A highly selective and sensitive colorimetric sensor for iodide detection based on anti-aggregation of gold nanoparticles

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ABSTRACT

In this study, a simple and rapid colorimetric iodide (I^-) sensor based on the anti-aggregation of gold nanoparticles (Au NPs) was presented. This assay relied upon the distance-dependent optical properties of gold nanoparticles, the combination of mercapto-functionalized thymine on Au NPs, and the stronger affinity between I^- and mercury ions (Hg^{2+}). Hg^{2+} was employed as cross-linking agent for pairs of modified Au NPs by the coordination between Hg^{2+} and thymine. In the simultaneous presence of I^- and Hg^{2+}, the aggregation of Au NPs could not occur because of the preferential formation of HgI_2 complex. Thus, the sensing of I^- based on anti-aggregation of Au NPs was developed with the color of the Au NPs changing from blue to red, which was readily seen by the naked eye. The colorimetric sensor exhibited high sensitivity with a low detection limit of 10 nM. Notably, a highly selective recognition of I^- was shown against other halogen anions (F^-, Cl^-, Br^-). It was further proved that this simple and quick determination of iodide had possibilities for applying to environmental applications.

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1. Introduction

Gold nanoparticles (Au NPs) have been widely used as attractive colorimetric reporters because of their excellent and distinctive optical properties such as high visible-region extinction coefficients and distance-dependent optical properties [1–4]. Au NPs in aqueous solutions exhibit distinctive colors according to their morphology because of their surface plasmon resonance. Whereas well-dispersed Au NPs in solution are red in color, aggregated Au NPs appear bluish purple color [5–7]. A series of gold nanoparticle-based colorimetric sensors have been investigated involving the formation of interparticle bridging structures composed of analytes and special functional ligands. When analytes were added to a solution, these analytes interacted with the functional ligands adsorbed on the surface of Au NPs, resulting in the assembly of the Au NPs changing the solution color from red to blue (or purple). Many special ligands as analyte-receptors functionalized Au NPs were developed for the detection of ions [8–17] and small molecules [18–21]. For example, glutathione functionalized Au NPs for detection of Pb^{2+} [10], mercaptopropionic acid for Hg^{2+} [12], 5,5′-dithiobis(2-nitrobenzoic acid) for Cr^{3+} [14], 1-(2-mercaptoethyl)-1,3,5-triazinane-2,4,6-trione for melamine [20]. These colorimetric sensors exhibited high sensitivity and selectivity toward target analytes relying on the Au NPs and the especially collected ligands. Hence, red-to-blue colorimetric sensors based on the morphological change of Au NPs from a dispersed to an aggregated state have been widely investigated.

Compared to red-to-blue colorimetric sensors based on Au NPs, very few blue-to-red colorimetric sensors have been reported, although they are more attractive in distinctive color change. Our group has investigated a blue-to-red colorimetric sensor that was based on the Hg^{2+} and Ag^+ deposition on the gold surface which could inhibit the cysteine-induced aggregation of Au NPs [22].

The development of highly sensitive and selective analytical methodology for the detection of trace levels of iodide (I^-) is of significant research interest. As we all know, iodide is essential for normal human growth and plays important role in thyroid gland function [23–25]. Both iodide deficiency and excessive intake could lead to thyroid diseases. In addition, elemental iodine is used in various applications, such as synthesizing organic chemicals and medicine [26]. Traditional analytical methods for the determination of iodide involved complicated sample preparation or sophisticated instrumentation, such as ion chromatography [27], capillary electrophoresis [28], and indirect atomic absorption spectrometry [29]. Fortunately, the gold nanoparticle-based colorimetric sensors provided an alternative to sense iodide in aqueous solution.

Herein, we used mercapto-functionalized thymine as the competitive ligand, which could modify Au NPs surface by Au—S bonds and also could coordinate with Hg^{2+}, to develop a colorimetric sensor for the quantitative detection and highly selective recognition

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of I⁻ against other halogen anions (F⁻, Cl⁻, Br⁻). In the presence of I⁻, Hg²⁺-induced aggregation of modified Au NPs was decreased to some extent. Because the aggregation was inhibited by iodide, the Au NPs solution exhibited a color gradation between blue and red in accordance with the iodide concentration. The experimental results proved that the present sensing system provided a good performance in terms of selectivity, sensitivity, linearity and detection limit for the determination of I⁻ in aqueous solutions.

2. Experiments

2.1. Chemicals

Hydrogen tetrachloroaurate(III)tetrahydrate (HAuCl$_4$·4H$_2$O), sodium citrate, Tween 20, NaF, KCl, KBr, NaHCO$_3$, Na$_2$SO$_4$·10H$_2$O, Na$_3$PO$_4$, NaNO$_3$, Na$_2$CO$_3$, NaAc were received from Sinopharm Chemical Reagent Co., Ltd., China. HgCl$_2$ and KI were purchased from Aladdin. All of the reagents were of analytical grade and used without further purification and deionized ultra-filtered water was used throughout the experiments. N-1-(2-mercaptoethyl)thymine was synthesized as our previous report [30].

2.2. Instrumentation

Deionized water (18.2 MΩ cm specific resistances) was purified by a Cascada TM LS Ultrapure water system (Pall Corp., USA). TEM analysis was performed on a JEM-1230 electron microscope (JEOL, Ltd., Japan) operating at 100 kV. UV–vis absorption spectra were measured on a Thermo Scientific NanoDrop 2000/2000 C spectrophotometer (USA). Size distribution measurements were performed on a Malvern Zetasizer Nano-ZS90 (ZEN3590). All glassware used in the following procedure was cleaned in a bath of freshly prepared 3:1 HCl–HNO$_3$, rinsed thoroughly in water and dried in air.

2.3. Gold nanoparticle synthesis and surface modification

Gold nanoparticles (Au NPs) with diameters 13 nm were synthesized by the citrate-mediated reduction of HAuCl$_4$ according to the published protocol [31,32] with necessary modifications. Briefly summarized, an aqueous solution of 1 mM HAuCl$_4$ (100 mL) was heated to reflux with vigorous stirring in a round-bottom flask fitted with a reflux condenser; 38.8 mM sodium citrate (10 mL) was then rapidly added to the boiled solution. The mixed solution was boiled for another 30 min and become wine red. The obtained solution was cooled to room temperature and stored at 4 °C. The size of Au NPs was measured using TEM.

The modified Au NPs were prepared at 38 °C by mixing 10 mL the above gold colloids and 1 mL of 1 mM N-1-(2-mercaptoethyl)thymine aqueous solution (as-synthesized ligand) under stirring. After reaction for 3 h, the mixture was subsequently left overnight without disturbance at room temperature. After centrifugation for 20 min at 14,000 rpm to remove the free ligands, the pellet was re-suspended in 0.05‰ Tween 20 solution.

2.4. Detection of I⁻ using modified Au NPs

The detection was performed in PBS buffer solution. For I⁻ sensing, the I⁻ were first added to a buffer solution (1 mL) containing modified Au NPs (1.4 nM), and then Hg²⁺ was added to the solution. After equilibrating at room temperature for the optimum incubation time, the UV–vis absorption spectra of the resulting solutions were recorded.

2.5. Analysis of real samples

Tap water sample obtained from our institute and pond water sample collected from a pond on the campus of Yantai University (Yantai, China) were filtered through a 0.2 μm membrane. The water samples were spiked with standard Hg²⁺ solutions at certain concentrations and then mixed with the stock solutions containing the Au NPs and PBS buffer solution.

3. Results and discussion

3.1. Sensing mechanism of I⁻ sensor

A schematic representation of the mechanism of the colorimetric sensing I⁻ is illustrated in Fig. 1. It is well known that thymine could complex with mercury ions in a ratio of 2 thymine ligands to each mercury ion [33–36]. The thiol group of as-synthesized thymine ligand exhibited intriguing reactivity with Au NPs. The mercapto-functionalized thymine could bind onto the surface of gold surface through the sulfur atom and the Au NPs were modified with ligands. Thus Hg²⁺ can act as cross-linking agent for pairs of thymine-coated Au NPs, inducing the aggregation of Au NPs. This caused a rapid, red-to-blue (or purple) color change as our previous report [30]. The formation constant for HgI$_2$ (8.3×10^{23}) and that for HgI$_4^{2-}$ (5.6×10^{29}) is higher than that for T–Hg–T (10^6) [37–39], which means that Hg²⁺ has a greater affinity for I⁻. As shown in Fig. 1, when enough I⁻ were injected to the gold colloid followed by the addition of Hg²⁺, the Au NPs still retained red color due to the preferential formation of HgI$_2$. This property was employed to design our nanoparticle-based colorimetric sensor for I⁻.

In the simultaneous presence of I⁻ and Hg²⁺ in the sensing solution, the aggregation of Au NPs induced by Hg²⁺ would be prevented because of the formation of HgI$_2$ complexes. As shown in Fig. 2A, the only modified Au NPs in red color showed an absorption band at 524 nm (curve a), with the addition of Hg²⁺, a new absorption band emerged at about 645 nm (curve b) and the color changed to blue, indicating the aggregation of Au NPs by the linkage of Hg²⁺. But, in the presence of I⁻, the Hg²⁺ could be prior to chelating with I⁻. As a result, the ratio of aggregated to dispersed Au NPs would decrease with the increasing of I⁻. As indicated by curve c in Fig. 2A, most of Au NPs remained dispersed state as reflected by the single absorption band at about 524 nm and the color of colloidal solution was still red. This dramatic anti-aggregation induced by I⁻ was further evidenced by TEM images. As clearly shown in Fig. 2B, the only modified Au NPs as blank sample were in dispersed state (a), in the presence of only Hg²⁺, Au NPs became aggregated (b), and Au NPs remained dispersed with the addition of I⁻ and Hg²⁺ (c) due to the preferential formation of HgI$_2$. Moreover, a group of reliable data was obtained by dynamic light scattering (DLS) measurement. It tends to overestimate the diameters of Au NPs measured by TEM images because DLS measures hydrodynamic diameters of gold nanocomposites [21]. Nevertheless, a pronounced difference in the above stated Au NPs was observed. As shown in Fig. 3, the intensity contribution versus diameters of Au NPs displayed the different dominant distribution peaks, around 23 nm, 128 nm, and 33 nm, respectively, thereby suggesting the effective anti-aggregation of I⁻.

The results described above indicated that iodide could effectively complex with Hg²⁺, thereby decreasing the aggregation of Au NPs and retaining the red color of gold colloid. Thus, a new colorimetric sensor based on iodide-indirectly prevented aggregation of Au NPs would be existed for an alternative approach for I⁻ detection.
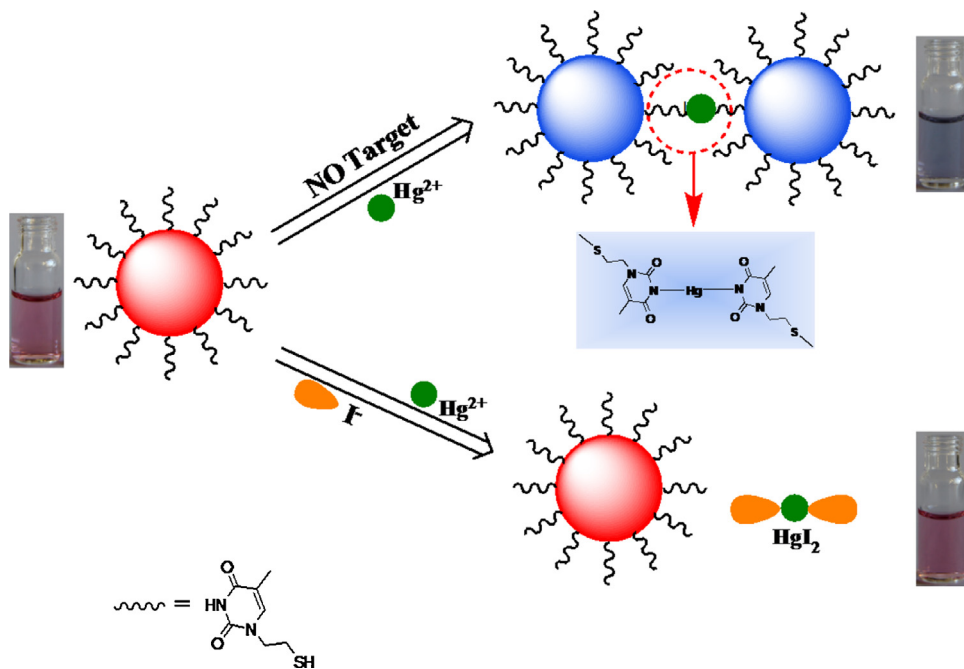
Fig. 1. Schematic illustration of the analytical process for detecting iodide based on the anti-aggregation of modified Au NPs.
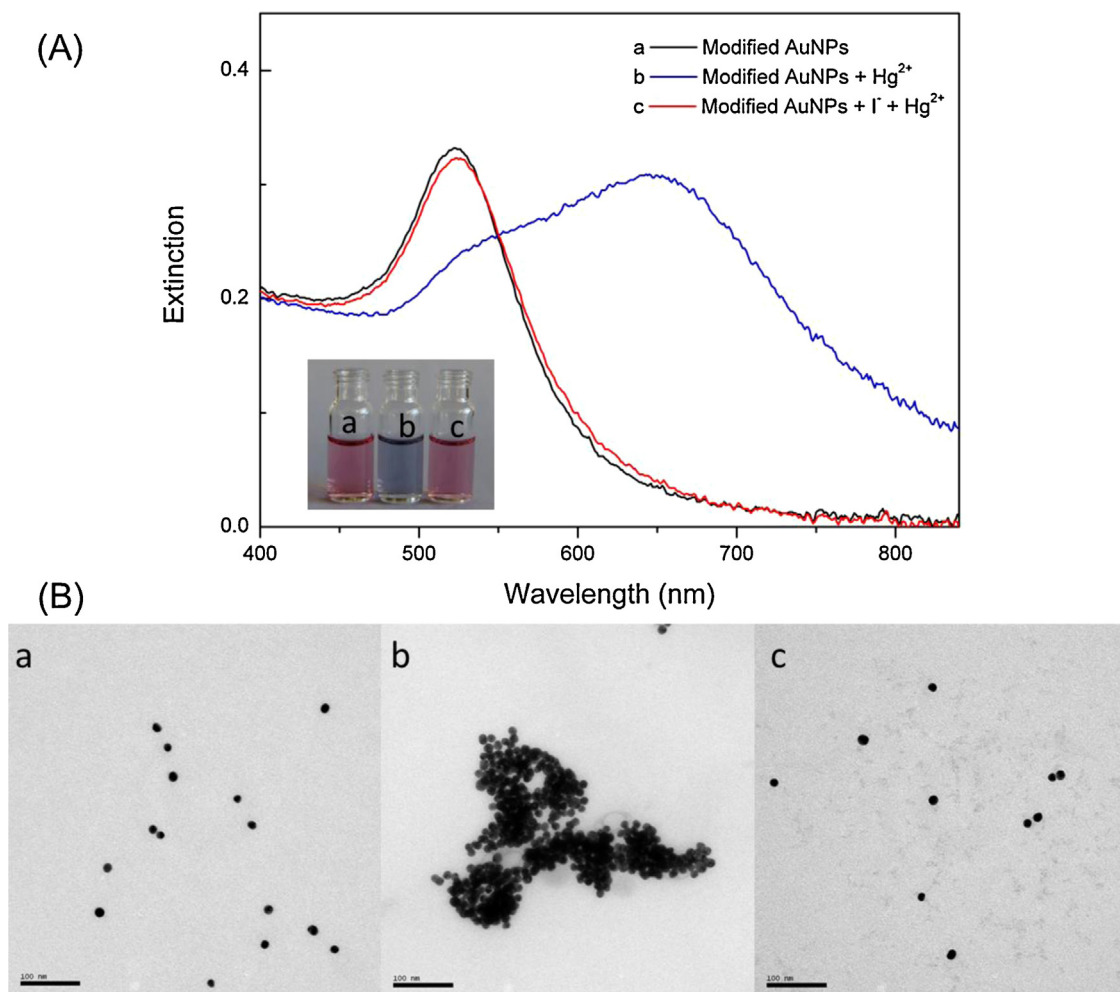

Fig. 2. (A) UV–vis absorption spectra of modified Au NPs (a) in the absence of I^-, (b) in the presence of 300 nM Hg^{2+}, (c) in the presence of 500 nM I^- and 300 nM Hg^{2+}, inset image is the corresponding photographs of gold colloid; (B) TEM images of Au NPs, corresponding to (A).
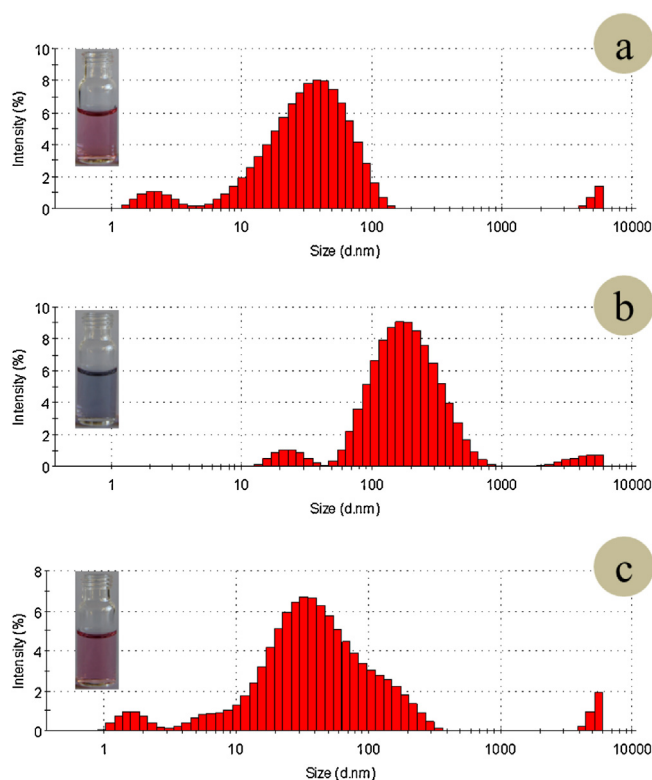
Fig. 3. Histogram of intensity contribution versus diameter of Au NPs: (a) modified Au NPs only; (b) modified Au NPs in the presence of only 300 nM Hg^{2+}; (c) modified Au NPs in the presence of 500 nM I^- and 300 nM Hg^{2+}.

3.2. Optimization of the responsive conditions

It is necessary to examine the optimum conditions for a sensor with better performance. Herein, we investigated several responsive conditions in our sensor, including solution pH, incubation time, and the concentration of Hg^{2+}. The value of Ex_{524}/Ex_{645}, which could characterize the ratio of the dispersed to the aggregated forms of Au NPs, was used as indicator for performance appraisal. The response of Ex_{524}/Ex_{645} was achieved over the pH range of 5.8–8.9 (Fig. 4a and b). To obtain a better performance, we chose the pH at 7.4, avoiding the protonation of the nitrogen atoms of the thymine at lower pH or the interference of OH^- induced by higher solution pH [40,41]. In all subsequent experiments, we used 20 mM PBS buffer solution to keep the pH value at 7.4.

The absorption spectra of the sensing system in the presence of I^- changed with time. Fig. 4c displayed the time-dependent changes of Ex_{524}/Ex_{645} in the absence and presence of I^-. It attained equilibrium during 2–8 min, however, considering the operation and measurement time-consuming, 5 min incubation time was chosen for further studies.

We also investigated the optimum Hg^{2+} concentration to bring the aggregation of Au NPs. The calibration curve of Hg^{2+} in modified Au NPs solutions was shown in Fig. 4d. We noted that Hg^{2+} concentration higher than 300 nM did not induce obviously notable differences, whereas the concentration lower than 300 nM would be less efficient and unfavorable to lower detection limit. Therefore, in all the following studies, the concentration of Hg^{2+} at 300 nM was employed for the detection of I^-.

3.3. Sensitivity of the sensor

In order to evaluate the sensitivity of this colorimetric system for I^-, a series of different concentrations of I^- ranging from 10

to 600 nM were introduced to the sensing system and the UV–vis spectra were recorded after incubation for 5 min. As expected, it exhibited different anti-aggregations in the presence of different concentrations of I^-. With the addition of I^-, the absorption band of Au NPs changed gradually from 524 nm to longer wavelengths, finally reached a maximum of 645 nm. The absorbance value of Au NPs solutions at 524 and 645 nm is related to the quantities of dispersed and aggregated Au NPs, respectively. As shown in Fig. 5a, with the addition of I^-, the absorbance at 645 nm gradually decreased, which suggested I^- had chelated with Hg^{2+} and efficiently prevented the aggregation of Au NPs. Moreover, the solution color dramatically changed from blue to red along with the increase of I^- concentration, which was easily read out by naked eyes as shown in the inset of Fig. 5a. Thus, the extinction ratio of Ex_{524}/Ex_{645} was employed to estimate the extent of anti-aggregation. As displayed in Fig. 5b, the ratio of Ex_{524}/Ex_{645} increased linearly with the I^- concentration in the range 10–600 nM ($R = 0.995$). The experiment results clearly demonstrated that this blue-to-red response can be used for the quantitative analysis of I^- as low as 10 nM in aqueous solution.

3.4. Selectivity of the sensor

To investigate the selectivity of the sensor toward I^- over other anions, UV–vis spectra of Au NPs in the presence of other anions, including F^-, Cl^-, Br^-, SO_4^{2-}, Ac^-, HCO_3^-, NO_3^-, CO_3^{2-}, were recorded. As demonstrated in Fig. 6, for other anions, the value of Ex_{524}/Ex_{645} was almost equal to the blank one and negligible compared to that for I^-. These results indicated that only I^- can prevent the Au NPs from Hg^{2+}-induced aggregation by the formation of HgI_2 complexes. Notably, a highly selective recognition of I^- against other halogen anions (F^-, Cl^-, Br^-) was obtained. The corresponding color change exhibited this bright distinction, the sensing system with I^- remained red while others were blue. Moreover, the satisfying response of the system toward I^- in the presence of the mixture of all the mentioned anions was observed, suggesting that the simultaneous presence of other competitive anions did not interfere the sensing of I^-. The color distinctions were clearly shown in the inset of Fig. 6. Evidently, the colorimetric method demonstrated here enables high selectivity toward I^- and good resistance to interference.

3.5. Sensing performance in real water samples

To evaluate the application of the presented method in real samples, we utilized it to sense I^- in tap water and pond water samples. Satisfying recoveries were obtained in the two different real samples; 89–109.4% for tap water samples and 92–112.3% for pond water samples (see Table 1). The experimental results clearly demonstrated that this colorimetric assay provided a potential application for the detection of I^- in environmental samples.

Table 1
Recoveries for the determination of I^- in real water samples ($n = 3$).

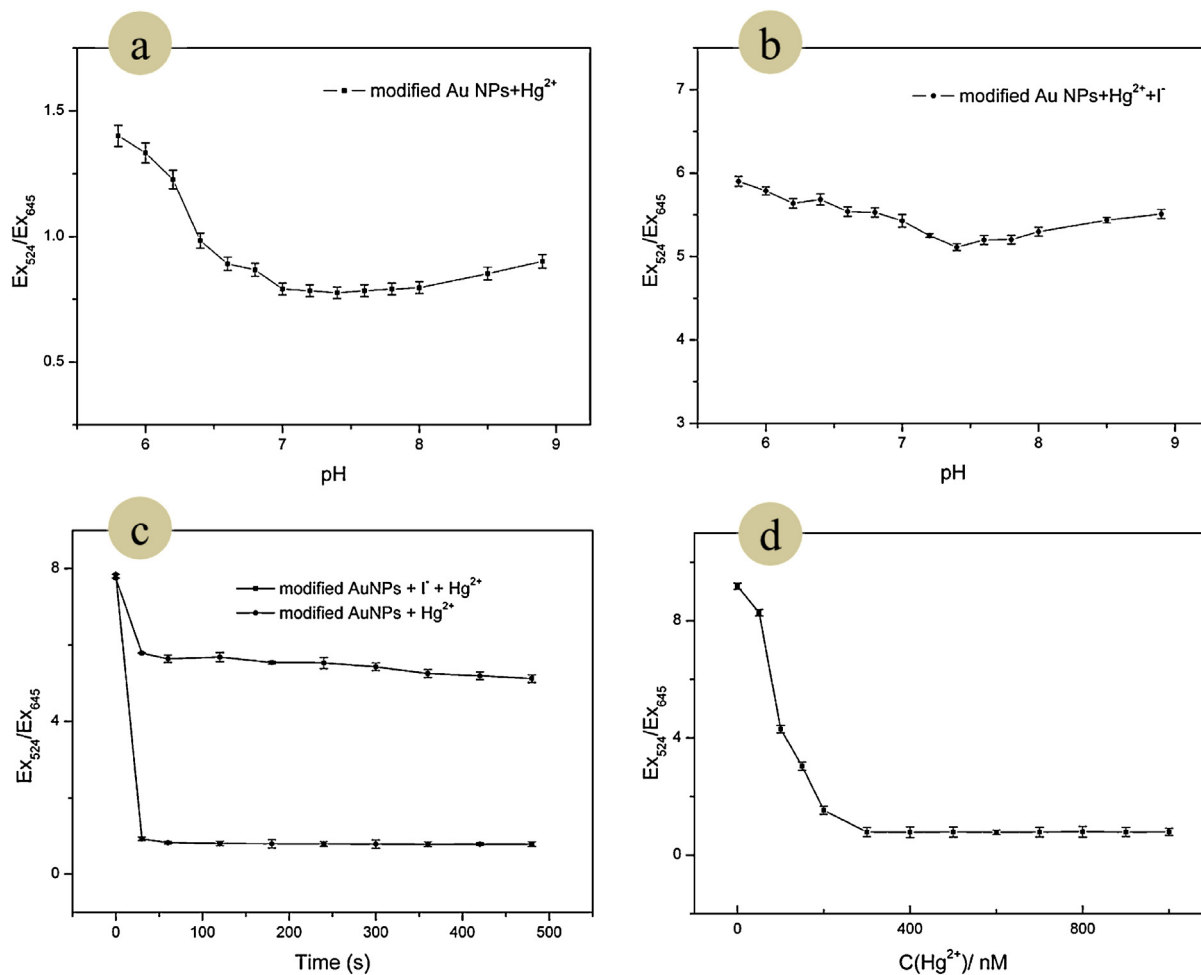| Samples	Spiked (nM)	Found (nM)	Recovery (%)
Tap water	0	nd[a]	–
	50	44.5	89.0
	100	96.2	96.2
	200	218.8	109.4
Pond water	0	nd[a]	–
	50	46.0	92.0
	100	90.4	90.4
	200	224.6	112.3

[a] nd, not detected.

Fig. 4. Optimization of assay conditions: the absorption ratio of Ex_{524}/Ex_{645} as a function of pH value in the presence of only Hg^{2+} (a) and in the presence of I^- and Hg^{2+}; effect of reaction time (c) and the concentration of Hg^{2+} (d). Time-course measurements of Ex_{524}/Ex_{645} for Au NPs after the addition of I^- (500 nM) and Hg^{2+} (300 nM).
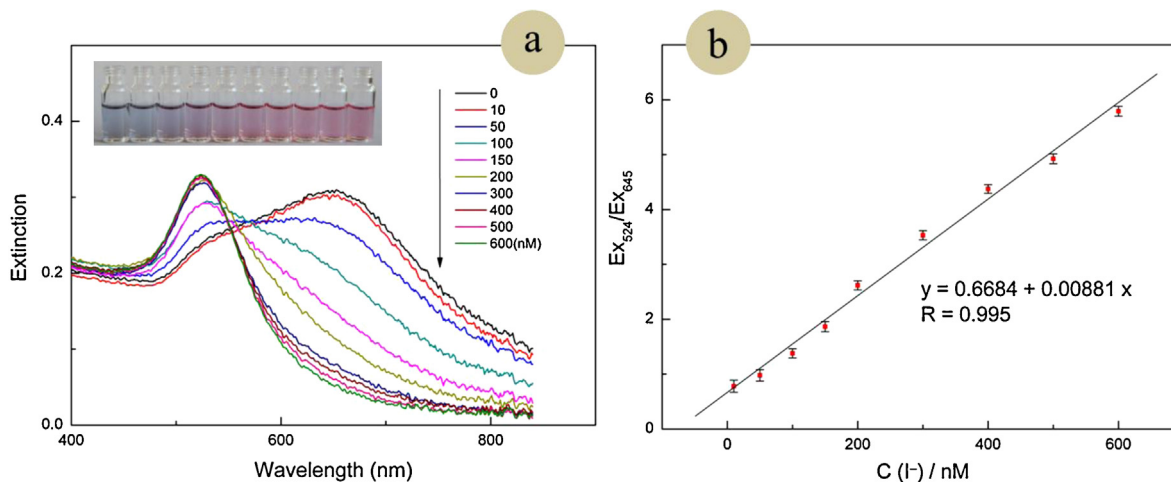

Fig. 5. (a) UV–vis absorption spectra of modified Au NPs before and after addition of different concentrations of I^-, and (b) plots of Ex_{524}/Ex_{645} of the absorption spectra of Au NPs as a function of the concentration of I^-.
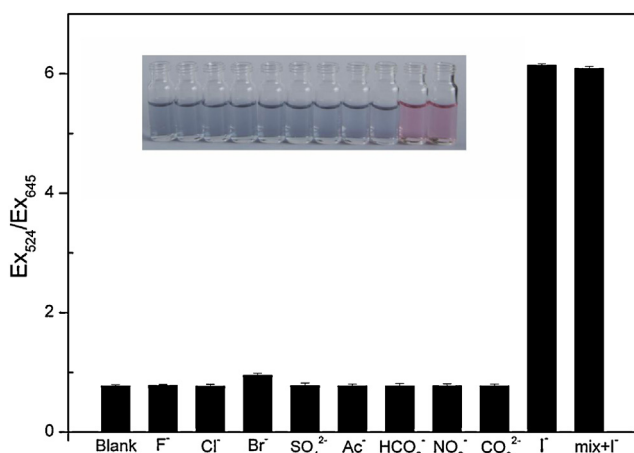
Fig. 6. The value of Ex_{524}/Ex_{645} and photographic images of modified Au NPs in the presence of 500 nM I^- and 100-fold other anion ions respectively and the mixture of I^- and all other competitive ions.

4. Conclusions

In summary, we take advantage of the color change of gold nanoparticles induced by I^- recognition to develop a novel nanoparticle-based colorimetric sensor for visual detection of I^-. This new method offered several advantages over current I^- detection techniques. First, the colorimetric method did not require complicated and expensive instruments, which can be readily seen by the naked eye or with the aid of simple UV–vis spectrometer, simplified operations and reduced the cost. Second, the method allowed the detection concentration as low as 10 nM to achieve with the naked eye within 5 min, which was useful for rapid and ultrasensitive detection of I^-. Finally, this sensor exhibited excellent selectivity for I^- over other anions, especially against other halogen anions (F^-, Cl^-, Br^-). These advantages substantially made this method quite promising for rapid detection of I^- in aqueous solution.

Acknowledgements

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