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The colorimetric detection of Pb^{2+} by using sodium thiosulfate and hexadecyl trimethyl ammonium bromide modified gold nanoparticles†

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A simple, rapid colorimetric detection method for Pb^{2+} in aqueous solution has been developed by using sodium thiosulfate (Na$_2$S$_2$O$_3$) and hexadecyl trimethyl ammonium bromide (CTAB) modified gold nanoparticles (Au NPs). Na$_2$S$_2$O$_3$ was added into the Au NP solution and thiosulfate ions (S$_2$O$_3^{2-}$) were adsorbed on the surface of the Au NPs due to electrostatic interactions. Au atoms on the surface of the Au NPs were then oxidized to Au(I) by the O$_2$ that existed in the solution in presence of thiosulfate. The addition of Pb^{2+} (the final concentration was lower than 10 μM), accelerated the leaching of the Au NPs, and Pb–Au alloys also formed on the surface of the Au NPs. There was an obvious decrease in the surface plasmon resonance (SPR) absorption of the Au NPs. The lowest concentration for Pb^{2+} that could be detected by the naked eye was 0.1 μM and using UV-vis spectroscopy was 40 nM. This is lower than the lead toxic level defined by the US Environmental Protection Agency (US EPA), which is 75 nM. In this method, CTAB, as a stabilizing agent for Au NPs, can accelerate the adsorption of S$_2$O$_3^{2-}$ on the surface of the Au NPs, which shortened the detection time to within 30 min. Moreover, this detection method is simple, cheap and environmentally friendly.

Introduction

Pb(II), as one of the most toxic metallic ions, is well-known to be non-degradable. It has posed a serious threat to the environment and human health due to its accumulation.[1,2] Pb pollution not only damages the kidneys, liver, gastrointestinal tract and neurotoxic system, but can also affect hemoglobin production.[3] It is worth noting that Pb can inhibit brain development in children. The US Environmental Protection Agency (US EPA) defined that the lead toxic level was 75 nM.[4] The determination of trace levels of Pb has attracted extensive attention in recent years.[5] Although traditional detection methods, such as atomic absorption/emission spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectrometry (XRF) and anodic stripping voltammetry (ASV) are sensitive and accurate, they require expensive and sophisticated instruments and a complicated sample preparation process. Therefore traditional detection methods are not suitable for rapid on-site analysis.

Noble metal nanoparticles have unique surface plasmon resonance absorption properties due to their size, shape and inter-particle distances.[6] They have been extensively used to explore colorimetric sensors for the sensitive and selective detection of oligonucleotides,[7] proteins[8] and heavy metallic ions such as Hg^{2+},[9–11] Cd^{2+}[12] and Cr(VI).[13,14] Thus far, several colorimetric sensing methods for Pb^{2+} based on gold nanoparticles (Au NPs) have also attracted considerable attention.[15] A series of functional DNAzyme-based sensors using Au NPs were developed by the Lu[16–20] and Dong[21] research groups. Although these sensors demonstrate high sensitivity and selectivity, they require complex labeling or surface functionalization chemistry and the synthesis of DNA oligomers is complex and expensive. Moreover, the stability of the DNA sensors limits their applications in real samples. Thomas *et. al.*, researched a gallic acid functionalized Au NPs system for Pb^{2+} that showed low sensitivity.[22] The Jiang[23] group detected Hg^{2+}, Pb^{2+} and Cu^{2+} simultaneously based on the color change induced by the aggregation of papain functionalized Au NPs, and they found that the lowest detectable concentration of Pb^{2+} was 0.2 μM. The Li[24] group designed podand triazole linked Au NPs and used them as colorimetric probes for Pb^{2+}; and they found that the lowest detectable concentration was 7 μM. They also reported an ultrasensitive dynamic light scattering assay for Pb^{2+} with pM sensitivity by using aza-crown-ether-modified silver nanoparticles.[25] Several molecules

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involving thiol end groups, such as 11-mercaptoundecanoic acid,[26] glutathione[27] and thiol alkyl phosphate,[5] were also used to modify Au NPs for the detection of Pb^{2+}. However, thiol end groups are easily oxidized. Although the above methods have different characteristics, they all need to be improved to be suitable for practical applications. In addition to these detection methods based on the aggregation of Au or Ag NPs, Huang and coworkers[28] developed a colorimetric and non-aggregation based Au NPs probe for the detection of Pb^{2+}, with a limit of detection (LOD) of 0.5 nM, based on the fact that Pb^{2+} ions and 2-mercaptoethanol accelerated the leaching rate of Au NPs. However, this method is complicated and it needs nearly 2 h to detect Pb^{2+}, which is not suitable for a rapid detection assay.

In this paper, we present a simple colorimetric probe for the rapid detection of Pb^{2+} based on the leaching of hexadecyl trimethyl ammonium bromide (CTAB) modified Au NPs induced by $Na_2S_2O_3$ and Pb^{2+}.[28] The quantification of Pb^{2+} can be obtained according to the change in the surface plasmon resonance (SPR) absorption of the Au NP solutions. This detection method is simple (as it is without complicated synthesis and modification techniques), cheap (as it uses an inorganic sulfur compound – $Na_2S_2O_3$, and not DNAzyme), and environmentally friendly (sulfhydryl molecules, which are noxious and easily oxidized are not used) and the use of a positively charged surfactant (CTAB) shortens the detection time, to within 30 min.

Results and discussion

Sensing strategy

In recent years, thiosulfate, as an alternative leachant for the extraction of gold, has attracted much attention.[28] The sensing strategy of this study is shown in Scheme 1. Firstly, CTAB modified Au NPs were synthesized, which was followed by the adsorbtion of $S_2O_3^{2-}$ onto the surface of the CTAB modified Au NPs via electrostatic interactions. A redox reaction occurred at the solid–liquid interface and $Au(S_2O_3)_2^{3-}$ complexes formed immediately on the surface of the Au NPs. The addition of Pb^{2+} caused an acceleration in the leaching of the Au NPs, which caused a decrease in the SPR absorption of the
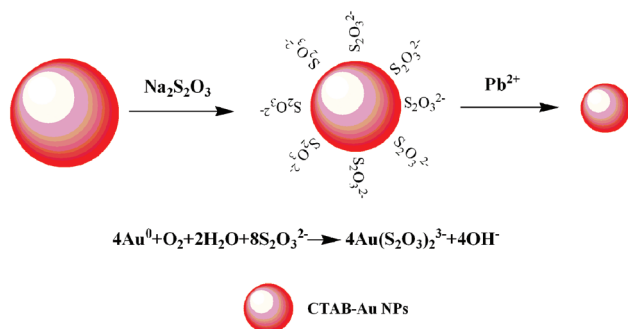
Au NPs. The quantity of Pb^{2+} can be obtained according to the change in the SPR absorption. The color of the Au NP solution gradually became lighter due to the leaching of the Au NPs, and this can semi quantify the amount of Pb^{2+} in aqueous solution.

Characterization

The transmission electron microscopy (TEM) images of Au NPs, $Na_2S_2O_3$–Au NPs and $Na_2S_2O_3$–Au NPs + Pb^{2+} in Fig. 1 reveal the corresponding morphologies and sizes of the Au NPs. When $Na_2S_2O_3$ was added to the CTAB modified Au NP solutions, the size of the Au NPs decreased from 14.2 to 12.6 nm (Fig. 1a and 1b) which is due to the redox reaction between O_2 and the gold atoms on the surface of the Au NPs in presence of thiosulfate. After the addition of Pb^{2+}, the diameter of the Au NPs continued to diminish to 11.2 nm (when the concentration of Pb^{2+} is 1 μM) and 9.6 nm (when the concentration of Pb^{2+} is 50 μM) (Fig. 1c and 1d), which is also consistent with the phenomenon reported in the literature.[28] The phenomenon is due to the leaching of the Au NPs. The particle size of the sample with 50 μM Pb^{2+} is smaller than that with 1 μM Pb^{2+} because more Au NPs have been dissolved with the increase in the Pb^{2+} concentration.

The effect of $Na_2S_2O_3$ and pH

In this work, many factors such as the concentration of $Na_2S_2O_3$ and pH influenced the detection of Pb^{2+}. Fig. S1a (in the ESI†) reveals that the higher the concentration of $Na_2S_2O_3$, the lighter the solution's color. Although higher concentrations of $Na_2S_2O_3$ are beneficial for the sensitivity of the detection of Pb^{2+} (Cu^{2+}, Co^{2+}, Cd^{2+} will affect the detection of Pb^{2+} when the concentration of $Na_2S_2O_3$ is too high), there is no benefit to the selectivity. A lower concentration of $Na_2S_2O_3$
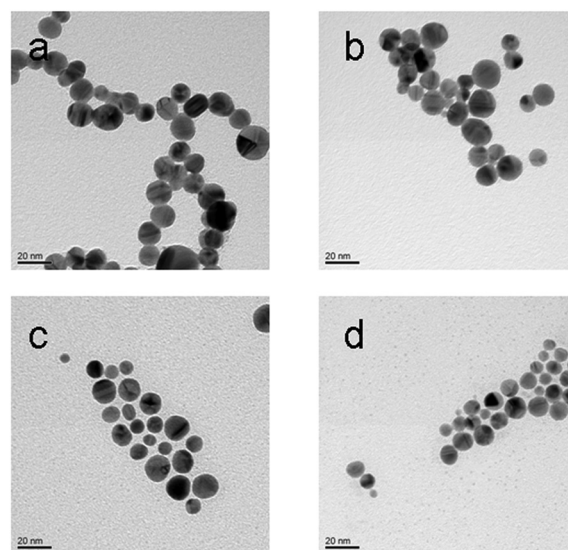
Fig. 1 TEM images of the Au NPs in samples of (a) Au NPs, (b) $Na_2S_2O_3$–Au NPs, (c) $Na_2S_2O_3$–Au NPs + Pb^{2+} (the final concentration is 1 μM) (d) $Na_2S_2O_3$–Au NPs + Pb^{2+} (the final concentration is 50 μM).

$$4Au^0 + O_2 + 2H_2O + 8S_2O_3^{2-} \longrightarrow 4Au(S_2O_3)_2^{3-} + 4OH^-$$

CTAB-Au NPs

Scheme 1 A strategy for the colorimetric detection of Pb^{2+}.

is not propitious for the sensitivity. Therefore, a $Na_2S_2O_3$ concentration of 0.1 M was used in the experiment.

$S_2O_3^{2-}$ ions will decompose and form sulfide, sulfate, sulfite, tetrathionate, trithionate, polythionates and polysulfides in acidic media. Therefore, high pH values may increase the stability of the $S_2O_3^{2-}$ ions and the $S_2O_3^{2-}$–Au NPs. However, passive layers of $Pb(OH)_2$, PbO or $Au(OH)_3$ may form on the surface of the CTAB–Au NPs when the pH value is too high, which will retard the leaching of the Au NPs.[28] Fig. S1b† shows that the color of the solution is at its lightest when the pH value is 9. That is to say that we can get the highest sensitivity when the pH value is about 9. After optimization, a pH of 8.95 was used in this experiment.

Sensitivity

According to the above optimized experimental conditions, the minimum detectable concentration of Pb^{2+} was recorded *via* the color change of the Au NP solution. It is clearly observed that the color of the solutions became lighter when the concentration of Pb^{2+} was increased from 0–8 μM (Fig. 2a). The detection limit of Pb^{2+} was 0.1 μM by the naked eye, which can be seen from Fig. 2b (blank sample and 0.1 μM Pb^{2+}).

The SPR absorption of the $Na_2S_2O_3$–Au NP solutions with various concentrations of Pb^{2+} was also recorded in a quantitative assay (Fig. 3a). It was clearly observed that the SPR absorption decreased dramatically with an increase in Pb^{2+} concentration, which is due to the fact that the Pb^{2+} ions accelerated the leaching of the Au NPs in the presence of thiosulfate.[28] A linear relationship between $(Ex_{530}^0 - Ex_{530})/Ex_{530}^0$ and the Pb^{2+} concentration was obtained over the range from 1 to 6 μM with a linear coefficient of 0.99 (Ex_{530} means absorbance of the Au NP–$Na_2S_2O_3$ solution after Pb^{2+} was added, Ex_{530}^0 means absorbance of the Au NP–$Na_2S_2O_3$ solution without Pb^{2+}). The lowest detectable concentration of Pb^{2+} is 0.04 μM, which is lower than the allowed maximum level of 0.75 μM by the US EPA.[4] Furthermore, from Fig. 4 it can be seen that the absorbance intensity of the $Na_2S_2O_3$–Au NPs in the presence of 2 μM Pb^{2+} decreased with time and was almost constant after 30 min. This means that the colorimetric method is a rapid method for detecting Pb^{2+} in aqueous solutions.

However, when the concentration of Pb^{2+} was higher than 8 μM, the color of the Au NP solution gradually became purple and the SPR absorption increased and was red shifted (Fig. 2a and Fig. S2†). This may be due to the fact that PbO or PbO_2

formed on the surface of the Au NPs, which retarded the leaching of the Au NPs.[29] This conclusion can be confirmed by the X-ray photoelectron spectroscopy (XPS) data (Fig. 5), using the binding energy (285 eV) of the alkyl chain C 1s orbital as an internal reference. In Fig. 5b, it is shown that the binding energy of Pb $4f_{7/2}$ is 138 eV. Compared with Fig. S3a† (Pb_3O_4), we can conclude that PbO and PbO_2 exist on the surface of the Au NPs when the concentration of Pb^{2+} is too high. This result also means that some Pb^{2+} was oxidized to Pb^{4+}.

Fig. 5c shows two sets of 2p doublet peaks for sulfide and sulfate at about 162 and 168 eV, respectively, which are due to the existence of $Na_2S_2O_3$ (Fig. S3b†). After Pb^{2+} was added, the intensity of the peak at 168 eV decreased relative to the peak at 162 eV, which means that part of the plus six valent S was deoxidized, and this result supports the fact that some Pb^{2+} was oxidized to Pb^{4+}.

XPS was also used to investigate the oxidation states on the surface of the Au NPs in the absence and presence of $Na_2S_2O_3$ (Fig. 5a). The binding energy for Au $4f_{7/2}$ in the Au NPs without $Na_2S_2O_3$ is 83.8 eV, which corresponds to a polynuclear Au(I)–ligand complex.[30] After reacting with $Na_2S_2O_3$, the binding energy of the Au NPs increased due to the passivation of the surface of the Au NPs by $S_2O_3^{2-}$,[28] which is also consistent with the data reported in the literature.[28]

Selectivity

The selectivity of the proposed detection method was evaluated by adding various types of metal ions (Ca^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+}, K^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Hg^{2+}, Al^{3+} and Mg^{2+}) and anions (SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-, $C_2O_4^{2-}$, CO_3^{2-} and $Cr_2O_7^{2-}$) into the detection system ($Na_2S_2O_3$–Au NPs) separately. The final concentrations of the metallic ions and anions in the detection system were 10 μM and 50 μM, respectively. The corresponding photo images and UV-vis spectra are shown in Fig. 6. It is clear that only the sample containing Pb^{2+} faded compared with the blank sample, all other metal ion and anion samples retained their red color (Fig. 6a and 6b). The absorbance intensity of the sample containing Pb^{2+} showed an obvious decrease compared with the blank sample, and the other metal ion and anion samples under the same conditions (Fig. 6c). These results mean that the sensing system has an excellent selectivity for Pb^{2+} in aqueous solution.
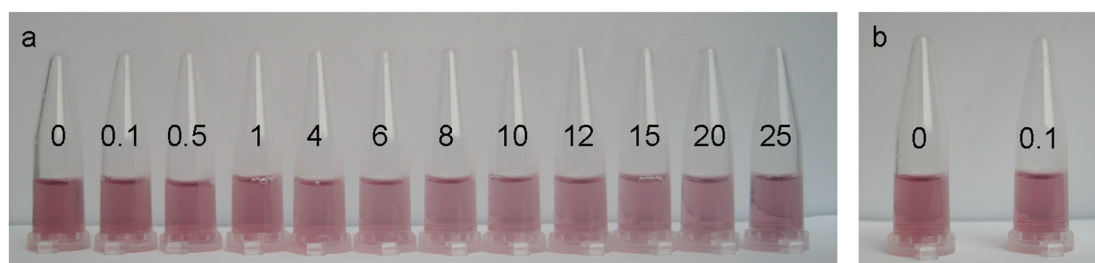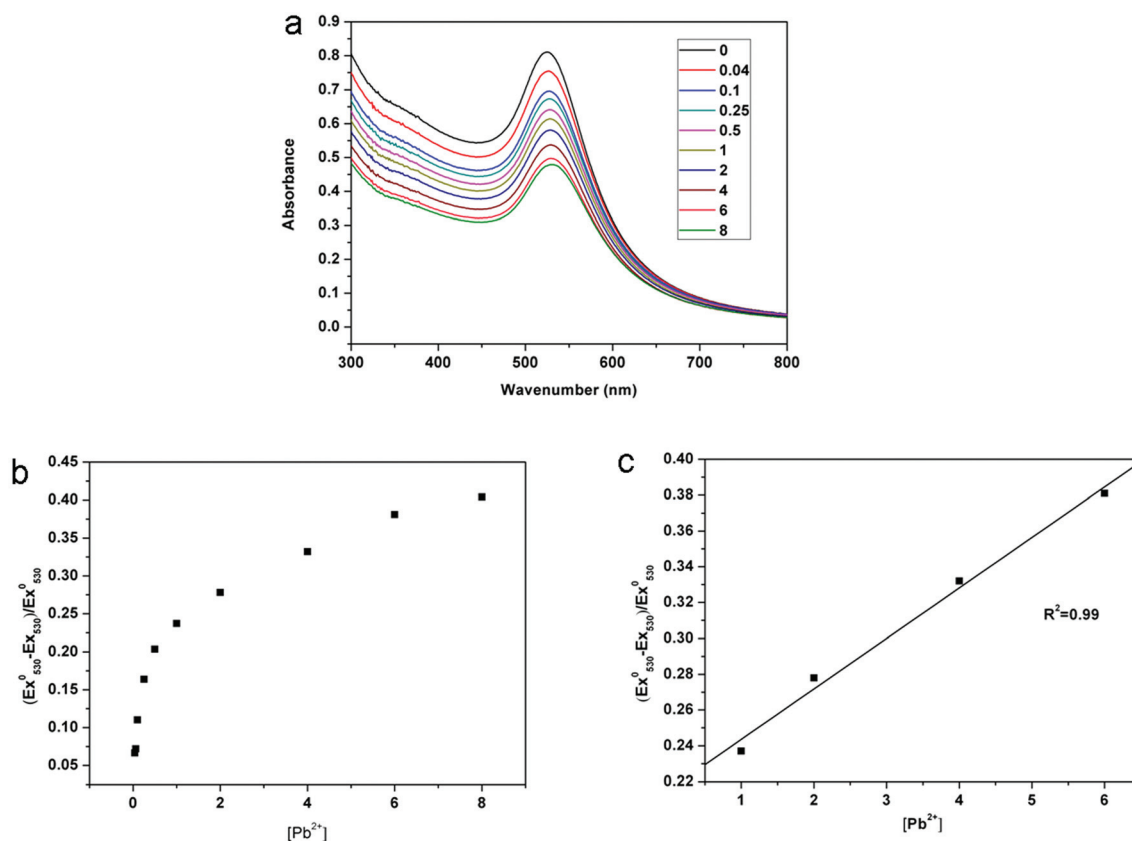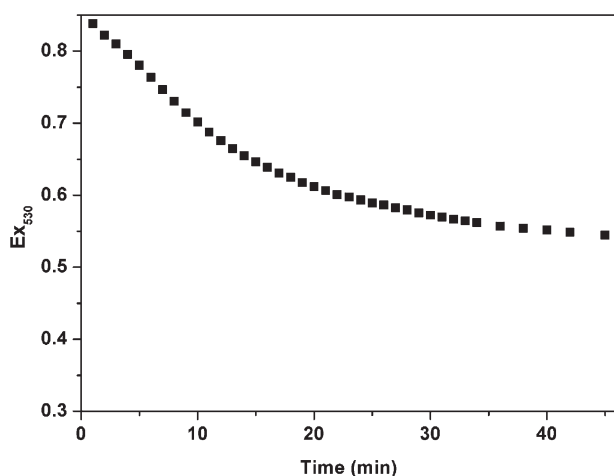

Fig. 2 The corresponding photo images of different concentrations of Pb^{2+} (0, 0.1, 0.5, 1, 4, 6, 8, 10, 12, 15, 20 and 25 μM).

Fig. 3 (a) The UV-vis absorption spectra of samples with different concentrations of Pb^{2+} (0, 0.04, 0.1, 0.25, 0.5, 1, 2, 4, 6 and 8 μM). (b) $(Ex^0_{530} - Ex_{530})/Ex^0_{530}$ of $Na_2S_2O_3$–Au NPs in the presence of Pb^{2+} (0–8 μM). (c) A plot of $(Ex^0_{530} - Ex_{530})/Ex^0_{530}$ *versus* the concentrations of Pb^{2+} in the range of 1–6 μM.

Fig. 4 Absorbance changes of the Au NPs at 530 nm in the presence of 2 μM Pb^{2+}.

The detection mechanism

From the UV-vis spectra, TEM images and XPS data, we can deduce a detection mechanism for our study. When the concentration of Pb^{2+} is lower than 8 μM, the Pb^{2+} ions accelerate the leaching of the Au NPs in the presence of thiosulfate and Pb–Au alloys formed on the surface of the Au NPs, which led

to the dramatic decrease of the SPR absorption of the Au NPs. When the concentration of Pb^{2+} is higher than 8 μM, Pb^{2+} and thiosulfate caused the leaching of the Au NPs, PbO and PbO_2 formed on the surface of the Au NPs, and the leaching of the Au NPs was retarded.

Practical applications

To validate the practicability of this detection method, the concentration of Pb^{2+} in a real environmental water sample (Ningbo Environment Monitoring Center, Ningbo, China) was measured by applying this method. As the real water sample contained no Pb^{2+}, we added a certain amount of $Pb(NO_3)_2$ to the real water sample. The detection result of Pb^{2+} ranged from 4 μM to 6 μM (Fig. S4†), and this result agrees well with that obtained from inductively coupled plasma-atomic emission spectrometry (ICP-AES) (5.5 μM).

Conclusions

A rapid, highly sensitive and selective colorimetric sensor for the detection of Pb^{2+} has been developed on the basis of the leaching of CTAB modified Au NPs induced by $Na_2S_2O_3$ and Pb^{2+}, which led to color fading and a decrease in the absorption intensity of the Au NP solution. The detection method is simple, and does not use expensive reagents or organic
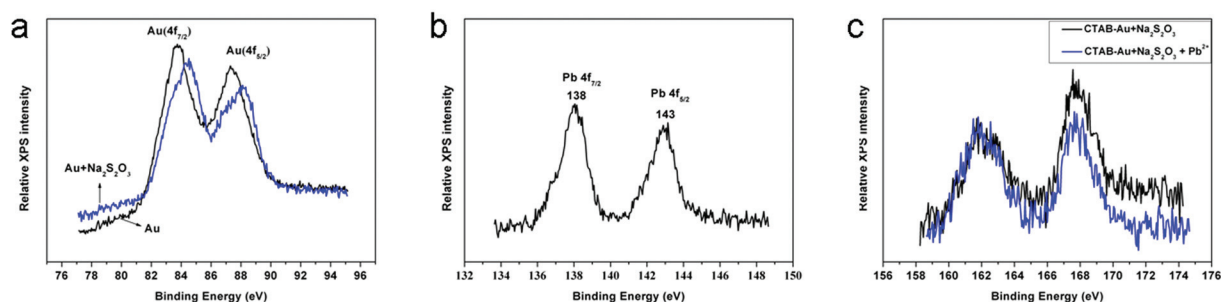
Fig. 5 (a) Au 4f core-level photoelectron spectra of Au NPs before and after reacting with $Na_2S_2O_3$, (b) Pb 4f XPS spectrum of the sample containing $Na_2S_2O_3$–Au NPs + Pb^{2+} (the final concentration is 50 μM), (c) XPS spectra of sulfur.
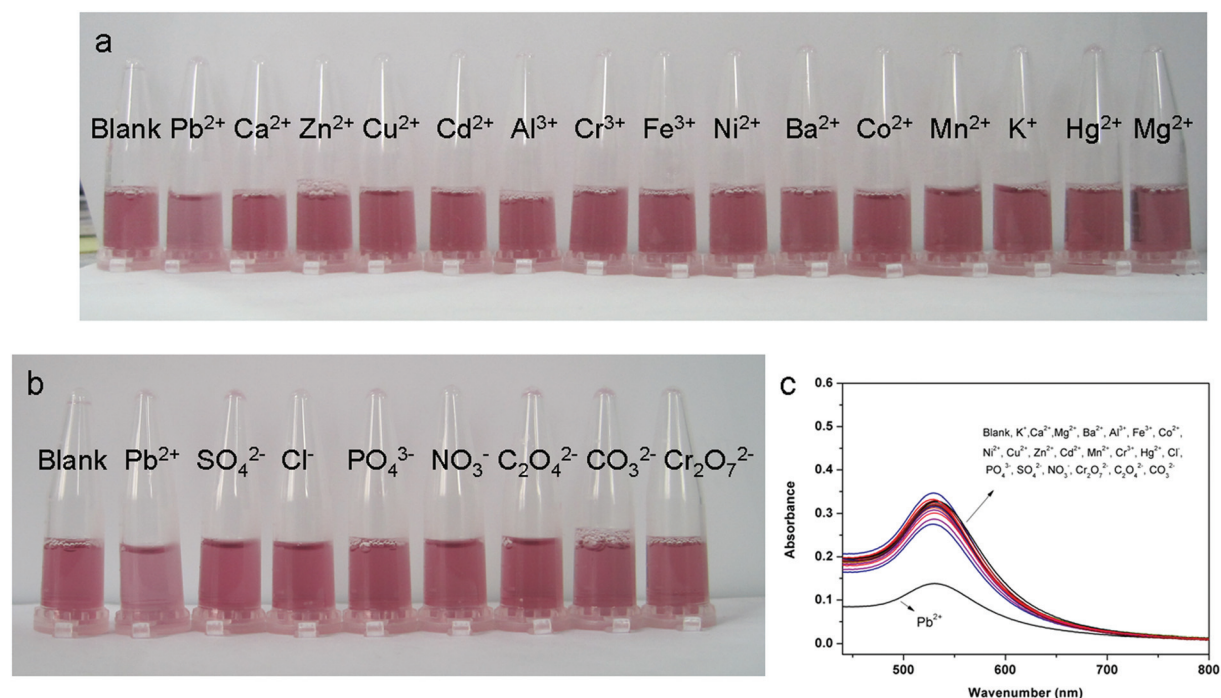
Fig. 6 (a), (b) The corresponding photo images and (c) UV-vis absorption spectra of the Au NP solutions containing 10 μM metal ions and 50 μM anions, respectively.

reagents which are easily oxidized. Under optimal conditions, the colorimetric method has high sensitivity for Pb^{2+} (LOD = 40 nM) with short detection time (within 30 min). The colorimetric detection method for Pb^{2+} has a promising practicality in real environmental samples.

Experimental

Chemicals

All analytical reagent-grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). These chemicals were used as received without further purification. Mill-Q water (18 MΩ cm resistance) was used to prepare all the solutions in this work.

Preparation of CTAB modified Au NPs

CTAB modified Au NPs were prepared according to Murphy's method with some modifications.[31] Specifically, 8 mL of 5 mM $HAuCl_4 \cdot 3H_2O$ aqueous solution was added to 85 mL of Mill-Q water; 4 mL of 20 mM CTAB aqueous solution was injected into the mixture with vigorous stirring. Then 2.4 mL of freshly prepared 0.1 M sodium hydroborate aqueous solution was added dropwise and the reaction was left for 1 h.

Detection of Pb^{2+}

The pH of the CTAB modified Au NP solution was first adjusted to 8.95 using 0.1 M NaOH aqueous solution. 40 μL of freshly prepared 0.1 M $Na_2S_2O_3$ aqueous solution was added to 560 μL of the above Au NP solution; the mixture solution was

shaken and stored for 5 min at room temperature. Different concentrations of Pb^{2+} were added to each of mixture solutions. UV-vis absorption spectra were recorded after 30 min. The selectivity of the detection method for Pb^{2+} over other metal ions (Ca^{2+}, Cd^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Mn^{2+}, K^+, Cu^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Al^{3+}, Mg^{2+} and Hg^{2+}) and anions (SO_4^{2-}, Cl^-, PO_4^{3-}, NO_3^-, $C_2O_4^{2-}$, CO_3^{2-} and $Cr_2O_7^{2-}$) was investigated under the same conditions. The final concentrations of metallic ions and anions were 10 μM and 50 μM, respectively.

Characterization

TEM images were recorded on a Tecnai F20 TEM instrument with an acceleration voltage of 200 kV. UV-vis spectra were recorded with a Lambda 950 UV-vis spectrophotometer from Perkin Elmer in the range of 300–800 nm. XPS was performed using an AXIS Ultra DLD instrument with Mg Kα radiation as the X-ray source.

Acknowledgements

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