0.5–50.0 μ M	0.2 μ M	[36]
Colorimetric method using AMTD-AuNPs	0.2–2.6 μ M	0.08 μ M	This work

S–Au, which was not enough for the aggregation to form another peak at 650 nm. Based on these results, 0.1 mM AMTD was chosen for the following experiments.

3.3.2. The Effect of pH

The pH value is a crucial factor of sensitivity in our method. Therefore, the pH condition for colorimetric detection of isoprenaline was optimized over the range from 2.0 to 11.0. Obviously, the highest absorbance ratio (A_{650}/A_{524}) is obtained at pH 7.0. However, the absorbance ratio (A_{650}/A_{524}) is quite low in strong acidic solution (pH < 3), where isoprenaline and AMTD are protonized that is undesirable for the hydrogen-bonding interactions. When the pH is 5.0, the AMTD-AuNPs is stable within several weeks, because the strong electrostatic repulsion between the particles prevents them aggregated together. However, with the decrease of pH below 5.0, the AuNPs is tending to aggregate together, owing to the formation of AMTD intermolecular hydrogen band in acidic solution. So, AMTD-AuNPs is unstable in pH < 5.0 and the instability increases in strong acidic solution (pH < 3). Furthermore, the AMTD-AuNPs are unstable in strong basic media, and easily aggregated even without isoprenaline. Also, pK_a isoprenaline is 8.6 and absorbance ratio (A_{650}/A_{524}) is low in strong basic media due to deprotonation of isoprenaline that is undesirable for the hydrogen-bonding interactions [31,32]. Thus, pH 7.0 was selected for the subsequent experiments considering the preferable sensitivity (Fig. 5).

3.3.3. The Effect of the Incubation Time

The effect of the incubation time on the absorption spectra of AMTD-AuNPs in the presence of 1.7 μ M isoprenaline was investigated and the results showed that maximum signal at A_{650}/A_{524} was observed after 20 min and the signals were stable afterward (Fig. 6).

3.4. Colorimetric Detection of Isoprenaline Using the AMTD-AuNPs

Under the optimum conditions, the absorption spectra and the color changes of the AMTD-AuNPs with increasing amounts of isoprenaline were recorded (Fig. 7). Fig. 7A reveals that with the increase of isoprenaline concentration, a clear color change from wine red to purple and blue could be easily differentiated by the naked eye. It can be seen that the increase in intensity of the 650 nm peak, is accompanied by a corresponding decrease in the 520 nm SPR peak with increasing concentration of isoprenaline, which is ascribed to the aggregation of AMTD-AuNPs. The absorbance ratio (A_{650}/A_{524}) shows linear response towards isoprenaline in the range from 0.2 to 2.6 μ M ($R = 0.997$, Fig. 7B). The detection limit is 0.08 μ M when the ratio of signal to noise is 3 ($S/N = 3$) and the relative standard deviation is 1.4% for the determination of 1.5 μ M isoprenaline ($n = 9$). The analytical performance of the present method has been listed and compared with several other methods for the detection of isoprenaline in the literature (Table 1). From Table 1, it can be seen that the detection limit of our proposed method (0.08 μ M) is lower than those of other methods and the linear range of our work is relatively wider.

3.5. Selectivity Study

As signal responses are based on the specific target binding-induced aggregation of AuNPs, the colorimetric probe should be comparatively insensitive to nonspecific binding. To examine the specificity of the proposed colorimetric probe for detection of isoprenaline, the interferences of some compounds and common ions in biological samples were investigated under the optimum conditions. As shown in Fig. 8, we could see that the responses to the interferences, except human serum albumin (HSA) and bovine serum albumin (BSA), are almost equal to the

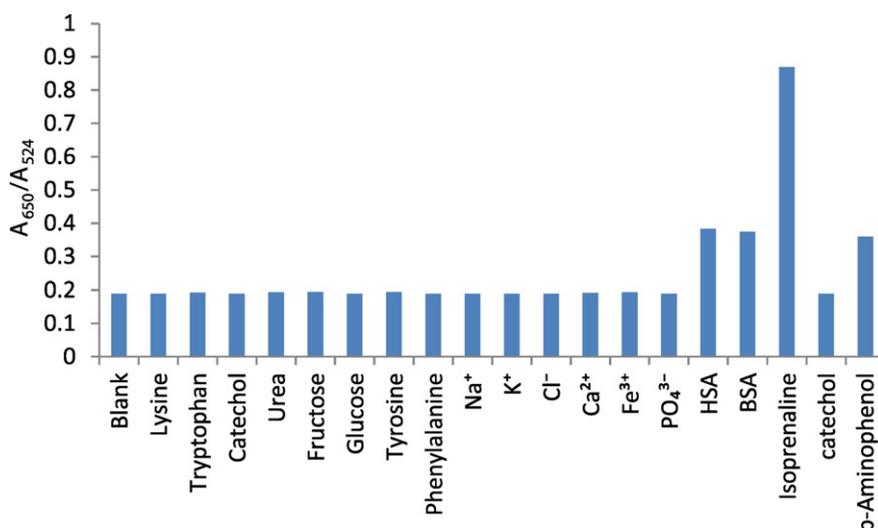


Fig. 8. The absorbance ratio (A_{650}/A_{524}) of the AMTD-AuNPs in the presence of 2 μ M isoprenaline, or other interferences (the concentrations of ions were 200 μ M, the concentrations of HSA and BSA were 5 μ M and the concentrations of all other interferences were 20 μ M). The concentration of catechol and *p*-Aminophenol were 2 μ M.

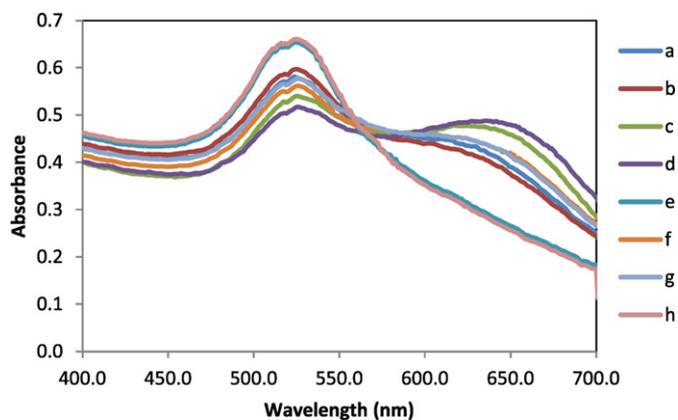


Fig. 9. The UV-vis absorbance spectra of the AMTD-AuNPs in spiked serum and urine samples for determination of isoprenaline. (a: serum (2); the added amount of isoprenaline: 1.3 μM , b: urine (2); the added amount of isoprenaline: 1.3 μM , c: serum (2); the added amount of isoprenaline: 2 μM , d: urine (2); the added amount of isoprenaline: 2 μM , e: serum (1); the added amount of isoprenaline: 0.6 μM , f: serum (1); the added amount of isoprenaline: 1.5 μM , g: urine (1); the added amount of isoprenaline: 1.5 μM , h: urine (1); the added amount of isoprenaline: 0.6 μM).

blank. However, in the presence of 5 μM HSA and 5 μM BSA a change in A_{650}/A_{524} was observed. Note that the concentration of HSA and BSA used in these studies does not reflect the actual concentration in the real samples. The actual concentration of serum albumin in the real sample is in the range of 3–5 g dL^{-1} . The interferences of HSA and BSA can be easily eliminated either by dilution of serum samples with PBS/saline or by filtration and precipitation procedures [37]. These results indicate that our proposed colorimetric sensor was appropriate for the high selective recognition of isoprenaline. As mentioned in Section 3.1 the control experiments with catechol and *p*-Aminophenol were performed to further elucidate the principle of isoprenaline detection.

3.6. Colorimetric Detection of Isoprenaline in Biological Fluids

To evaluate the efficiency of the proposed method in a real sample, it was successfully applied to detection of isoprenaline in human urine and serum samples. The real samples were pretreated and deproteinized according to the procedure described in the Experimental section. UV-vis spectra of the solutions were measured after the incubation of 20 min (Fig. 9). The analytical results of several spiked samples are summarized in Table 2. As can be seen, recoveries are in the range from 95.5 to 108.7%, which confirm the successive applicability of the proposed method in real samples.

4. Conclusion

In this work, a simple, rapid, sensitive and cost effective colorimetric assay using AMTD modified AuNPs was proposed for detection of isoprenaline. The hydrogen bonding interactions between AMTD and isoprenaline rapidly induce the aggregation of AMTD-AuNPs and leading to a color change from red to blue. No complicated instrumentation was required and no special additives or organic solvents are involved in this method. The as-prepared optical assay has great potential for the detection of isoprenaline in biological fluids.

Table 2

Analytical results for determination of isoprenaline in serum and urine samples.

Sample	Added (μM)	Found (μM)	Recovery (%)
Serum(1)	0	<LOD	–
	0.6	0.626	104.3
	1.5	1.631	108.7
Serum(2)	0	<LOD	–
	1.3	1.401	107.8
	2	1.927	96.4
Urine(1)	0	<LOD	–
	0.6	0.573	95.5
	1.5	1.536	102.4
Urine(2)	0	<LOD	–
	1.3	1.276	98.15
	2	2.16	108

References

- [1] L.S. Goodman, A. Gilman, *The Pharmacological Basis of Therapeutics*, 9th ed. McGraw-Hill, New York, 1996 105–109.
- [2] K.O. Lupetti, I.C. Vieira, O. Fatibello-Filho, *Talanta* 57 (2002) 135–143.
- [3] D. Voet, J.G. Voet, *Biochemistry*, Wiley, New York, 1995.
- [4] G.J. Zhou, G.F. Zhang, H.Y. Chem, *Anal. Chim. Acta* 463 (2002) 257–263.
- [5] A.A. Al-Warthan, S.A. Al-Tamrah, A. Al-Akel, *Anal. Sci.* 10 (1994) 449–452.
- [6] C. Zhang, J. Huang, Z. Zhang, M. Aizawa, *Anal. Chim. Acta* 374 (1998) 105–110.
- [7] A. Kutluay, M. Aslanoglu, *Acta Chim. Slov.* 57 (2010) 157–162.
- [8] J.L. Elrod, J.L. Schmit, J.A. Morley, *J. Chromatogr. A* 723 (1997) 235–241.
- [9] A.A. Ensafi, E. Khoddami, H. Karimi-Maleh, *Int. J. Electrochem. Sci.* 6 (2011) 2596–2608.
- [10] P. Solich, C.K. Polydorou, M.A. Koupparis, C.E. Efstathiou, *J. Pharm. Biomed. Anal.* 22 (2000) 781–789.
- [11] J.J.B. Nevado, J.M.L. Gallego, P.B. Laguna, *Anal. Chim. Acta* 300 (1995) 293–297.
- [12] J.R. Watson, R.C. Lawrence, *J. Pharm. Sci.* 66 (1977) 560–564.
- [13] J.A. Clements, K. Hassan, G. Smith, *J. Chromatogr. A* 189 (1980) 272–275.
- [14] D. Liu, Z. Wang, X. Jiang, *Nano* 3 (2011) 1421–1433.
- [15] W. Chansuvarn, A. Imyim, *Microchim. Acta* 176 (2012) 57–64.
- [16] B. Liu, H. Tan, Y. Chen, *Microchim. Acta* 180 (2013) 331–339.
- [17] C.A. Mirkin, R.L. Letsinger, R.C. Mucic, J.J. Storhoff, *Nature* (1996) 607–609.
- [18] M.E. Stewart, C.R. Anderton, L.B. Thompson, J. Maria, S.K. Gray, J.A. Rogers, R.G. Nuzzo, *Chem. Rev.* 108 (2008) 494–521.
- [19] S. Vantasin, P. Pienpinijtham, K. Wongravee, C. Thammacharoen, S. Ekgasit, *Sensors Actuators B Chem.* 177 (2013) 131–137.
- [20] M. Cho, M.S. Han, C. Ban, *Chem. Commun.* 38 (2008) 4573–4575.
- [21] Z. Jiang, Y. Fan, M. Chen, A. Liang, X. Liao, G. Wen, X. Shen, X. He, H. Pan, H. Jiang, *Anal. Chem.* 81 (2009) 5439–5445.
- [22] J. Du, B. Zhu, X. Chen, *Small* 9 (2013) 4104–4111.
- [23] Y. Zheng, Y. Wang, X. Yang, *Sensors Actuators B* 156 (2011) 95–99.
- [24] M.R. Hormozi-Nezhad, S. Abbasi-Moayed, *Plasmonics* 10 (2015) 971–978.
- [25] W. Li, L.Y. Feng, J.S. Ren, L. Wu, X. Qu, *Chem. Eur. J.* 18 (2012) 12637–12642.
- [26] J. Sun, L. Guo, Y. Bao, J. Xie, *Biosens. Bioelectron.* 28 (2011) 152–157.
- [27] G. Frens, *Nat. Phys. Sci.* 241 (1973) 20–22.
- [28] W. Haiss, N.T.K. Thanh, J. Aveyard, D.G. Fering, *Anal. Chem.* 79 (2007) 4215–4221.
- [29] Y. Guo, Z. Wang, W. Qu, H. Shao, X. Jiang, *Biosens. Bioelectron.* 26 (2011) 4064–4069.
- [30] C. Pezzato, S. Maiti, J.L. Chen, A. Cazzolaro, C. Gobbo, L.J. Prins, *Chem. Commun. (Camb.)* 51 (2015) 9922–9931.
- [31] A.J. Wang, H. Guo, M. Zhang, D.L. Zhou, R.Z. Wang, J.J. Feng, *Microchim. Acta* 180 (2013) 1051–1057.
- [32] A. Mahal, L. Tandon, P. Khullar, G.K. Ahluwalia, M.S. Bakshi, *ACS Sustain. Chem. Eng.* 5 (2017) 119–132.
- [33] V.G. Bonifacio, L.H. Marcolino, O.F. Filho, *Anal. Lett.* 37 (2004) 2111–2124.
- [34] V.G. Bonifacio, L.H. Marcolino, F.S.M. Teixeira, O.F. Filho, *Microchem. J.* 78 (2004) 55–59.
- [35] S. Damiri, H. Shamlouei, *ACAJ* 10 (2011) 781–791.
- [36] A.A. Ensafi, H. Karimi-Maleh, *Int. J. Electrochem. Sci.* 5 (2010) 1484–1495.
- [37] N.I. Govorukhina, A. Keizer-Gunnink, A.G.J. van der Zee, S. de Jong, H.W.A. de Bruijn, R. Bischoff, *J. Chromatogr. A* 1009 (2003) 171–178.