Red to brown to green colorimetric detection of Ag⁺ based on the formation of Au-Ag core-shell NPs stabilized by a multi-sulphydryl functionalized hyperbranched polymer

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Abstract: The hyperbranched polyethylenimine (HPEI) derivative with thiol (SH) terminals was synthesized and used as multidentate ligand to stabilize AuNPs/analyte composites. A facile and rapid colorimetric method for the sensitive and selective detection of Ag⁺ based on the formation of Au-Ag core-shell NPs with three color changes (red through brown to green) was developed. Successive multiple color changes can greatly improve the specificity and selectivity of this colorimetric sensor owing to the lower possibility of false positive results. Other environmentally relevant metal ions did not interfere with the determination of Ag⁺. The response (i.e., the absorbance at 600 nm, A_{600 nm}) was linearly proportional to the Ag⁺ concentration in a range from 8.76×10⁻⁹ to 1.27×10⁻⁴ M with a detection limit of 8.76×10⁻⁸ M by the naked eyes and 8.76×10⁻⁹ M by the UV-vis spectra. For the first time, this novel colorimetric sensor based on multiple color changes was developed and successfully applied to detect Ag⁺ in real samples.

Keywords: multidentate ligand, colorimetric sensor, multiple color changes, AuNPs

1. Introduction

Noble metal nanoparticles (NPs) with their associated unique optical and catalytic properties are exploited for a wide variety of applications in sensing,^[1-3] medicine,^[4, 5] catalysis,^[6, 7] etc. In particular, the colorimetric detection based on gold nanoparticles (AuNPs) or conjugated polymer^[8] has generated increased interest because of its simplicity, rapidity, visualization and low cost. Over the past several years, different AuNPs- or AuNPs composites-based colorimetric assays have been used in the detection of Ag⁺.^[9-13] The detection mechanisms of these assays are all based on the color change of red-to-blue (purple) or blue-to-red induced by the aggregation-to-dispersion or dispersion-to-aggregation of AuNPs in the presence of Ag⁺. However, the aggregated state is usually unstable and the instability of the AuNPs aggregates can greatly limit their sensing applications because of the short persistence time of the color change and limited observing time for recording the color change phenomenon before the color fades. In addition, so far most reported colorimetric sensors only exhibit one color change from red-to-blue or red-to-purple or blue-to-red in detection process, which results in the poor specificity and selectivity for Ag⁺ detection. For instance, many other external factors can also trigger the aggregation of AuNPs with red-to-blue color change, such as an acid environment, high ionic strength and so on. Design and fabrication of AuNPs-based colorimetric sensors, which not only maintain their high stability before and after the sensing but also improve their specificity and selectivity by means of three color changes during the detecting process, are meaningful and will definitely promote great progress in the field of colorimetric sensor monitoring technology.

So far, different functional decorators have been developed to stabilize or achieve strong coupling AuNPs and target analyte. Most decorators are all ligands containing functional groups such as carboxyls, aminos, thiol groups with O, N, and S atoms. In particular, thiol group is the most popular decorator due to the strong Au-S bond. For instance, 11-mercaptoundecanoic acid,^[14] 3-mercaptopropionic acid,^[15] dithioerythritol^[16] and alkanethiols with different chain lengths (2-mercaptoethanol, 4-mercaptobutanol, 6-mercaptohexanol, and 11-mercaptoundecanol)^[17] have been applied to AuNP-based colorimetric systems. However, these monodentate ligands as capping agents can readily desorb or decompose upon heating, and be displaced from the AuNPs surface over time,^[18-21] therefore hindering and limiting their application in sensing analyte.

To enhance the stability of decorators/AuNPs composites, multiple binding interactions between the decorators and AuNPs are an effective strategy. For AuNPs stabilized by multidentate ligands with a large number of binding groups, the probability of having all binding groups desorbed from the surface of AuNPs simultaneously would be much lower than that with only one binding group.^[21, 22] Therefore, the enhanced stability of AuNPs/analyte composites formed from multidentate ligands permits the development of colorimetric sensor that is more practical and sensitive than those derived from monodentate ligands. Recently, our group has reported the colorimetric sensor for Ag⁺ based on hyperbranched polyethylenimine (HPEI) as multidentate ligand, which exhibited an unusual color change from red to brown and drastically extended observing time due to the high stability of the AuNPs/analyte composites.^[23] In the process of sensing, amine groups form stable monolayer on AuNPs, and the binding of amine to AuNPs is described by a weak non-covalent binding.^[24] However, the binding strength of the amine groups to the Au is weaker than that of the thiol groups. It has been reported that the order of the binding strength is Au-S > Au-NH₂ > Au-COOH.^[25, 26] Therefore, the hyperbranched polyethylenimine derivative with a large number of thiol groups (HPEI-SH) as multidentate ligand will further improve the stability of AuNPs/analyte composites and be benefit for testing.

Herein, for the first time, the hyperbranched polyethylenimine derivative with thiol terminals was synthesized and used as multidentate ligand to stabilize AuNPs/analyte composites. This colorimetric sensor based on the binding and stabilization of multi-thiol groups to AuNPs/analyte composites has several advantages and great potential for monitoring Ag⁺: (1) There are three color changes successively during the detecting process, which can greatly improve the specificity and selectivity of this colorimetric sensor owing to the lower possibility of false positive results; (2) The multidentate ligand (i.e., HPEI-SH) not only achieves the binding of AuNPs to target Ag⁺ but also maintains their high stability for a long time after the sensing, which is convenient to record and observe the changes of the color and spectra; (3) Utilization of multidentate hyperbranched polymer instead of organic small molecules can easily vary the size, composition of the nanoparticles, and their interparticle distance, causing nanoparticles exhibit unique optical properties; (4) This colorimetric sensor exhibits high sensitivity and excellent selectivity toward Ag⁺; (5) The sensing process is very fast at room temperature, which is practical and convenient for colorimetric detection of Ag⁺; (6) Unique core-

shell nanostructures can increase the SPR absorption due to the interaction of neighboring AuNPs and synergistic effects of the AuNPs with AgNPs, generating dual signals by this special structure.

To the best of our knowledge, this is the first colorimetric sensor for Ag⁺ detection based on three color changes induced by multidentate ligand. This colorimetric sensor could achieve a fast readout, which is suitable for low-cost point-of-care diagnostics instead of the conventional optical imaging/detection methodologies.

2. Experimental Section

2.1 Materials.

Hyperbranched polyethylenimine ($M_n = 10^4$ g/mol, Aldrich) was dried under vacuum for 3 h at 45 °C prior to use. Polyethylene glycol (PEG, M.W. 1000) and polyvinylpyrrolidone (PVP, M.W. 10000) were purchased from Alfa Aesar. Gold(III) chloride hydrate ($\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$, Tianjin Yinda chemical company) was used as purchased. Methyl mercaptoacetate, ascorbic acid (AA), bovine serum albumin (BSA), sodium citrate and other chemicals were purchased from Shanghai Sinopharm Chemical Reagent Corporation. Wastewater containing silver was provided by Yantai Yuntong Plating Co., Ltd. The water used in the experiments was doubly distilled.

2.2 Apparatus and instruments

¹H NMR spectra of the HPEI-SH were carried out on a Varian INOVA 500MHz spectrometer. Electronic spectra of the particles were recorded on a T6 UV/Vis Spectrophotometer (Purkinje General, China). TEM images were carried out on a Philips TECNAI G2 F20 transmission electron microscope. The hydrodynamic size of the particles was determined by dynamic light scattering measurements (Zetasizer Nano-ZS90, Malvern Instruments). The concentration of Ag⁺ was determined by an Inductively Coupled Plasma spectrometer (ICP-9000, Shimadzu).

2.3 Synthesis of HPEI with 2-mercapto acetamide (SH) terminals (HPEI-SH).

Under a nitrogen atmosphere, a solution of methyl mercaptoacetate (0.62 g) in 5 mL water was added dropwise to 5 mL aqueous solution of HPEI (0.5013 g) at 25 °C with vigorous stirring. The mixture was allowed to photophobic react for 24 h. Then the reaction mixture was purified by dialysis against water through bag filter (MWCO 1000 g/mol) for 2 days and kept in dark. Finally, the solvent was removed under reduced pressure, and the obtained product was dried in vacuum at 40 °C for 24 h.

2.4 Preparation of citrate-capped AuNPs.

The preparation of AuNPs was similar to previous report.^[23] Briefly, 6.0 mL of HAuCl_4 solution (0.22%) was added to 115 mL of distilled water boiling in a three-necked flask. Then, 10 mL of sodium citrate solution (0.9%) was added while stirring vigorously. After continuous boiling for 20 min, it was allowed to cool to ambient temperature. The concentration of the AuNPs was estimated by Lambert-Beer's law (the extinction coefficient of ca. 13 nm AuNPs is $2.7 \times 10^8 \text{ M}^{-1} \text{ cm}^{-1}$ at 520 nm).^[27]

2.5 Colorimetric sensing of Ag⁺.

For Ag⁺ sensing, 1.5 mL of AA solution (0.06 mM to 2.5 mM) was added to the mixture of citrate-capped AuNPs (0.5 mL) and Ag⁺ (1.5 mL) at different concentrations (4.38 nM to 13 μM). After equilibrating at room temperature for 2 min, the first color change of the solution was recorded by a digital camera and a UV-vis spectrophotometer, respectively. Then, 1.5 mL of HPEI-SH (0.3 mg/mL) was added to the above solution. After equilibrating at room temperature for 2 min, the second color change of the mixture was recorded again. All detecting experiments were performed in triplicate. For TEM testing, the resulting mixture was subjected to centrifugation at 17 000 rpm for 10 min, removing the free HPEI-SH polymer.

2.6 Ag⁺ detection in real wastewater samples.

To evaluate the practicality of this colorimetric sensor, the HPEI-SH/AuNPs were used for the detection of Ag⁺ in real wastewater (Yantai Yuntong Plating Co., Ltd). The actual concentration of Ag⁺ was determined by an Inductively Coupled Plasma spectrometer.

3. Results and discussion

3.1 Synthesis and characterization of HPEI-SH

Scheme 1. Preparation of HPEI-SH and proposed Ag⁺ sensing mechanism based on the formation of core-shell Au-Ag NPs

Fig. 1. ¹H NMR spectra of (A) HPEI-SH and (B) HPEI

HPEI-SH was prepared (Scheme 1) and characterized by ¹H NMR spectroscopy. Compared with that of HPEI (Fig. 1B), the ¹H NMR spectrum of HPEI-SH exhibits a new signal located at 3.42 ppm (f in Fig. 1A), which is attributed to the methylene proton of the thiol ethyl amide groups, i.e., -NH-CO-CH₂-SH, indicating the successful attachment of SH groups to the HPEI. From the integration (*I*) ratio of the signals originated from the methylene proton of the thiol ethyl amide groups to that from the methylene proton of the HPEI in ¹H NMR spectra (Fig. 1A), the substitution degree of the SH groups on the surface of the HPEI can be calculated according to the equation (1). The degree of thiolation is about 26.32%, indicating that the HPEI-SH has a large number of thiol groups that can facilitate the further application as multidentate ligand.

$$\text{Degree of substitution} = (I(f)/2)/(I(g+h+i+j)/4) \quad (1)$$

where *I*(f) is the integral of the methylene protons of the thiol ethyl amide group; *I*(g+h+i+j) is the total integral of the methylene protons adjacent to the amine and amide groups of HPEI-SH.

3.2 Sensing Mechanism.

Fig. 2. TEM images of (A) AuNPs, (B) Au-Ag core-shell NPs and (C) larger Au-Ag core-shell NPs stabilized by HPEI-SH. DLS diagram of (D) AuNPs, (E) Au-Ag core-shell NPs and (F) larger Au-Ag core-shell NPs stabilized by HPEI-SH.

Fig. 3. Colorimetric response: (A) color changes and (B) absorption spectra of (a) the mixture of 0.65 nM citrate-capped AuNPs and HPEI-SH (66.7 mg/L); (b) 0.65 nM AuNPs with 6.3 mM AA in the presence of 4.38 μM Ag^+ with a red to brown color change; (c) HPEI-SH (66.7 mg/L) was added into the mixture of 0.65 nM AuNPs, 6.3 mM AA and 4.38 μM Ag^+ with a red to brown and brown to green color change; (d) 0.65 nM AuNPs with 6.3 mM AA in the presence of 4.38 μM Ag^+ after 24 h at room temperature;

Scheme 1 shows the sensing mechanism of the HPEI-SH/AuNPs as a colorimetric assay for Ag^+ detection. The prepared citrate-capped AuNPs with an average diameter of 12.5 ± 1.5 nm were highly dispersed and randomly distributed (Fig. 2A) because of the electrostatic repulsion of the anionic citrate on the AuNPs surface; they showed a surface plasmon resonance (SPR) peak at 520 nm (a in Fig. 3B) and appeared red (a in Fig. 3A). When AA was added into the AuNPs solution in the presence of Ag^+ , the color of AuNPs solution immediately changed from red to brown (b in Fig. 3A) and two new plasmon bands at 400 and 500 nm (b in Fig. 3B) were formed. This was because of the formation of Au-Ag core-shell NPs [23, 28-30] and such behavior was referred to as plasmon hybridization.[31] Also, the formation of Au-Ag core-shell NPs was confirmed by TEM (Fig. 2B), which showed that $\text{Ag}(0)$ was deposited onto the AuNPs surface through the strong affinity between Au and Ag,[9, 10] causing the red color of the AuNPs solution turned the brown color of the Au-Ag core-shell NPs solution. Importantly, after adding the HPEI-SH, the color of the Au-Ag core-shell NPs solution immediately changed from brown to green. This was because of the formation of larger Au-Ag core-shell NPs with attractive green (c in Fig. 3A).[32] The HPEI-SH with rich sulfur and nitrogen atoms had strong affinity with Au-Ag core-shell NPs due to the strong Ag-S covalent bond[33] and noble metal NPs-NH- covalent binding interaction,[26] causing the formation of the larger Au-Ag core-shell NPs and the color change of this system. TEM images (Fig. 2B and 2C) also supported the formation process. From Fig. 2B and 2C, it can be seen that most of the nanoparticles had a darker central part (Au as core) and a clearer outer part (Ag as shell), indicating the formation of the core-shell structure. After adding the HPEI-SH, the mean diameter of the Au-Ag core-shell nanoparticles was 103 ± 9 nm (Fig. 2C), which was larger than that (21.2 ± 2 nm, Fig. 2B) without HPEI-SH. The HPEI-SH with a large number of thiol groups, amino groups and a high steric hindrance effect not only induced Au-Ag core-shell NPs to aggregate larger Au-Ag core-shell NPs, but also stabilized them, thereby protecting NPs against further aggregation. However, the Au-Ag core-shell NPs would aggregate and precipitate out over time in the absence of the HPEI-SH, which was observed by the red shift of the absorption band (Fig. 3B Curve d) and a red-to-blue color change (Fig. 3A Picture d). Moreover, these change processes can also be evidenced by the DLS measurements. The DLS plots (Fig. 2D-2F) demonstrated the AuNPs, Au-Ag core-shell NPs and the larger Au-Ag core-shell NPs possessed average dynamic size of ca. 17.5 ± 3.2 , 27.2 ± 5.5 and 141 ± 12 nm, respectively, which were slightly larger than the corresponding results obtained from TEM. It

is because DLS measured the hydrodynamic diameter/radius and the NPs are suspended in water with a loose nanostructure.^[10]

In this sensing system, HPEI-SH with a large number of thiol groups and amino groups took the role of induced aggregation reagent and stabilizing reagent, simultaneously. We performed a preliminary study on the detection of Ag^+ according to the same operation based on the other polymer (e.g. PEG, PVP) and protein (BSA). As shown in Fig. S1, the colors of the Au-Ag core-shell NPs solution in the presence of PEG, PVP or BSA were always brown or pale yellow, not changing from brown or pale yellow to other color. Thus, the multidentate ligand (i.e., HPEI-SH) included in the assay is important and indispensable, which can induce the Au-Ag core-shell NPs to aggregate the larger core-shell NPs and stabilize them. Therefore, the changes in the solution color and UV-vis spectra, induced by the HPEI-SH, allowed the colorimetric sensing for Ag^+ in aqueous solution by naked eyes or UV-vis spectroscopy.

3.3 Effect of the concentration of AA.

Fig. 4. Effect of the concentration of AA on (A) the color changes (B) the absorption spectra and (C) the response ($A_{600\text{ nm}}$) of 0.65 nM AuNPs and 4.38 μM Ag^+ in the presence of HPEI-SH (66.7 mg/L).

From the sensing mechanism analysis, we can see that the AA played a role in reducing Ag^+ to $\text{Ag}(0)$, which can then directly deposit onto the AuNPs surface to form the Au-Ag core-shell NPs because of the high affinity between Au and Ag. As the concentration of AA increased, the deposition of reduced Ag^+ on the surface of the AuNPs increased.^[23] Previous works have shown that the resonant wavelength (i.e., $\lambda_{\text{Au-Ag}}$) can be approximately expressed as a linear fit of the Ag shell thickness.^[34, 35] In this sensing system, the Au-Ag core-shell NPs showed a broad resonance plasmon band and a gradual increase in absorbance at 550 to 700 nm (Fig. 4B) with color change from red through brown and finally to green or blue-green (Fig. 4A). Thus, the sensor responses can be expressed by the absorption value at 600 nm ($A_{600\text{ nm}}$). According to Fig. 4C, the $A_{600\text{ nm}}$ values went up sharply as the AA concentration increased from 0.62 mM to 20.2 mM and reached a maximum value of about 0.126. After the AA concentration was more than 20.2 mM, the $A_{600\text{ nm}}$ value did not significantly change. This was because AA could not only reduce the Ag^+ but could also react with the amino groups of HPEI-SH due to the acid-base interaction. When the concentration of AA reached 20.2 mM, all of the Ag^+ could be reduced completely and the $A_{600\text{ nm}}$ values were no longer changing. In fact, the redox potential of Ag^+ increases with the decrease in pH, so more Ag^+ can be reduced at low pH, thus leading to a stronger response. From Fig. S2, pH of 4.2 (i.e., 20.2 mM of AA) was selected for the following experiments.

3.4 Effect of the AuNPs and HPEI-SH concentration on detection of Ag^+ .

Fig. 5. Photographs of 20.2 mM AA and 4.38 μM Ag^+ solutions with different AuNPs and HPEI-SH concentrations in the (A) presence and (B) absence of 4.38 μM Ag^+ . Absorption spectra of 20.2 mM AA and

4.38 μM Ag^+ solutions with different AuNPs and HPEI-SH concentrations in the (C) presence and (D) absence of 4.38 μM Ag^+ . ($[\text{AuNPs}]/[\text{HPEI-SH}]=1\text{ nM}/102.7\text{ mg/L}$).

It is well known that the sensitivity of colorimetric sensor is highly dependent on the AuNPs concentration.^[10] In this sensing system, we investigated the concentrations of AuNPs (0.075 to 0.8 nM) and HPEI-SH (16.7 to 166.7 mg/L) with a $[\text{AuNPs}]/[\text{HPEI-SH}]$ ratio of 1 nM/102.7 mg/L on the response of the colorimetric assay in the presence and absence of Ag^+ . By comparing the changes of the color (Fig. 5A and 5B) and absorption spectra (Fig. 5C and 5D) before and after sensing, we can see that the optimum concentration of AuNPs for sensing Ag^+ was above 0.3 nM. At relatively high concentrations of AuNPs, the deposition of reduced $\text{Ag}(0)$ on the surface of a single Au particle decreased, taking a long time to occur a distinct color change of the AuNPs solution from red through brown to green. At relatively low concentration of AuNPs, the plasmon resonance of the AuNPs was rapidly masked or attenuated by that of the growing Ag deposition, thus taking a shorter time to occur a distinct color change. However, when the concentration of the AuNPs was lower than 0.3 nM, the red and the plasmon resonance peak of the AuNPs were not obvious (Fig. 5B and 5D). Therefore, the concentration of AuNPs was fixed at 0.3 nM in the follow experiments.

3.5 Sensitivity of the colorimetric sensor.

Fig. 6. (A) Photographs and (B) Absorption spectra of 0.3 nM AuNPs and 20.2 mM AA with different Ag^+ concentrations. (C) The $A_{600\text{ nm}}$ values versus the concentrations of Ag^+ .

Fig. 6 shows the changes in the solution color and absorption spectra at different concentrations of Ag^+ , ranging from 8.76×10^{-9} to 1.27×10^{-4} M. As the concentration of the Ag^+ increased, the color of the AuNPs rapidly changed from red through brown to blue-green or green at Ag^+ concentrations of 1.09×10^{-5} to 1.27×10^{-4} M and red through pale-brown to pale-green at Ag^+ concentrations of 8.76×10^{-9} to 5.47×10^{-6} M (Fig. 6A), suggesting the Ag^+ concentration-dependent colorimetric response of AuNPs. As shown in the absorption spectra of the AuNPs solutions (Fig. 6B), the absorbance of the broad resonance plasmon peak at 550 to 700 nm gradually increased with increasing Ag^+ concentration. We observed that the $A_{600\text{ nm}}$ values increased linearly with increasing Ag^+ concentration within the range of 8.76×10^{-9} to 1.27×10^{-4} M with a correlation coefficient of 0.9937 (Fig. 6C). The limit of detection (LOD) of Ag^+ under the optimum conditions was estimated to be 8.76×10^{-8} M by the naked eyes and 8.76×10^{-9} M by the UV-vis spectra, which were significantly lower than that of the United States Environmental Protection Agency standard limit in drinking water ($0.1\text{ mg/L}\approx920\text{ nM}$).^[36] To explore the practicality of the developed colorimetric sensor, we compared the obtained results with that of other reported colorimetric methods (Table S1). This LOD was below that of the many other colorimetric sensors reported previously.

3.6 Selectivity of the colorimetric sensor for determination of Ag^+ .

Fig. 7. Selectivity of the sensor: (A) Photographs, (B) Absorption spectra and (C) Response ($A_{600\text{ nm}}$) of 0.3 nM AuNPs and 20.2 mM AA solutions containing Ag^+ (4.4 μM) and several other metal ions (44 μM) in the presence of HPEI-SH (66.7 mg/L).

To evaluate the selectivity of HPEI-SH/AuNPs to Ag^+ , other metal ions including Na^+ , Cs^+ , Mg^{2+} , Sr^{2+} , Ba^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Mn^{2+} , Cu^{2+} and Hg^{2+} were tested. As shown in Fig. 7, the addition of 10-fold higher concentrations of other metal ions to the system could not cause obvious changes in the color (Fig. 7A) and UV-vis absorption spectrum (Fig. 7B) of the AuNPs solution except Ag^+ and Hg^{2+} . After addition of 4.4 μM Ag^+ , the color of the AuNPs solution changed from red through to green due to the formation of large Au-Ag core-shell NPs. In the presence of 43.8 μM of the remaining metal ions, the colors of the AuNPs solutions were all similar to that of the blank except for Hg^{2+} , which only changed from red to fawn. It's worth mentioning that Hg^{2+} and Ag^+ usually would interfere with each other in colorimetric sensing system based on the AuNPs.^[9, 10] However, in our system, the color change of the solution and the UV-vis absorption spectrum were all different in the presence of Hg^{2+} and Ag^+ , so there was no need to choose masking agents. We tested several Hg^{2+} solutions varied from 109 nM to 43.8 μM . As shown in Fig. S3A, an obvious color change from red to pale yellow was observed in the presence of Hg^{2+} , which was different from that from red through brown to green in the presence of Ag^+ . In addition, the UV-vis absorption spectra also have significant difference between Hg^{2+} (Fig. S3B) and Ag^+ (Fig. 7B) system. Thus, this colorimetric assay showed a high and attractive selectivity toward Ag^+ , with no need for masking agents. Fig. 7C showed that the $A_{600\text{ nm}}$ value of the colorimetric assay was up to 0.17 upon the addition of Ag^+ , but the values for other metal ions were all about 0.015 except 0.079 of Hg^{2+} . As observed from the comparative results, as a new sensing strategy, all other tested metal ions did not interfere with the determination of Ag^+ . This colorimetric sensor based on three color changes of AuNPs induced by the multidentate ligand (HPEI-SH) showed good selectivity for Ag^+ detection.

3.7 Ag^+ detection in real wastewater samples.

Fig. 8. Absorption spectra and Photographs (inset) of real silver-containing wastewater, 0.3 nM AuNPs and 20.2 mM AA in the presence of HPEI-SH.

To evaluate the practicality of the developed colorimetric sensor, we applied HPEI-SH/AuNPs in the detection of Ag^+ in real wastewater. As shown in Fig. 8, the $A_{600\text{ nm}}$ values of the sample 1 and 2 were 0.166 and 0.117, respectively. Based on the linear relationship in Fig. 6C, the concentrations of the Ag^+ should be 71.3 and 43.5 μM , respectively, which were similar to that (74.8 and 45.6 μM) measured by ICP. The experimental data of the practical applications demonstrated this colorimetric sensor could be used for Ag^+ detection in real sample.

4. Conclusions

A new multidentate ligand (i.e., HPEI-SH) with a large number of thiol and amine groups was successfully prepared and characterized. In this work, we have developed a novel colorimetric method for the sensitive and selective detection of Ag^+ based on three color changes of the AuNPs solution. The proposed method with color change from red through brown to green was different from that of usual colorimetric assays with color change from red to blue or red to purple of previous reported AuNPs. HPEI-SH not only achieves the binding of Au-Ag core-shell NPs but also maintains their high stability for a long time after the sensing, providing drastically extended observing time for operator. The sensing probe showed high sensitivity with a LOD of 8.76×10^{-8} M by the naked eyes and 8.76×10^{-9} M by the UV-vis spectra and a good linear relationship ($R^2=0.9937$) ranging from 8.76×10^{-9} to 1.27×10^{-4} M. The proposed method had three color changes during the detecting process, which can greatly improve the specificity and selectivity to Ag^+ over several other metal ions. Furthermore, this simple and rapid approach can be used for Ag^+ detection in real sample using only the naked eye and UV-vis spectra. As such, the multidentate ligand supported colorimetric sensor has a great and broad application prospect in the analytical field.

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Scheme 1

Fig. 1

Fig. 2

Fig. 3

Fig.4

Fig. 5

Fig.6

Fig. 7

Fig. 8

Graphical Abstract

The novel red to brown to green colorimetric sensor for Ag⁺ detection based on the multidentate ligand stabilized Au-Ag core-shell NPs showed high sensitivity and selectivity.