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Single Molecular Functionalized Gold Nanoparticles for Hydrogen-Bonding Recognition and Colorimetric Detection of Dopamine with High Sensitivity and Selectivity

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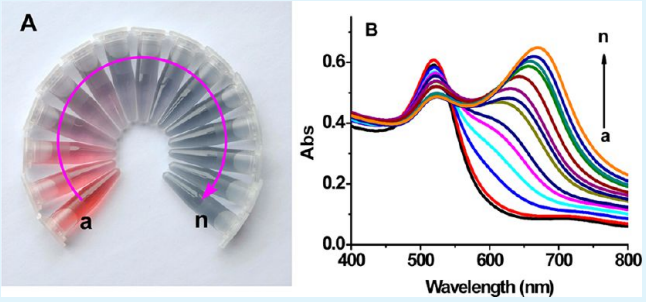
Supporting Information

ABSTRACT: In this work, we developed a low-cost, facile, sensitive, and selective colorimetric method for the quantitative determination of dopamine, based on 4-amino-3-hydrazino-5-mercapto-1,2,4-triazol (AHMT) functionalized gold nanoparticles (AHMP-AuNPs) as a model probe. Dopamine could induce the aggregation of the AHMT-AuNPs through hydrogen-bonding interactions, which caused the colloidal solution changed from red to blue. And the color change was in situ monitored for the quantitative determination of dopamine in human serum and urine samples. The developed approach is simple, without using complex financial instruments and adding other metal salts or ions for improving sensitivity.



KEYWORDS: *4-amino-3-hydrazino-5-mercapto-1,2,4-triazol, gold nanoparticles, dopamine, hydrogen-bonding interactions*

INTRODUCTION

Dopamine, a biogenic catecholamine, is an important neurotransmitter of the central and peripheral nervous systems.[1] Normal level of dopamine in brain allows usual freedom of movement, whereas excess dopamine in brain often cause pleasurable, rewarding feelings, and sometimes even euphoria.[2] The deficiency of dopamine in brain may cause Parkinson's disease and schizophrenia.[3] Up to now, many methods have been developed for the quantitative determination of dopamine,[4] such as electrochemistry,[5,6] chemiluminescence,[7] high-performance liquid chromatography,[8,9] capillary electrophoresis,[10] and spectroscopic approaches.[11,12] However, most of the above methods require expensive equipment and/or complicated procedures, as well as some organic solvent. Thus, it is still urgent to develop a fast, facile, low-cost, sensitive, and selective method for the detection of trace dopamine in biologic fluids.

Recently, gold nanoparticles (AuNPs) have attracted great interests as a colorimetric probe, which can directly detect analytes by monitoring the color change, using UV–vis spectroscopy, or even with naked eyes. Apparently, nearly no complicated instruments are involved in the detection procedures.[13,14] Furthermore, the color change is highly sensitive to the size, shape, capping agent, medium refractive index, and state of AuNPs.

Many successful examples have been reported in the detection of analytes regarding to diagnosis of diseases,[15] environmental contaminations,[16,17] and food safety.[18] Jiang et al. have reviewed recent advances of the AuNPs-based colorimetric assays for cations, anions, and small organic compounds.[19] Lately, Escarpa discussed the development of sensing colorimetric approaches based on gold and silver nanoparticles aggregation.[20]

Among them, quantitative determination of dopamine has received great success until now. Tian and his co-workers designed the AuNPs coated with 4-mercaptophenylboronic acid and dithiobis(succinimidylpropionate) succinimidyl-propionate) for doubly molecular recognition and quantitative determination of dopamine.[21] Zhang et al. designed a method based on the aggregation of AuNPs induced by Cu^{2+} ion.[22] Yang and his co-workers developed a method using dopamine-binding DNA aptamer as a recognition element and citrate coated AuNPs as a probe.[23] Although these AuNP-based probes displayed good selectivity and sensitivity, they are somewhat complicated such as using double molecular modified AuNPs or adding other metal salts or ions.

Herein, we develop a rapid, simple, sensitive, and selective approach for the colorimetric detection of dopamine using 4-amino-3-hydrazino-5-mercapto-1,2,4- triazol (AHMT) functionalized AuNPs (AHMT-AuNPs) as a probe. Dopamine is

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used as a "molecular bridge" between the AHMT-AuNPs, leading to the aggregation of AHMT-AuNPs through hydrogen-bonding interactions. The aggregated AHMT-AuNPs caused color change that can be used for the quantitative determination of dopamine in human serum and urine samples.

EXPERIMENTAL DETAILS

Reagents. Dopamine, $HAuCl_4$, 4-amino-3-hydrazino-5-mercapto-1, 2, 4-triazol (AHMT), sodium citrate, histidine, tyrosine, tryptophan, phenylalanine, lysine, catechol, glutamic acid, acrobatic acid, glucose, fructose, glutathione, 2,3,4-trihydroxybenzoic acid, gallic acid, ferulic acid, uric acid, urea, histamine, serotonin, catechol, epinephrine, isoprenaline, and norepinephrine were purchased from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). All the other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with twice-distilled water.

Apparatus. UV−vis spectra were recorded on a TU-1901 UV−vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., Beijing, China). Transmission electron microscopy (TEM) measurements were carried out on a JEOL-2100F transmission electron microscope operated at an accelerating voltage of 200 kV. Dynamic light scattering (DLS) spectroscopy was monitored using a Malvern Zetasizer Nano instrument (Zetasizer Nano S90). The photographs were taken with Nikon D90 digital camera. The pH measurements were performed on a model PHS-3E digital ion analyzer (Jiangshu Instruments, Jiangshu, China).

Preparation of Functional AuNPs with AHMT. Prior to use, all glassware was cleaned in a bath of freshly prepared 3:1 HNO_3−HCl (3:1, V/V), thoroughly rinsed with water, and dried in air.

The AuNPs were prepared by citrate-mediated reduction of $HAuCl_4$ according to literature.[24] 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 concentrations of the AuNPs were measured by UV−vis spectroscopy using the molar extinction coefficients at the maximum absorption band of gold colloid.[25]

The AuNPs coated with AHMT (denoted as AHMT-AuNPs) were obtained via ligand exchange reaction by putting 0.1 mM AHMT into the colloidal AuNPs solution (10 nM, 300 mL). The mixtrue was reacted in dark for 2 h under stirring at room temperature to ensure self-assembly of AHMT onto the surface of the AuNPs. After the ligand exchange reaction, no color change or aggregation was observed when more AHMT was existed. The AHMT-AuNPs were purified by centrifugation and the deposition was washed several times by water to remove free AHMT molecules in solution. The AHMT-AuNPs colloid was diluted to original volume with 10 mM HEPES buffer. The surface coverage ratio of the AHMT-AuNPs is about 91.5%, which is consistent with only 6-mercaptonicotinic acid-functionalized AuNPs.[26] It is ascribed to both the −SH and nitrogen atom in molecular AHMT can bind with the AuNPs. Thus-prepared AHMT-AuNPs have good stability, and no aggregation was observed within 3 months.

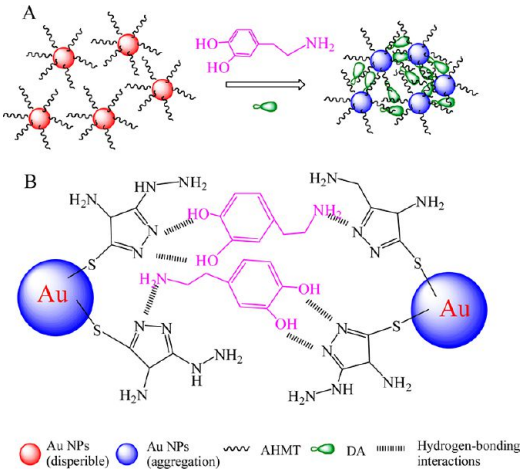
The AHMT-AuNPs were characterized by TEM and UV−vis microscopy, and DLS, respectively. The pH values of the colloidal solution was controlled using several different buffers (formic acid/formate buffer for pH 2.0 and 3.0, acetic acid/acetate buffer for pH 4.0 and 5.0, MES buffer for pH 6.0, HEPES buffer for 7.0, EPPS buffer for 8.0, AMPSO buffer for 9.0, AMPSO buffer for 10, and CAPS buffer for 11.0). The concentration of the buffers are 10 mM.

Colorimetric Detection of Dopamine in Biological Fluids. Human serum and urine samples were collected from healthy adult volunteers. All samples were subjected to a 100-fold dilution before analysis, and no other pretreatments were required. Specifically, certain amounts of dopamine standard solutions or samples (0.5 mL) were sequentially put into 8 mL 20 nM AHMT-AuNPs solution. The mixture was diluted to 10 mL with water. The reaction temperature was controlled at 35 °C. UV−vis spectra of the AHMT-AuNPs solution were rapidly measured after the incubation of 30 min. The concentrations of dopamine were obtained through the absorption ratio of A_{650}/A_{520}.

RESULTS AND DISCUSSION

Principle of dopamine detection using the AHMT-AuNPs. Scheme 1 shows the mechanism for the detection of dopamine. The as-prepared AHMT-AuNPs are stable in aqueous solution, due to the electrostatic repulsion of the positive capping agent against van der Waals attraction between AuNPs. Furthermore, the AHMT-AuNPs solution shows a particular color, because suitable visible light induces the collective oscillations of the surface electrons that is highly dependent on the interparticle distance.[27]

Scheme 1. Colorimetric Detection of Dopamine Using AHMT-AuNPs as a Probe



It is known that dopamine molecules contain one amine group and two hydroxyl groups. And each dopamine molecule has three equivalent sites to form hydrogen bonds of NH···O and NH···N. In our system, the adjacent AHMT-AuNPs can be cross-linked together by hydrogen bonds between dopamine and AHMT molecules (Scheme 1), leading to the aggregation of the AHMT-AuNPs. The mechanism is similar to the Lu's group work. In their work, 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione (MTT) modified AuNPs was used for visual detection of melamine, based on the hydrogen-bonding recognition-induced color change.[18]

Control experiments were conducted to further elucidate the principle of dopamine detection. Epinephrine, norepinephrine, and isoprenaline, as three other neurotransmitters with similar molecule structures to dopamine, can also induce the color change in the colloidal AuNPs solution to some extent (Figure 1), but lower sensitivity are obtained for epinephrine and isoprenaline, in comparison with that of dopamine. This is ascribed to dopamine with one primary amino group, while epinephrine containing one secondary amine group of $-NH-CH_3$ and isoprenaline including one $-NH-CH_2-(CH_3)_2$, respectively. In the case of norepinephrine with similar structures to dopamine (containing catechol and primary amine groups), the UV−vis spectra change of the AHMT-AuNPs is weaker, compared to that of dopamine, while other conditions are kept constant. Specifically, the absorption ratio (A_{650}/A_{520}) of norepinephrine is only half of the one produced by dopamine (Figure 1), owing to weaker hydrogen-bonding interactions of norepinephrine, since the dissociation constant

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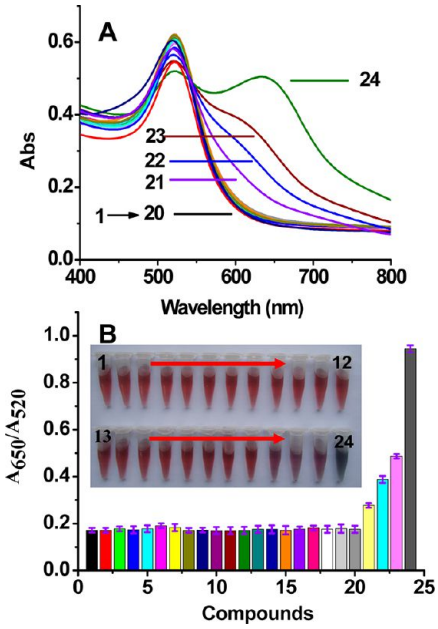

Figure 1. (A) UV−vis spectra of the AHMT-AuNPs solution with different analytes. Analysts (curve 1−24): AHMT-AuNPs solution-(blank, 1), histidine (2), tyrosine (3), tryptophan (4), phenylalanine (5), lysine (6), catechol (7), glutamic acid (8), acrobatic acid (9), glucose (10), fructose (11), glutathione (12), 2,3,4-trihydroxybenzoic acid (13), gallic acid (14), ferulic acid (15), uric acid (16), urea (17), histamine (18), serotonin (19), catechol (20), epinephrine (21), isoprenaline (22), norepinephrine (23), and dopamine (24). The concentrations of dopamine, epinephrine, isoprenaline are 0.90 μM, the others are all 9.0 μM. (B) The absorbance ratio (A_{650}/A_{520}) of the AHMT-Au NPs after the addition of different analysts. Inset photographs of the AHMT-AuNPs in the presence of different analysts.

value (pK_a) of norepinephrine is 8.40, smaller than that of dopamine (pK_a = 8.89). Meanwhile, nearly no color change is observed after the addition of 2,3,4-trihydroxybenzoic acid, gallic acid, and ferulic acid, respectively. It is due to that carboxylic acid groups are existed instead of the amine groups in these molecular structures. Similar observations occurred with histamine and serotonin only containing one hydroxyl group.

Taken together, the AHMT-AuNPs can recognize dopamine because of the particular dopamine structures, where the primary amine group and two hydroxyl groups play key roles. In our study, dopamine is used as a "molecular bridge", which can form NH···O and NH···N hydrogen bonds with the AHMT-AuNPs, shorten the interparticle distance, and induce the aggregation of the AHMT-AuNPs. As a result, a rapid, simple, and colorimetric method was developed for the detection of dopamine.

Meanwhile, TEM experiments were conducted to deeply understand the microstructures of the AHMT-AuNPs in the absence (Figure 2A) and presence of 0.20, 0.50, and 0.80 μM (Figure 2B−D) dopamine, respectively. Notably, without dopamine, the AHMT-AuNPs are well monodispersed (Figure 1A). Nevertheless, in the presence of 0.20 μM dopamine, the AHMT-AuNPs start to aggregate together and the aggregations of the AHMT-AuNPs are more and more severe with the increase of dopamine from 0.20 to 0.80 μM. The TEM results are similar to those reported previously on the aggregated AuNPs cross-linked by other molecules[28,29] or ions.[17,26] In addition, DSL experimental results are also supported the TEM observations, where the sizes of the AHMT-AuNPs are also increased with the increase of dopamine (Figure 3).

Responses of the AHMT-AuNPs. In our work, we applied the above property to develop a colorimetric method for the detection of dopamine using AHMT-AuNPs as a probe. We first checked some biomolecules including amino acids and

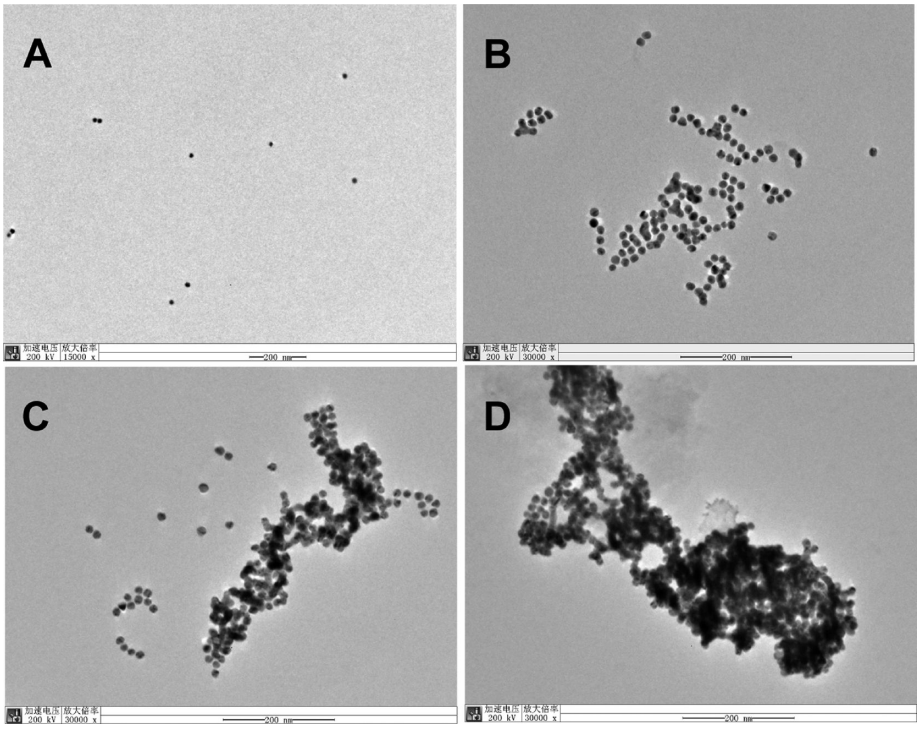

Figure 2. TEM images of the AHMT-AuNPs in the (A) absence and presence of (B) 0.3, (C) 0.5, and (D) 0.8 μM dopamine, respectively.

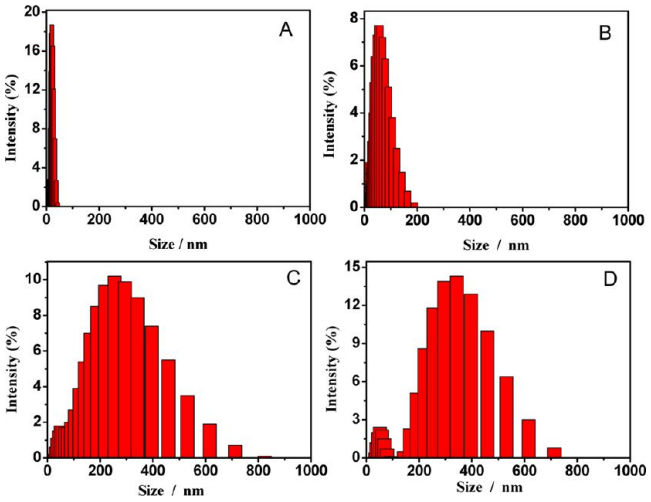

Figure 3. Size distribution of the AHMT-AuNPs measured by DLS in the (A) absence and presence of (B) 0.18, (C) 0.30, and (D) 0.80 μM dopamine.

peptides, drugs such as neurotransmitters, and common ions in biological samples (Figure 1). The UV–vis curves of AHMT-AuNPs have significant red-shift in the presence of dopamine. Meanwhile, the AHMT-AuNPs solution became purple or even blue, which was different from the red colloidal solution of AHMT-AuNPs in the absence of dopamine. The changes in the UV–vis spectra are negligible with histidine, tyrosine, tryptophan, phenylalanine, lysine, catechol, glutamic acid, acrobatic acid, glucose, fructose, glutathione, 2,3,4-trihydroxybenzoic acid, gallic acid, ferulic acid, uric acid, urea, and histamine, (for 10-fold dopamine concentration). Interestingly, the presence of acrobatic acid or uric acid causes only a slight color change in the colloidal AHMT-AuNPs solution, because of their weak interactions with the AHMT-AuNPs, although their electrochemical property is similar to that of dopamine. Therefore, high selectivity is possible for dopamine detection in acrobatic acid solution, using the AHMT-AuNPs as a probe. Meanwhile, we also investigated the responses of the AHMT-AuNPs in the presence of other neurotransmitters such as norepinephrine, epinephrine, isoprenaline, serotonin, and catechol. The color of the AHMT-AuNPs did not change in the presence of serotonin and catechol (10-fold the concentration of dopamine). However, it was found that the AHMT-AuNPs also had responses to three neurotransmitters such as norepinephrine, epinephrine, and isoprenaline to some extent. Among these neurotransmitters, the absorption ratio (A_{650}/A_{520}) of dopamine was maximum (Figure 1). In this work, we tried to develop a low-cost, facile, sensitive, and selective colorimetric sensing for dopamine using single molecular functionalized AuNPs. We tried to ignore the effects of epinephrine and isoprenaline, because the level of dopamine in the brain is higher than those of norepinephrine, epinephrine, and isoprenaline.

Optimization of the Experimental Parameters. The performance of the as-developed dopamine detection is strongly influenced by the experimental conditions such as reaction temperature, stirring, reaction time, and pH in the colloidal solution. Therefore, each detection parameter was optimized in our study, while keeping the other parameters constant.

The reaction temperature has great effects on hydrogen-bonding interactions. As displayed in Figure 4 and Figure S1

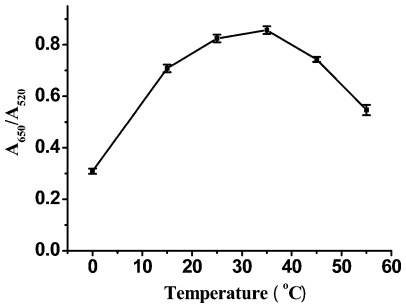

Figure 4. Absorption ratio (A_{650}/A_{520}) of the AHMT-AuNPs at different reaction temperature in the presence of 0.80 μM dopamine.

(see the Supporting Information), the absorption ratio (A_{650}/A_{520}) quickly increased, reached a maximum at 35 °C, and dropped down steeply when the reaction temperature was above 35 °C. Thus, 35 °C was chosen as the optimal reaction temperature in the experiments.

As expected, stirring and incubation time also influence the colorimetric responses of the AHMT-AuNPs in the presence of dopamine. Without stirring (Figure 5A), the absorbance peak at

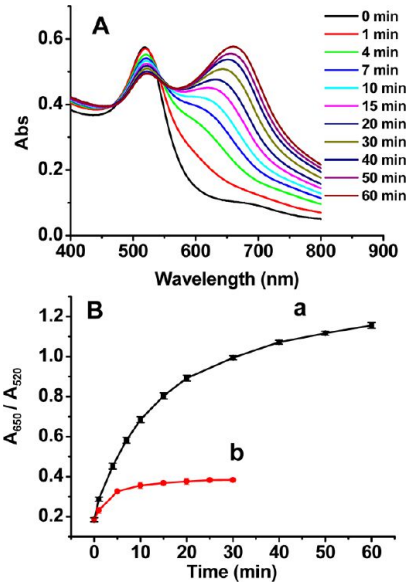

Figure 5. (A) Time-dependent absorption spectra for incubation without stirring. (B) Time-absorbance ratio of A_{650}/A_{520}. Data was obtained in 20 nM AHMT-AuNPs solution containing 0.80 μM dopamine after incubation (a) without and (b) with stirring.

520 nm gradually decreased when extending the incubation time. Meanwhile, another should peak emerged in the spectral range of 600–700 nm, slowly red shifted, and became stronger gradually. As a result, the UV–vis spectra changed greatly and the absorption ratio (A_{650}/A_{520}) quickly increased within the initial 30 min, whereas it became weak and slow when the incubation time was more than 30 min (Figure 5B, curve a). Therefore, 30 min was chosen for the optimal incubation time in the experiments.

On the contrary, in the case of stirring, the UV–vis curves change slowly and the absorption ratio (A_{650}/A_{520}) is much lower, compared to that without stirring, whereas other

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conditions are constant (see Figure S2 in the Supporting Information, Figure 5B, curve b). These results indicate that stirring is unfavorable for the hydrogen-bonding interactions of the AHMT-AuNPs with dopamine. The reason might be that stirring would deteriorate the balance of dopamine as a "molecular bridge" between the AHMT-AuNPs.

The amount of the AHMT-AuNPs also affects the dopamine detection in the range of 2.5−50.0 nM. With insufficient AHMT-AuNPs, it is difficulty for accurate dopamine detection with good performance. However, the AHMT-AuNPs become unstable when the AHMT-AuNPs is more than 40 nM. High sensitivity is obtained within the AHMT-AuNPs range from 10 to 15 nM, and thereby 15 nM was chosen in the following experiments.

In addition, the pH also influences the interactions of the AHMT-AuNPS with small molecules. We investigated the pH effects from 2.0 to 11.0, while keeping the dopamine concentration unchanged. Obviously, the highest absorption ratio (A_{650}/A_{520}) is obtained at pH 7.0. However, the absorption ratio (A_{650}/A_{520}) is quite low in strong acidic solution (pH <3.0), where dopamine and AHMT are protonized that is unfavorable for the hydrogen-bonding interactions. On the other hand, the AHMT-AuNPs are unstable in strong basic media, and easily aggregated even without dopamine. Thus, pH 7.0 was chosen in the following experiments.

Colorimetric Detection of Dopamine Using the AHMT-AuNPs. As shown in Figure 6, a colorimetric sensor is developed for the quantitative determination of dopamine, based on the AHMT-AuNPs as a probe under optimal conditions (e.g., incubation time of 30 min, without stirring, 15 nM of AHMT-AuNPs, and pH 7.0). As can be seen, the photographs clearly display the color changes form red to blue with the increase of dopamine concentrations. The detection can be easily followed by the naked-eye towards the change of color in the colloidal solutions. Besides, the absorbance peak at 650 nm significantly red-shifts and becomes broad. Furthermore, the absorption ratio (A_{650}/A_{520}) linearly increases with the increase of dopamine in the range from 0.20 to 1.10 μM. The detection limit is 0.07 μM (S/N = 3), and the relative standard deviation is 1.3% for the determination of 0.80 μM dopamine (n = 11). These results demonstrate that this method has a better sensitivity towards the quantitative determination of dopamine, in comparison with those in the literature.[11,30] As shown in Table S1 (see the Supporting Information), the linear range of this approach is wider than those of other AuNPs as colorimetric probes.[21,22] The detection limit is lower than that of the aptamer-AuNPs.[23]

The developed colorimetric sensor based on the AHMT-AuNPs was applied to selective and sensitive detection of dopamine in biological fluids such as human urine and serum samples (Table 1). The spiked samples were obtained using an appropriate dilution of urine and serum by adding the standard solution of dopamine. The recoveries are within the range from 104.6 to 108.9%. Thus, the as-prepared sensor has promising feasibility for rapid detection of dopamine in biological fluids.

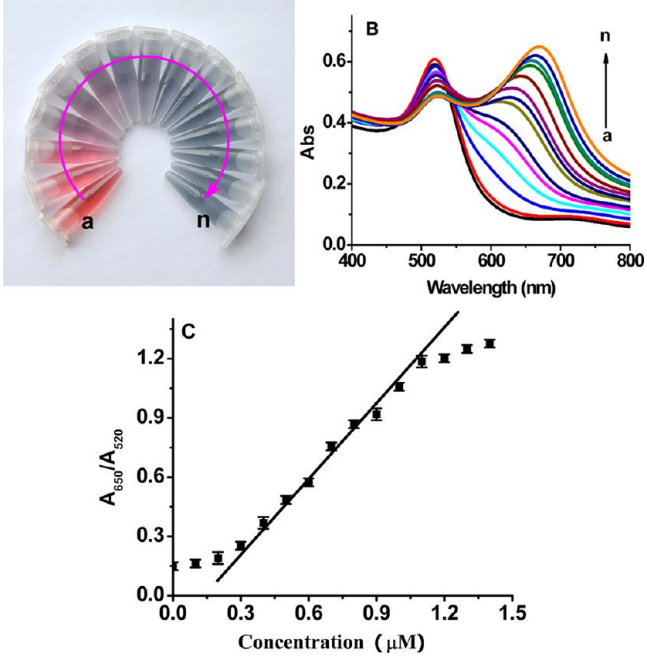

Figure 6. (A) AHMT-AuNPs with different concentrations of dopamine. (B) UV−vis spectra of the AHMT-AuNPs with different amount of dopamine. (C) Plots of the absorption ratio (A_{650}/A_{520}) vs. dopamine concentrations. The concentrations of dopamine (curves a−n): 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1.10, 1.20, 1.30, and 1.40 μM, respectively.

Table 1. Results for the Determination of Dopamine in Human Urine and Serum Samples

samples	spiked amount (μM)	found amount[a] (μM)	recovery[a] (%)
human urine	0	not detected	
	0.150	0.160 ± 0.005	106.4 ± 3.4
	0.250	0.261 ± 0.005	104.6 ± 2.0
human serum	0	not detected	
	0.150	0.163 ± 0.007	108.9 ± 4.6
	0.250	0.267 ± 0.006	106.2 ± 2.5

[a]Mean ± std, n = 5.

CONCLUSIONS

In this study, a rapid, simple, sensitive, and selective optical sensor was developed for colorimetric detection of dopamine in human serum and urine samples, based on the aggregation of the AHMT-AuNPs without any additives such as metal salts or ions. No complex instrumentation was required. The as-prepared dopamine sensor takes advantage of the formation of hydrogen-bonding recognition between the AHMT-AuNPs and dopamine, which provides a potential application for monitoring dopamine related to physiological and pathological events in brain chemistry.

ASSOCIATED CONTENT

Supporting Information

Time-dependent absorption spectra for incubation with stirring, UV−vis spectra of the AHMT-AuNPs with different the reaction temperature, and comparison of this work with some established methods using gold nanoparticles as probe to detect dopamine. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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