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Highly selective and sensitive visualizable detection of Hg^{2+} based on anti-aggregation of gold nanoparticles

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ABSTRACT

For the widely used gold nanoparticles (AuNPs)-based colorimetric probes, AuNPs generally change from dispersion to aggregation state accompanying with corresponding color turning from red to blue. Although colorimetric probes based on the anti-aggregation of AuNPs show exceptional selectivity and sensitivity, few examples have been reported in literature. A facile but highly sensitive and selective colorimetric probe based on the anti-aggregation of AuNPs transferred from the deactivation of aggregation agent 4,4′-dipyridyl by Hg^{2+} was developed in this work. This reported probe is suitable for real-time detection of Hg^{2+} in water with a detection limit of 3.0 ppb for Hg^{2+}, and exhibits a selectivity toward Hg^{2+} by two orders of magnitude over other metal ions. The dynamic range of this probe can be conveniently tuned by adjusting the amount of 4,4′-dipyridyl used.

1. Introduction

Optical probes can overcome the limitations caused by the traditional instrumental analytical methods because no sophisticated instrumentation or sample preparation is required in their procedures, and accordingly the fluorescent or colorimetric probes have attracted great attention in the past two decades [1]. Colorimetric probes are extremely attractive because signaling the targeted event can be visualized by naked eyes and thus can make on-site, real-time detection possible [2,3]. Gold nanoparticles (AuNPs) are emerging as an important type of colorimetric reporter due to their intrinsically exploitable properties of the high extinction coefficient and of the distinct variation in color associated with the transition of the nanoparticles from dispersion to aggregation state or vice versa [4–8]. AuNP-based colorimetric probes have been applied for sensing a series of biological and chemical matters such as proteins [9–13], oligonucleotides [14–17], metal ions [18–24], and some other small molecules [25–30]. Most AuNP-based colorimetric probes rely on the rational modification of AuNPs surface with specific binding-ligands, and the interaction between target analytes and ligands can then change the dispersion/aggregation state of the AuNPs accompanied with the color change [7–30]. Among these probes, AuNPs generally change from dispersion to aggregation state and the color turns from red to blue concomitantly. It should be noted that AuNPs aggregation processes are not selective, because many other external factors, which are not easy to be excluded in real applications, can trigger the aggregation of AuNPs. In order to achieve higher selectivity, the AuNPs colorimetric probe based on anti-aggregation or re-dispersion of AuNPs becomes a good alternative. However, to our knowledge, only very few colorimetric probes based on the anti-aggregation of AuNPs were reported, where AuNPs were generally modified by functional DNAs [31–35]. This increases the tedious labor and the corresponding cost.

Herein, for the first time we report an AuNPs colorimetric probe suitable for the facile, sensitive and selective detection of Hg^{2+} by means of the anti-aggregation of AuNPs with the use of a commonly available small organic molecule 4,4′-dipyridyl (DPy). The sensing mechanism as outlined in Scheme 1 is based on the anti-aggregation of AuNPs transferred from the deactivation of the aggregation reagent by target analyte Hg^{2+}. In the absence of Hg^{2+}, DPy molecules can induce the aggregation of AuNPs due to strong coordinative ability, therefore replacing the original capping ligand citrate moieties on AuNPs surface. However, AuNPs can disperse in DPy solution under the coexistence of Hg^{2+} because of the deactivation of DPy by Hg^{2+} due to the formation of the Hg–DPy complex. Thus this system can be used to develop a Hg^{2+} probe. The high affinity of DPy for Hg^{2+} combined with the high extinction coefficient of AuNPs substantially enables this probe with a low detection limit (3.0 ppb) and excellent selectivity toward Hg^{2+}. The dynamic range of these assays can be conveniently tuned by adjusting the amount of aggregation reagent DPy. In addition, this

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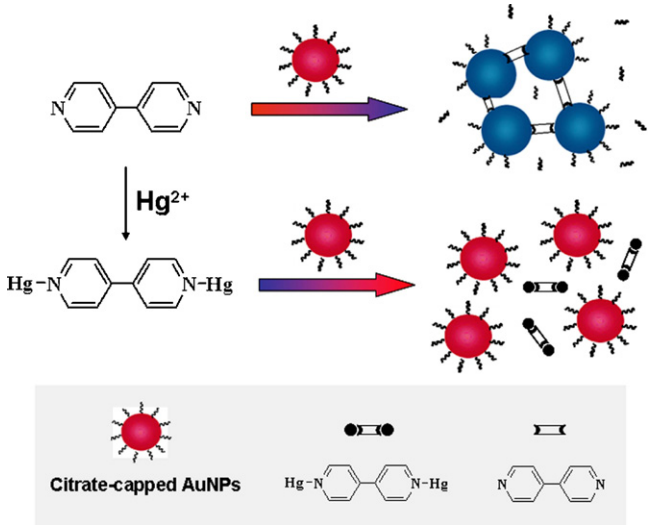

Scheme 1. Anti-aggregation of AuNPs for the detection of Hg^{2+}.

method remains much simpler and more cost-effective than the other existing methods for Hg^{2+} assay, without the requirement of much instrumentation or designing and synthesizing fluorophore or chromophore molecules to achieve the required sensitivity and selectivity [36–42].

2. Experimental

2.1. Chemicals and apparatus

UV–vis spectra were obtained on a Shimadzu UV-2450 spectrophotometer. 4,4′-Dipyridine (DPy), hydrogen tetrachloride ($HAuCl_4$), and trisodium citrate were obtained from Sigma–Aldrich and all metal salts were purchased from Sinoreagent, China. All other reagents were of analytical reagent grade and used without further purification. Milli-Q ultrapure water was used throughout unless otherwise stated.

2.2. Preparation of AuNPs

13-nm AuNPs were synthesized by sodium citrate reduction of $HAuCl_4$ following a literature procedure [43]. Briefly, trisodium citrate (5 mL, 38.8 mM) was rapidly added to a boiling solution of $HAuCl_4$ (50 mL, 1.0 mM), and the solution was kept continually boiling for another 30 min to give a wine-red solution. After filtering the solution through a 0.45-μm Millipore syringe to remove the precipitate, the filtrate was stored at 4 °C. DPy and Hg^{2+} stock solutions were prepared by dissolving DPy and $HgCl_2$ in water, respectively.

2.3. Detection of Hg^{2+}

For the detection of Hg^{2+}, different concentrations of Hg^{2+} were firstly mixed well with the DPy solution (5.2 μM) in 350 μL of Tris–HCl buffer (10 mM, pH 7.0) for 5 min, and then the DPy–Hg solution was added into the AuNPs nanodispersion (300 μL). The total volume of the solution was 650 μL and the final concentrations of AuNPs and DPy were ca. 5 nM and 2.5 μM, respectively. Photographs and UV–vis spectra of the AuNPs solution were recorded 30 min later. For detection of Hg^{2+} in tap water or spring water samples, Hg^{2+} and DPy stock solutions were prepared using the tap water or spring water instead of Milli-Q water and then the above general procedures were followed.

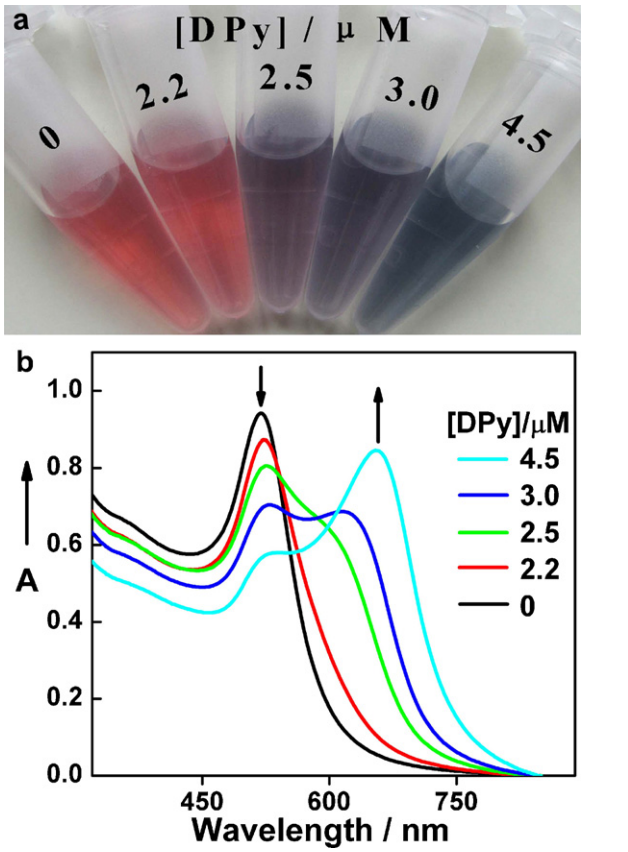

Fig. 1. Photographic images (a) and corresponding UV–vis spectra (b) of AuNPs nanodispersion under different concentrations of DPy: 0, 2.2, 2.5, 3.0, and 4.5 μM respectively.

3. Results and discussion

3.1. Aggregation of AuNPs induced by DPy

The citrate-stabilized AuNPs were prepared through the classic citrate reduction of $HAuCl_4$ [43]. The rather loose shell of citrate ions on the AuNPs surfaces is easily displaced by other desired ligands with valuable function (e.g. heterocyclic N and SH groups). Amines with electron-rich nitrogen atoms are easy to be bound onto the surface of metal nanoparticles through the coordinating interactions between nitrogen atoms in amines with the electron-deficient surface of metal nanoparticles, in particular, the ring nitrogen of hybrid aromatics exhibits much stronger binding ability/affinity to AuNPs [44–46]. Accordingly, the adopted DPy molecule with two sp^2 hybrid-nitrogen may strongly coordinate to AuNPs via the replacement with weakly surface-bound citrate ions, and finally links neighboring AuNPs through the bridge coordination effect. Therefore, DPy is an effective aggregation reagent for AuNPs. The existence of DPy can induce the aggregation of AuNPs through the cross-linking effect. The aggregation of AuNPs by DPy can be visualized by naked eyes and can also be monitored quantitatively by UV–vis spectroscopy (Fig. 1). The as-prepared 13-nm AuNPs nanodispersion exhibits wine-red color and shows a strong extinction band at 520 nm in the UV–vis absorption spectrum. The extinction band at 520 nm is ascribed to the surface plasmon resonance (SPR) absorption band of dispersed AuNPs [4]. As illustrated in Fig. 1a, the addition of DPy (0–4.5 μM) to the AuNPs nanodispersion led to an observable aggregation of the AuNPs, and the solution color turned from the original wine-red to violet blue. In the corresponding UV–vis spectra (Fig. 1b), with the increase of DPy concentration the intensity of the absorption band at 520 nm

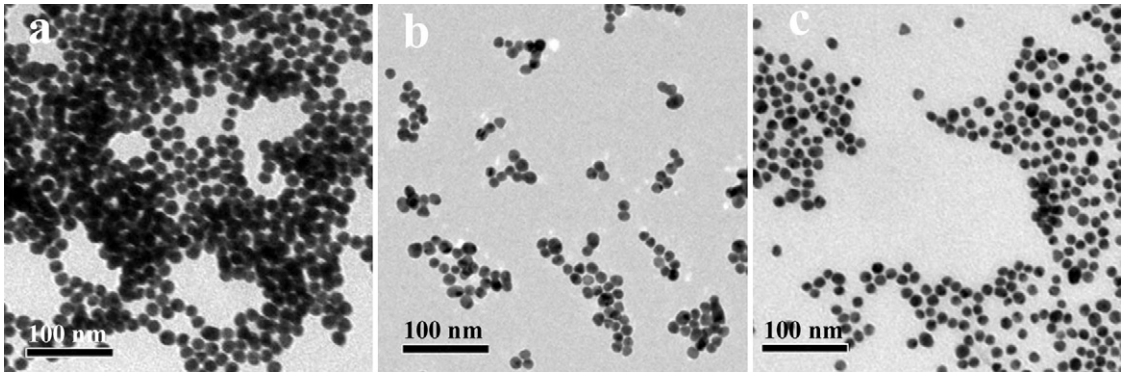

Fig. 2. The TEM images of AuNPs nanodispersion containing 2.5 μM DPy in the presence of 0 M (a), 370 nM Hg^{2+} (b), and 1.1 μM Hg^{2+} (c).

decreased systematically accompanied with the appearance of a new absorption band at ca. 650 nm, which originates from the interparticle coupled plasmon absorbance of the aggregated AuNPs [4]. The mutation point of color or spectrum variation is at ~2.5 μM DPy. Furthermore, TEM measurement also clearly demonstrated that the presence of DPy resulted in the aggregated state of AuNPs (Fig. 2a).

3.2. Anti-aggregation of AuNPs by Hg^{2+}

As mentioned above, in the absence of Hg^{2+}, the addition of DPy to the citrate-stabilized AuNPs nanodispersion led to the aggregation of AuNPs with concomitant color change from original wine red to blue with increase of the DPy concentration. Notably, when the DPy solution was firstly treated with Hg^{2+} followed by mixing with AuNPs nanodispersion, the color change of AuNPs went through a totally reverse process: with the increase of Hg^{2+} concentration, the color of AuNPs nanodispersion changed from blue to purple, and finally to wine red (inset of Fig. 3a), which corresponded to AuNPs changing from aggregation to dispersion state. The Hg^{2+} induced anti-aggregation of AuNPs was also confirmed by TEM measurement (Fig. 2b and c). This clearly demonstrates that Hg^{2+} ions take the role of anti-aggregation reagent and prevent the aggregation of AuNPs. The anti-aggregation role of Hg^{2+} toward AuNPs was derived from the deactivation of DPy by Hg^{2+} because of the stronger binding preference for DPy and Hg^{2+}.

Usually DPy is regarded as a common linear bidentate ligand and used in the construction of supramolecular system, where DPy links metal centers to form cross-linking networks [47]. A series of Hg^{2+} complexes coordinated by DPy have been isolated and characterized [48–51]. Furthermore, coordination chemistry tells us that the affinity of N-containing ligand for Hg^{2+} is superior to other transition metal ions [52], therefore, the deactivation of DPy by Hg^{2+} exhibits a specificity in coexistence of other metal ions. These intrinsic properties ensure the effect and specificity of the deactivation of DPy by Hg^{2+}. Since the color change of the AuNPs is directly dependent on the Hg^{2+} concentration, the AuNPs–DPy system can serve as a colorimetric probe for the quantitative detection of Hg^{2+}. To our best knowledge, the probes based on the AuNPs anti-aggregation process are still rare, among which the DNAzyme served as the aggregation reagent [31–34]. In comparison, in our system, the use of the small organic molecules in place of DNA-based detection setups simplifies the probe and may reduce overall cost.

3.3. Assay of Hg^{2+} concentration

As mentioned above, with the addition of the mixture solution containing DPy (2.5 μM) and Hg^{2+} to the AuNPs nanodispersion, the AuNPs nanodispersion color turned from blue to purple, and finally to red with the increase of Hg^{2+} concentration (the inset in Fig. 3a). The evolution of the corresponding UV–vis absorption spectra of the AuNPs nanodispersions in the presence of different concentrations of Hg^{2+} is shown in Fig. 3a. With the increase of Hg^{2+} concentration, the absorbance at 620 nm decreased systematically, while that at 520 nm varied in a contrary direction. Such a change in the spectrum coincides with the color change of solutions. Even the addition of nanomolar amount (40 nM) of Hg^{2+} led to a change in the solution color that could be distinguished from

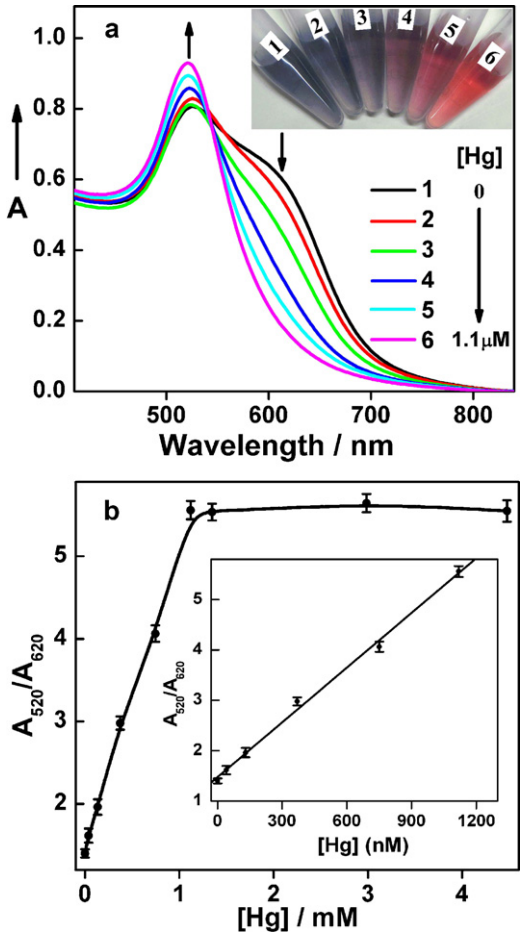

Fig. 3. (a) UV–vis spectra of AuNPs nanodispersion containing 2.5 μM DPy in the presence of Hg^{2+} concentration: (1) 0, (2) 40 nM, (3) 130 nM, (4) 370 nM, (5) 750 nM, and (6) 1.1 μM. Inset: AuNPs color dependent on Hg^{2+} concentration. (b) Calibration curve of A_{520}/A_{620} against Hg^{2+} concentration in the AuNPs nanodispersion containing 2.5 μM DPy. Inset: Linear dependence of A_{520}/A_{620} on the Hg^{2+} concentration.

that of the initial blank nanodispersion. This demonstrates that the probe could be used for direct detection of Hg^{2+} down to nanomolar level (ppb). When the Hg^{2+} concentration went up to 1.1 μM, the absorption spectrum recovered almost completely to that of bare AuNPs (without the addition of any other species).

The ratio of the absorbance at 520 nm (A_{520}) to that at 620 nm (A_{620}) was chosen to monitor the color variation caused by different concentrations of Hg^{2+}. A low ratio is associated with aggregated AuNPs of blue color, while a high one refers to dispersed AuNPs with red color. It should be noted that the selection of the peak position can only influence the value of the absorbance ratio, but has no effect on the detection of Hg^{2+}. With the increase of the Hg^{2+} concentration in the DPy–AuNPs system, this ratio increased linearly (linear correlation $R = 0.998$) from 1.4 to 5.8 corresponding to Hg^{2+} concentration of 40 nM and 1.1 μM, respectively (Fig. 3b). The limit of detection (LOD) of this probe for Hg^{2+} at a signal-to-noise ratio of 3, is approximately 15 nM (=3 ppb) Hg^{2+}, which is among the lowest values reported for a colorimetric Hg^{2+} sensing system and this value is closed to the upper limit (2 ppb) for Hg^{2+} in drinking water.

3.4. Mechanism of high sensitivity

The high sensitivity of this probe stems from three aspects: (i) AuNPs, (ii) aggregation reagent DPy, and (iii) anti-aggregation process. AuNPs with high extinction coefficients of 10^8–10^{10} M^{-1} cm^{-1} can act as an amplifier for the anti-aggregation of AuNPs transferred from the deactivation of the DPy induced by Hg^{2+} ions [4–8], thus allowing the detection limit of Hg^{2+} in nanomolar level. The fact that the anti-aggregation of AuNPs is transferred from the deactivation of DPy by Hg^{2+} plays furthermore amplification on the detection signal of Hg^{2+}. Since the concentration of DPy used (herein 2.5 μM) is just above the threshold value to trigger the AuNPs aggregation, if small part of the DPy molecules are coordinated and deactivated by Hg^{2+}, the aggregation of AuNPs induced by DPy will be invalidated. Thus the needed amount of Hg^{2+} to achieve the anti-aggregation of AuNPs will be much less than that of the aggregation reagent DPy. Similarly, the dynamic range of this probe for Hg^{2+} can be conveniently adjusted depending on the amount of aggregation reagent DPy used as discussed below.

3.5. Tuning dynamic range

A tunable dynamic range is important for practical applications as the concentration of the target analyte can be different in various samples. In order to tune the dynamic range and enable the probe for different detection requirements, we investigated if the amount of DPy can be used as a tunable parameter. Because the anti-aggregation of AuNPs was transferred from the deactivation of DPy by Hg^{2+}, we suppose that a higher concentration of Hg^{2+} should be needed to achieve the same deactivation effect on DPy if a higher concentration DPy is used. To confirm this hypothesis, we carried out the similar colorimetric sensing measurement as shown above, except that the concentration of DPy was adjusted to 10.0 μM instead of 2.5 μM. As shown in Fig. S1 (Supporting Information (SI)), the corresponding dynamic range was shifted to 4.2–8.5 μM. It was found that with the use of higher concentration aggregation reagent DPy, wider dynamic range can be achieved.

3.6. High selectivity

The selectivity of this probe for Hg^{2+} was evaluated by testing the response of the probe to other environmentally relevant metal ions, including Na^+, K^+, Mg^{2+}, Ca^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Cd^{2+}, and Pb^{2+}. Experimental results indicated that all

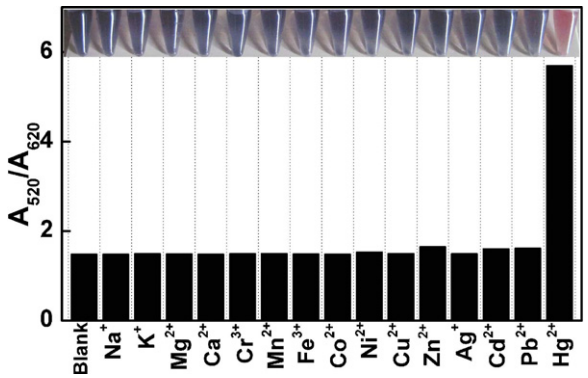

Fig. 4. Absorbance ratio of A_{520}/A_{620} and photographic images (inset) of solutions containing AuNPs, DPy (2.5 μM), and various metal ions (each 100 μM, except Hg^{2+} 1.0 μM).

the other metals ions with concentration up to 100 μM could not prevent the AuNPs aggregation under the coexistence of 2.5 μM DPy; while Hg^{2+} with concentration down to 1.0 μM could effectively induce an anti-aggregation of AuNPs and kept the NPs in dispersed state with red color. In Fig. 4, the absorbance ratios of A_{520}/A_{620} are depicted against corresponding metal ions with concentration of 100 μM except Hg^{2+} at 1.0 μM. The A_{520}/A_{620} values for samples containing all other metal ions are about 1.5, which is close to that of blank sample, while the value in the case of Hg^{2+} is 5.7. As stated above, the value of this ratio corresponds directly to the extent of AuNPs aggregation: a low value associated with a high extent of aggregation of the NPs. This means that our probe responds selectively toward Hg^{2+} by a factor of over 100-fold relative to the other metal ions. The discrimination of Hg^{2+} from the Cd^{2+} and Pb^{2+} in our probe is of particular importance since they are also highly toxic and difficult to be discriminated from each other due to their similar response as Hg^{2+} to many organic fluorescent probe [53]. The effects of some anion species, including Cl^-, NO^{3-}, $SO_4{}^{2-}$, CH_3COO^- and $PO_4{}^{3-}$ with concentration up to 100 μM have also been investigated. Our results show that the presence of these anions does not interfere with the detection of Hg^{2+}. This demonstrates the practicability of our proposed probe for Hg^{2+}.

The high selectivity of this probe is derived from the high affinity and selectivity of DPy for Hg^{2+}. Even though we cannot get the stability constants ($\log\beta_1 = [DPy-M]/[DPy][M]$) for the mononuclear complexes between DPy and different metal ion M^{n+} currently, from the $\log\beta_1$ values for M^{n+} and pyridine, a kind of structure analogue with DPy, we can find that the $\log\beta_1$ value for pyridine–Hg^{2+} has been estimated to be as much as three orders of magnitude greater than those of pyridine with other metal ions (Table S1) [54]. From these data we can deduce that DPy should also possess a high affinity and selectivity for Hg^{2+} in comparison with other metal ions. In a control experiment, different metal ions were added individually to a 1.0 mM DPy solution. Experimental results showed that 1.0 mM Hg^{2+} could form a precipitation in the reaction mixture. While for the other metal ions at least 100-fold higher concentrations were needed to cause the similar precipitation. The precipitate product in the $HgCl_2$–DPy system has been characterized to be two-dimensional $[HgCl_2(DPy)]_n$ neutral networks, based on an octahedral Hg atom coordinated by four μ_2-Cl atoms and two μ_2-DPy ligands in trans positions [48]. This result shows that the coordination selectivity of DPy for Hg^{2+} over other common metal ions is 100-fold high. In addition, the high selectivity of this probe is also benefited from the intrinsic advantage of the anti-aggregation process of AuNPs.

3.7. Detection of Hg^{2+} in real samples

In order to verify the performance of the probe for detection of Hg^{2+} in practical applications, the possible interferences of common metal ions as stated above were mixed together with Hg^{2+} in the tested samples. The results indicated that the coexistence of at least 100-fold excess of the interference ions did not affect the determination of Hg^{2+} (Fig. S2). Therefore, these excellent properties substantially enable the present probe work in the practical application for on-site, real-time detection of Hg^{2+}. To further investigate the potential practical application of this colorimetric method, the detection of Hg^{2+} in tap water and spring water samples were carried out. No change in the color or the UV–vis spectrum of the AuNPs nanodispersion was observed until the tap water or spring water sample was spiked with 40 nM Hg^{2+}. This result demonstrates the application of this probe for Hg^{2+} detection in real water samples.

4. Conclusions

In conclusion, we have developed a facile, sensitive and selective colorimetric probe for on-site and real-time Hg^{2+} detection. The proposed sensing assay is based on anti-aggregation of AuNPs transferred from the deactivation of the aggregation reagent DPy by Hg^{2+} due to the affinity preference between DPy and Hg^{2+}. The quantitative detection can be achieved by the simple introduction of aggregation reagent DPy into the as-prepared citrate-stabilized AuNPs nanodispersion. No pre-modification using specific binding-ligands is required in this probe. The reported probe has a LOD of 3.0 ppb, and exhibits a high selectivity toward Hg^{2+} by two orders of magnitude over other environmental relative metal ions. Furthermore, the dynamic range of this probe can be conveniently tuned by adjusting the amount of aggregation reagent used. This work not only provides an alternative colorimetric method suitable for the facile, cost-effective detection of Hg^{2+}, but also provides a general platform for sensing analytes based on the anti-aggregation of AuNPs transferred from deactivation of the aggregation reagent by target analytes. Higher sensitivity and selectivity of this kind of probe can be realized through adopting aggregation reagents with higher sensitivity toward AuNPs, with higher selectivity for target analyte and work along this direction is underway.

Acknowledgment

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.talanta.2011.01.037.

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