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ARTICLE TYPE

# A Label-free Colorimetric Sensor for Pb<sup>2+</sup> Detection Based on the Acceleration of Gold Leaching by Graphene Oxide

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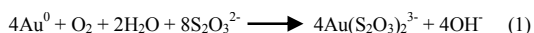
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**Abstract:** In this work, we developed a novel, label-free, colorimetric sensor for Pb<sup>2+</sup> detection based on the acceleration of gold leaching by graphene oxide (GO) at room temperature. Gold nanoparticles (AuNPs) can be dissolved in thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) aqueous environment in the presence of oxygen, however, the leaching rate is very slow due to the high activation energy (27.99 kJ/mol). In order to enhance the reaction, some accelerators should be added. Compared with the traditional accelerators (metal ions or middle ligands), we found that GO could efficiently accelerate the gold leaching reaction. Kinetic data demonstrate that the dissolution rate of gold in the Pb<sup>2+</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-GO system is 5 times faster than that without GO at room temperature. In addition, the effects of surface modification and the nanoparticle size on the etching AuNPs were investigated. Based on GO-accelerated concentration-dependent colour changes of AuNPs, a colorimetric sensor for the Pb<sup>2+</sup> detection was developed with a linear range from 0.1 to 20 μM and the limit of detection (LOD) was evaluated to be 0.05 μM. This colorimetric assay is simple, low-cost, label-free, and has a great potential applications in environmental field.

## Introduction

Over the past decades, gold nanoparticles (AuNPs)-based colorimetric assay is one of the most extensively studied colorimetric strategies in the fields of chemical, physical, material and biomedical science,<sup>1-3</sup> for their unique capability of visual detection by the naked eye. The colorimetric analytical platforms are mainly based on the distance-dependent optical property of the AuNPs.<sup>4</sup> Based on the different motives stimulated interparticle crosslinking aggregation mechanism, some simple, portable and cost-efficient colorimetric sensors have been developed for the detection of DNA,<sup>5</sup> metal ions<sup>6-8</sup> and small molecules, such as cysteine,<sup>9</sup> melamine,<sup>10</sup> cocaine,<sup>11</sup> ATP,<sup>12</sup> glucose,<sup>13</sup> and dopamine.<sup>14</sup> However, a significant drawback is that the undesirable aggregation of AuNPs may occur in real samples with high ionic strength or the existence of impurities. Therefore, some colorimetric strategies based on the non-aggregate AuNPs (for example, gold leaching) have also attracted fast-growing interest in recent years.



As shown in reaction (1), gold can be dissolved in thiosulfate (S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) aqueous solution in the presence of oxygen.<sup>15</sup> During this process, the concentration of AuNPs decreases and leads to the color change of the solution. However, the rate of the reaction (1) is so slow that the reaction time can be up to several hours because of the high activation energy (E<sub>a</sub> = 27.99 kJ/mol).<sup>16</sup> It was reported that metal ions and middle ligands could be

employed to accelerate the dissolution of gold in S<sub>2</sub>O<sub>3</sub><sup>2-</sup> leaching systems. Chen et al<sup>17</sup> found that Pb<sup>2+</sup> ions could accelerate the leaching rate of AuNPs with the help of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> and 2-mercaptoethanol and a colorimetric sensing strategy for Pb<sup>2+</sup> based on the catalytic etching AuNPs was developed for the first time. But the reaction time was about 2 hours and 2-ME was toxic. Lou et al<sup>18</sup> developed a colorimetric sensor for Cu<sup>2+</sup> based on the Cu<sup>2+</sup>-accelerated gold leaching using silver coated AuNPs as probes. The gold leaching was completed in 60 min by the accelerating of Cu<sup>2+</sup>. Hasab and coworkers<sup>19</sup> reported that gold could be dissolved in chloride/hypochlorite-sulfide system and the leaching reaction time was reduced as 45 min, however, hypochlorite is a strong oxidants which is environmental unfriendly. In Cu<sup>2+</sup>-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-NH<sub>3</sub> system, AuNPs was successfully dissolved within 30 min, however, the reaction temperature was up to 50 °C.<sup>20</sup> Therefore, it is still limited to the strategy for accelerating gold leaching in mild and green system with short reaction time.

The rise of graphene oxide (GO) with its amazing properties has stimulated exquisite interest in various fields, especially in the applications of sensing.<sup>21-24</sup> In our previous work, GO was used as an efficient fluorescence quencher and an accelerator to enhance the leaching of AuNPs for fluorescence detection of Pb<sup>2+</sup> ions.<sup>25</sup> Although this strategy was very sensitive for Pb<sup>2+</sup> determination, the fluorescent reporter, amino pyrene, should be labeled on AuNPs. Accordingly, the experimental procedure is complicated, and amino pyrene is toxic and hazardous to environment.

In this work, a simple, label-free, and sensitive colorimetric

sensor for  $\text{Pb}^{2+}$  was constructed based on the acceleration of gold leaching by GO at room temperature. Typically,  $\text{Pb}^{2+}$  could accelerate the leaching rate of gold because the activation energy is reduced accompanying with the generation of  $\text{AuPb}$ .<sup>15,26</sup> In addition, GO could enrich the reactants due to the large surface area and strong adsorption ability. Thus, the gold leaching process occurs rapidly and the reaction reaches the balance within 20 min. The effect factors for gold leaching in  $\text{Pb}^{2+}$ - $\text{S}_2\text{O}_3^{2-}$ -GO system are well investigated, such as the surface modification, size of AuNPs as well as reaction temperature. The colorimetric assay is simple, rapid, eco-friendly and low-cost, and has a great potential application in the environmental field.

## Experimental

### Reagents and Instruments

Hexadecyltrimethylammonium bromide (CTAB) was purchased from Sigma Aldrich (Shanghai, China). Gold chloride trihydrate, sodium citrate,  $\text{PbCl}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , ethanol and the other reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China). UV spectra were recorded on a Shimadzu UV-2550 spectrophotometer (Shimadzu, Japan). Dynamic light scattering (DLS) measurements were conducted using a Nano ZS zetasizer analyzer (Malvern, England). Transmission electron microscopy (TEM) images were performed on the JEM-2100F transmission electron microscope (JEM, Japan).

### Preparation of Bare AuNPs

Bare AuNPs were synthesized through the reduction of  $\text{NaBH}_4$  according to our previous work.<sup>25</sup> Briefly, 10  $\mu\text{L}$  aliquots of freshly prepared  $\text{NaBH}_4$  (0.1 M) were added slowly into  $\text{HAuCl}_4$  (0.25 mM, 8 mL) at 22 °C until a stable purple-colored colloid was observed, and the reaction was left for 24 h at 22 °C. The concentration of the AuNPs was calculated according to Beer's law as 2.3 nM.

### Preparation of CTAB modified AuNPs

CTAB modified AuNPs (CTAB-AuNPs) were synthesized by the method of Pastoriza et al.<sup>27</sup> Simply, CTAB was introduced in the procedure of preparation of bare AuNPs as above-mentioned step. The CTAB-AuNPs were centrifuged twice at 4500 rpm to remove excess polyelectrolyte, and redispersed in 5.0 mL of Milli-Q water.

### Preparation of citrate modified AuNPs with different sizes

Citrate modified AuNPs (citrate-AuNPs) with different sizes were synthesized following a protocol reported by Bastus et al.<sup>28</sup> Briefly, a solution of 2.2 mM sodium citrate in Milli-Q water (150 mL) was heated with a heating mantle in a 250 mL three-necked round-bottomed flask for 15 min under vigorous stirring. After boiling, 1.0 mL of  $\text{HAuCl}_4$  (25 mM) was injected. The color of the solution changed from yellow to bluish gray, and then to soft pink within 10 min. The as-prepared AuNPs (approximately 10 nm) were functionalized with negatively charged citrate ions and exhibited good dispersion.

AuNPs with larger sizes were obtained by a typical seeds growth method. Briefly, the obtained citrate-AuNPs solution was cooled until 90 °C. 1.0 mL of sodium citrate (60 mM) and 1.0 mL

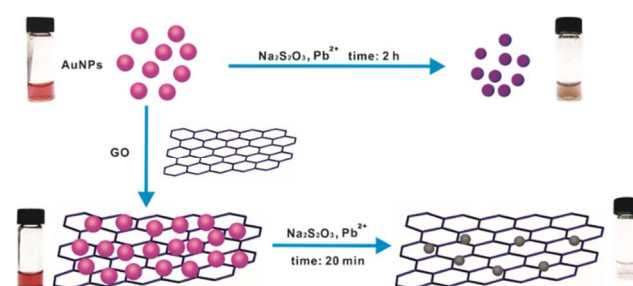
of a  $\text{HAuCl}_4$  solution (25 mM) were sequentially injected into the same reaction vessel, with a time delay of approximately 2 min. By repeating this growth process for 6 cycles (sequential addition of 1.0 mL of 60 mM sodium citrate and 1.0 mL of 25 mM  $\text{HAuCl}_4$ ), AuNPs with sizes from approximately 10 nm to 35 nm were obtained. These AuNPs were collected through centrifuging and sorted by the growth cycles ( $n=0, 1, 2, 3, 4, 5, 6$ ).

### Protocol of colorimetric assay

Gold leaching reaction was accelerated with the introduction of GO according to our previous work.<sup>25</sup> Firstly, 20  $\mu\text{L}$  of GO solution (0.5 mg/mL) was added to the as-prepared AuNPs solution overnight. Then 10  $\mu\text{L}$   $\text{Na}_2\text{S}_2\text{O}_3$  (0.1 mM) and different concentrations of  $\text{Pb}^{2+}$  were sequentially added into 1.0 mL of the GO-AuNPs aqueous solution, and were incubated at room temperature for 20 min. After that, the UV-vis absorption spectra were measured.

## Results and Discussions

Scheme 1 shows the colorimetric sensor of  $\text{Pb}^{2+}$  based on the gold leaching reaction. AuNPs can be dissolved in  $\text{Pb}^{2+}$ - $\text{S}_2\text{O}_3^{2-}$  system and the color of the AuNPs dispersion gradually changes from red to gray. However, this process is very slow and the solution color don't show any notable changes until 2 hours. When GO was introduced to the system, it was found that gold leaching was accelerated and distinctive color change was observed. The color of AuNPs colloids changed quickly from initial red to nearly colorless within 20 min.



Scheme 1. Schematic illustration of colorimetric sensing of  $\text{Pb}^{2+}$  based on the enhancement etching AuNPs with GO.

### Gold leaching in $\text{S}_2\text{O}_3^{2-}$ system

In order to understand the crucial roles of  $\text{Pb}^{2+}$  and GO for gold leaching, the surface plasma resonance (SPR) absorption of the AuNPs was investigated. Fig. 1a shows the UV-vis spectrum of AuNPs and typical SPR signal located at 520 nm is observed. After mixed with GO, ignorable SPR change is observed (Fig. 1b). It indicates that GO cannot induce the obvious changes in the proximity of Au colloids and lead to the interparticle distance-dependent color change. In addition, the absorbance intensities of both AuNPs and GO-AuNPs mixture show negligible changes for 4 hours, indicating the stability is very well. When 1.0 mM  $\text{S}_2\text{O}_3^{2-}$  was added to the system, the adsorption intensity decreased (Fig. 1c) because  $\text{S}_2\text{O}_3^{2-}$  could react with gold atoms in presence of  $\text{O}_2$  to form  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complexes (as described in reaction (1)) due to the low spin  $d_{10}$   $\text{Au}^+$  ions.<sup>29</sup> However, the  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complexes could densely cover the surface of AuNPs and retard the proceeding of the reaction. After the addition of  $\text{Pb}^{2+}$  (Fig.

1d), the SPR absorbance of AuNPs was further reduced, indicating a large amount of gold dissolution because of the  $\text{Pb}^{2+}$ -catalyzed leaching of AuNPs in the  $\text{S}_2\text{O}_3^{2-}$  system. Meanwhile, a slight red shift was observed. It might ascribe to the fact that  $\text{Pb}^{2+}$  could react with gold atom to form  $\text{AuPb}_2$ ,  $\text{AuPb}_3$  alloy or metallic Pb on the surfaces of AuNPs, which resulted in a slight aggregation of AuNPs.<sup>30,31</sup>

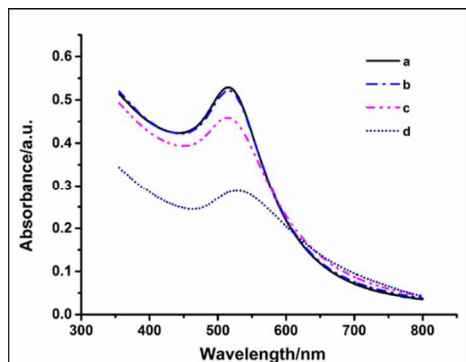


Figure 1. UV-vis spectra of (a) AuNPs and (b) GO-AuNPs, (c) GO-AuNPs- $\text{S}_2\text{O}_3^{2-}$ , and (d) GO-AuNPs- $\text{S}_2\text{O}_3^{2-}$ - $\text{Pb}^{2+}$ , respectively. The concentrations of GO,  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{PbCl}_2$  were 10  $\mu\text{g/mL}$ , 1.0 mM and 5.0  $\mu\text{M}$ , respectively.

The TEM image of the as-prepared AuNPs is shown in Fig. 2a. The morphologies of AuNPs are generally spherical and the particle sizes are approximately 10 nm. Fig. 2b shows the TEM image of the GO-AuNPs mixture. GO sheets display the paper-like morphology and AuNPs are densely adsorbed on the plane of GO. It can be easily observed that AuNPs are enriched on the surface of GO nanosheets. After addition of  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Pb}^{2+}$ , a great deal of AuNPs are leached and few AuNPs are observed on the surface of GO nanosheets (Fig. 2c). This phenomenon confirms the successfully etching of AuNPs.

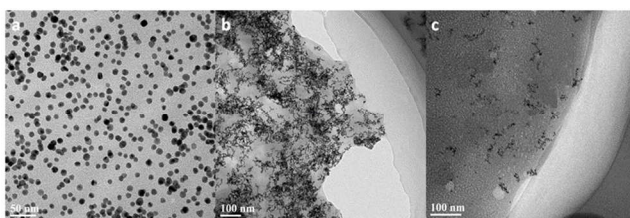


Figure 2. The TEM images of (a) AuNPs and (b) GO-AuNPs, (c) GO-AuNPs with  $\text{S}_2\text{O}_3^{2-}$  (1.0 mM) and  $\text{Pb}^{2+}$  (5.0  $\mu\text{M}$ ).

### The accelerating effect of GO

The leaching rate of AuNPs is quite slow because of the high activation energy of the reaction (1) ( $E_a=27.99$  kJ/mol). The leaching rate of gold is accelerated in the presence of metal mediators, such as  $\text{Pb}^{2+}$ , because the generation of  $\text{AuPb}_y$  can reduce the activation energy. Nevertheless, the leaching rate of AuNPs is still low. Although GO can accelerate the gold leaching process in the presence of  $\text{S}_2\text{O}_3^{2-}$  and  $\text{Pb}^{2+}$ , the mechanism remains unclear. Given the structure and strong adsorption properties of GO, we supposed that GO could enrich AuNPs and  $\text{Pb}^{2+}$ , which equivalently increases the concentration of reactants and induces stronger etching. Graphene and the derivatives have been reported to show well physisorption for AuNPs.<sup>32,33</sup> The TEM image of GO-AuNPs also demonstrates the enrichment of

AuNPs by GO (Fig. 2b). In addition, the enrichment effect of GO could not result in remarkable aggregation of AuNPs based on the SPR signal shown in Fig. 1b. Besides,  $\text{Pb}^{2+}$  could strongly bind to GO through metal-carbonyl coordination.<sup>34</sup> Overall, AuNPs and  $\text{Pb}^{2+}$  could be adsorbed on the surface of GO and facilitate the gold leaching. Moreover, some defects and oxygen containing groups of GO may act as complexing agents to improve the leaching rate of the AuNPs.

$$-\frac{d[A]}{dt} = k[A] \quad (2)$$

In order to in-depth evaluation the accelerating effect by GO, the kinetic analysis was applied to the system using the data at 25  $^\circ\text{C}$  (Fig. 3). The concentration of the AuNPs is calculated as 2.3 nM according to Beer's law using an extinction coefficient of  $3.7 \times 10^8$   $\text{M}^{-1} \text{cm}^{-1}$  for the 10 nm AuNPs.<sup>31</sup> The concentration of  $\text{H}_2\text{O}$  and  $\text{O}_2$  are considered as constant, while the concentration of AuNPs is much less than  $\text{Pb}^{2+}$  and  $\text{S}_2\text{O}_3^{2-}$ . Therefore, the gold leaching reaction is considered as pseudo-first order reaction.<sup>35</sup> Although Fig. 3 shows parabola curves in a long range reaction time, the experiment data of initial reaction display well linear regression (Insert a, b). According to the rate equation of first order reaction (2),  $-\ln([A]/[A_0])$  is linear regressed versus reaction time.<sup>36</sup> In both cases, correlation coefficient is higher than 0.99, which confirms the proposed kinetics for the gold leaching. Compared to the  $k$  values in the presence of GO, the gold leaching reaction is about 5 times faster than that in the  $\text{Pb}^{2+}$ - $\text{S}_2\text{O}_3^{2-}$  system.

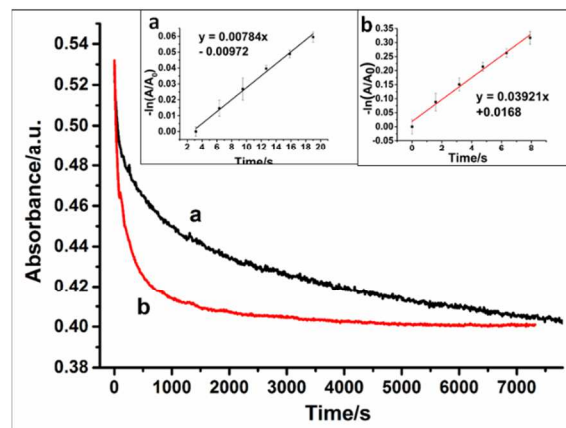


Figure 3. Time-dependent absorbance change of AuNPs after the addition of  $\text{S}_2\text{O}_3^{2-}$  (1.0 mM) and  $\text{Pb}^{2+}$  (5.0  $\mu\text{M}$ ) in the (a) absence and (b) presence of GO (10  $\mu\text{g/mL}$ ). Inset: the pseudo-first order rate constants of gold leaching reaction (a) without and (b) with GO.

### The influence of reaction temperature on gold leaching

Given temperature as a common critical factor for reaction rate, the time-dependent SPR changes of AuNPs in the presence and absence of GO were studied. As shown in Fig. 4, the absorbance intensity of AuNPs decreases as the reaction time increases due to the leaching of AuNPs by  $\text{Pb}^{2+}$ , and the decline rate increases with the increase of temperature. The gold leaching reaction couldn't reach equilibrium until 2 h at 15  $^\circ\text{C}$  in the absence of GO (Fig. 4a). However, when the temperature is up to 30  $^\circ\text{C}$ , the absorbance remains virtually unchanged within 20 min. It is indicated that reaction temperature is a key factor for gold



leaching. In the AuNPs-GO-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-Pb<sup>2+</sup> system, the leaching process reaches equilibrium within 20 min even at low temperature (Fig. 4b). Moreover, the reaction rate has hardly changed when the temperature exceeds 25 °C. Therefore, GO plays a significant role in the process of gold leaching and 25 °C is selected as the reaction temperature.

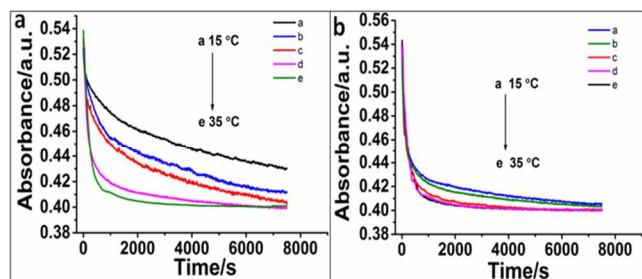


Figure 4. Time-dependent SPR changes of AuNPs after the addition of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (1.0 mM) and Pb<sup>2+</sup> (5.0 μM) in the (a) absence and (b) presence of GO (10 μg/mL) at different temperature: a) 15 °C, b) 20 °C, c) 25 °C, d) 30 °C, and e) 35 °C.

#### The influence of nanoparticle size on the leaching rate

In order to evaluate the effect of the nanoparticle size on leaching rate, citrate-capped AuNPs with different sizes were obtained by a typically seeds-growth procedure. The TEM images of citrate-AuNPs after different growth rounds are shown in Fig. 5a-d. It can be seen that the sizes of citrate-AuNPs vary from 10 to 33 nm. In addition, the sizes of AuNPs for different growth cycles are also measured by DLS and the results are shown in Table 1. These results are well consistent with these of TEM observation.

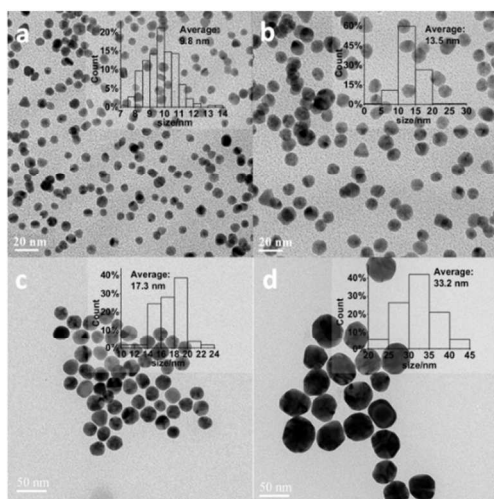


Figure 5. TEM images and corresponding size distribution of citrate-AuNPs after different growth cycles, a) n=0, b) n=2, c) n=4 and d) n=6.

Table 1 The DLS data of AuNPs after different growth cycles.

Cycles	0	2	4	6
Size/nm	9.3	12.4	19.0	35.0

The effect of nanoparticle size on the leaching rate is shown in Fig. 6. It is clearly seen that citrate-AuNPs with larger size show relatively lower leaching rate. Our results are well agreement with the work of Lou et al<sup>18</sup>, in which the leaching of Ag/Au NPs would lead to dramatic decrease in the SPR absorption as the size

of Ag/Au NPs decreased. It is because that the absorption coefficient of AuNPs increases with the increase of the nanoparticle size.<sup>31</sup> As a result, the concentration of AuNPs decreases with the increment of the nanoparticle size. Since the concentration of GO remains unchanged, the numbers of AuNPs on the GO nanosheets are reduced, which would slow down the leaching rate. Therefore, 10 nm AuNPs were selected as the probes in the further study.

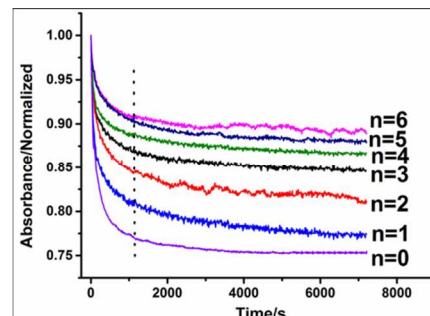


Figure 6. Time-dependent absorbance changes of AuNPs with different sizes in the GO-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-Pb<sup>2+</sup> system. The concentrations of GO, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and PbCl<sub>2</sub> were 10 μg/mL, 1.0 mM and 5.0 μM, respectively.

#### The influence of surface modification of AuNPs on the leaching rate

The effect of surface modification of AuNPs on the leaching rate was also investigated. The most common stabilizers for AuNPs, CTAB and citrate, are taken into consideration in this work. The time-dependent SPR changes of bare AuNPs, citrate-AuNPs and CTAB-AuNPs in the GO-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-Pb<sup>2+</sup> system are shown in Fig. 7. As a result, the fastest etching speed are observed for the bare AuNPs. We inferred that the surface modification by CTAB and citrate could stabilize the AuNPs, therefore, these stabilizers are not easy to be displaced by S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, which is an alternative leachant for the extraction of gold. Actually, CTAB is reported as a stronger stabilizer than citrate,<sup>37,38</sup> therefore, the slowest leaching rate is observed for CTAB-AuNPs. The resulting is also consistent with the work of Zhang et al., in which CTAB-AuNPs were etched by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and Pb<sup>2+</sup>, which led to relatively slow color fading and a decrease in the absorption intensity.<sup>39</sup> Therefore, 10 nm bare AuNPs obtained by the method of NaBH<sub>4</sub> reduction were selected as the colorimetric probes.

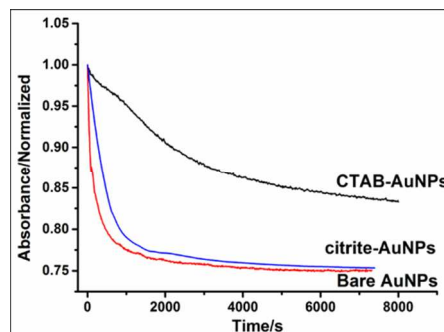


Figure 7. Time-dependent SPR absorbance of different AuNPs in the GO-S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-Pb<sup>2+</sup> system. The size for CTAB-AuNPs, citrate-AuNPs and bare AuNPs is about 10 nm. The concentrations of GO, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and PbCl<sub>2</sub> were 10 μg/mL, 1.0 mM and 5.0 μM, respectively.

#### Colorimetric sensing of Pb<sup>2+</sup>

In view of the above-mentioned investigation, a novel colorimetric strategy for  $\text{Pb}^{2+}$  measurement was developed on the basis of enhanced etching bare AuNPs (ca. 10 nm) by GO in the solution of  $\text{Na}_2\text{S}_2\text{O}_3$  at room temperature. In addition, the detection conditions were further optimized. We find that the concentration of GO could affect the performance of the  $\text{Pb}^{2+}$  sensor. With the increment of the concentration of GO from 2 to 14  $\mu\text{g}/\text{mL}$ , the enhancement leaching AuNPs was observed while the concentration is below 10  $\mu\text{g}/\text{mL}$ . However, higher concentration of GO could affect the naked-eye recognition of  $\text{Pb}^{2+}$  because of the color of itself. Therefore, the concentration of GO was selected as 10  $\mu\text{g}/\text{mL}$ . The pH of the solution also has effect on the response of the sensor. We find that the sensor shows best performance with solution pH about 8.0. Under the optimized condition, the naked-eye recognition of  $\text{Pb}^{2+}$  were shown in Fig. 8. It can be seen that the color of the aqueous solution gradually changed until nearly colorless with the increase of the concentration of  $\text{Pb}^{2+}$  ions. It is indicates that the proposed strategy could be used for naked-eye colorimetric detection  $\text{Pb}^{2+}$  ions.

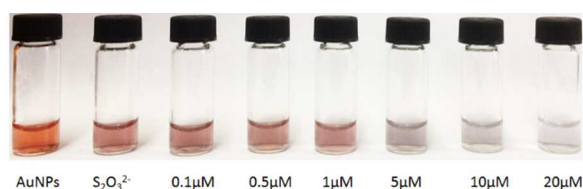


Figure 8. The solution color of AuNPs, AuNPs +  $\text{S}_2\text{O}_3^{2-}$  (1.0 mM), and AuNPs +  $\text{S}_2\text{O}_3^{2-}$  (1.0 mM) +  $\text{Pb}^{2+}$  (0.1, 0.5, 1, 5, 10, 20  $\mu\text{M}$ ) in the presence of GO (10  $\mu\text{g}/\text{mL}$ ).

Fig. 9 shows the UV-vis spectra of AuNPs with different concentration of  $\text{Pb}^{2+}$ . It can be seen that the absorbance peak shows slightly red-shift and the intensity decreases sharply, which ascribes to the  $\text{Pb}^{2+}$  catalyzed leaching of AuNPs with the help of GO. The extent of red-shifting and damping of the absorbance peak gradually increased as the increase of the concentration of  $\text{Pb}^{2+}$ . The absorbance displays a well linear response over the range from 0.1 to 20  $\mu\text{M}$  with a correlation coefficient (R) of 0.9913 (inset of Fig. 9). The limit of detection (LOD,  $S/N=3$ ) for  $\text{Pb}^{2+}$  ions is as low as 0.05  $\mu\text{M}$ .

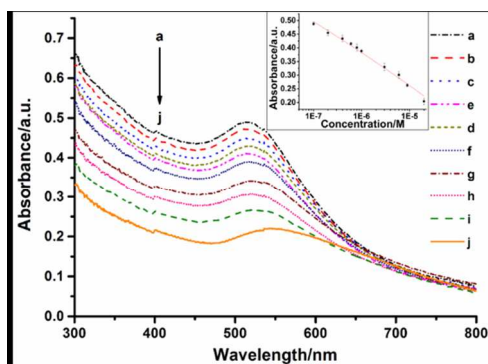


Figure 9. UV-vis spectra of AuNPs in GO (10  $\mu\text{g}/\text{mL}$ )- $\text{Na}_2\text{S}_2\text{O}_3$  (1.0 mM) with the addition of  $\text{Pb}^{2+}$  ions ( (a) 0, (b) 0.1, (c) 0.3, (d) 0.6, (e) 0.9, (f) 1, (g) 3, (h) 6, (i) 10 and (j) 20  $\mu\text{M}$ ). Inset: standard calibration curve for  $\text{Pb}^{2+}$  detection.

The complexity of environmental samples presents a great

challenge to the analytical methods for metal ion detection. Thus, the selectivity of the assay was carried out in the presence of other metal ions ( $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ) that may coexist in the samples to the leaching reaction solution. Remarkably, as shown in Fig. 10, no obvious UV-vis signal and color changes were observed for the other metal ions, compared with that obtained for  $\text{Pb}^{2+}$ . Furthermore, we find that the SPR response and the solution color of the mixture of  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  are the similar as that of  $\text{Pb}^{2+}$ . Besides, anions, such as  $\text{Cl}^-$  and  $\text{NO}_3^-$  are also investigated and no interference is observed. It indicates the proposed strategy shows excellent selectivity for the colorimetric measurement of  $\text{Pb}^{2+}$ .

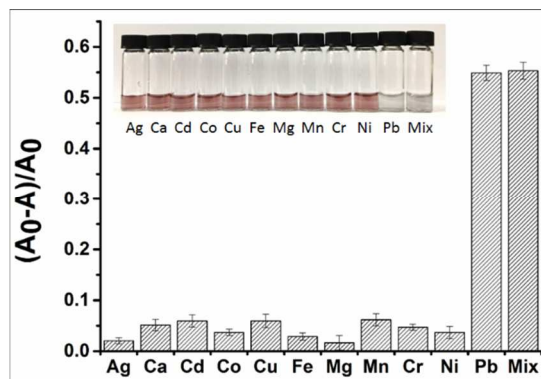


Figure 10. Relative UV-vis responses of AuNPs in GO (10  $\mu\text{g}/\text{mL}$ )+ $\text{Na}_2\text{S}_2\text{O}_3$  (1.0 mM) system towards various metal ions (10  $\mu\text{M}$  for  $\text{Ag}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$  and the mixtures of  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ).  $A_0$  is the absorbance of solution before leaching reaction and A is the absorbance of solution after leaching reaction. Inset: the corresponding color changes of AuNPs.

### $\text{Pb}^{2+}$ detection in real samples

To evaluate the applicability of the colorimetric assay toward real samples, drinking pure water and river water samples were tested. The standard addition method were applied for  $\text{Pb}^{2+}$  determination in the drinking pure water. As shown in Table 2, the recovery for  $\text{Pb}^{2+}$  is over the range of 93 to 105.3%. And  $\text{Pb}^{2+}$  was successfully detected in the 10-fold diluted river water with the concentration of 474.5  $\mu\text{g}/\text{L}$ . These results demonstrate the colorimetric sensing system is applicable for  $\text{Pb}^{2+}$  detection with good precision and accuracy even in real environmental samples.

Table 2. Recovery for  $\text{Pb}^{2+}$  detection in the drinking pure water and river water samples ( $n=3$ )

Samples	$\text{Pb}^{2+}$ ( $\mu\text{g}/\text{L}$ )	Addition ( $\mu\text{M}$ )	Recovery (%)	RSD (%) ( $n=3$ )
Drinking pure water	0	0.2	93	1.54
	0	5	102.4	7.23
	0	10	105.3	2.12
River water	474.5	-	-	3.73

### Conclusion

A simple, rapid, label-free and sensitive colorimetric sensing system is developed based on the enhancement leaching bare AuNPs induced by  $\text{Pb}^{2+}$  and GO. With the help of the GO, the  $\text{Pb}^{2+}$ -catalyzed gold leaching reaction was 5 times accelerated and

the procedure could be completed within 20 min. In addition, the etching process is environmental friendly and no toxic agent is used. The SPR change of AuNPs provides an excellent platform for rapid and selective measurement Pb<sup>2+</sup>. Under optimal conditions, the colorimetric sensing system shows a linear detection of Pb<sup>2+</sup> from 0.1 to 20 μM and a detection limit of 0.05 μM. This colorimetric sensor has the advantages of simplicity, rapidity, high sensitivity and selectivity. With respect to these merits, the sensing system shows potential application in a real sample without complicated processes of sample pretreatment. In addition, the strategy promises to be a practical tool for the in situ monitoring of Pb<sup>2+</sup> because no complicated instruments is demanded.

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## Notes and references

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## Table of Contents

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