Colorimetric assay for sulfate using positively-charged gold nanoparticles and its application for real-time monitoring of redox process

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Supporting Information

1. Characterization

The morphology and size of the cysteamine-capped AuNPs were characterized by transmission electron microscopy (TEM) and dynamics light scattering (DLS).

![Size Statistics Report by Number](image)

*Figure S1. Size characterization of the cysteamine-AuNPs by dynamics light scattering (DLS).

The FI-IR spectra of cysteamine-capped AuNPs can confirm the successful coating of cysteamine on the surface of AuNPs. As shown in Fig. S3, the IR data contain characteristic features of amine (-NH$_3^+$): the peaks at 3425 cm$^{-1}$. 
Figure S2. The FT-IR spectra of (A) cysteamine and (B) cysteamine-capped AuNPs.

Figure S3. Zeta potential of the (A) cysteamine-AuNPs and in the presence of (B) $\text{PO}_4^{3-}$, (C) $\text{CO}_3^{2-}$, (D) $\text{NO}_3^-$ or $\text{S}_2^-$, (E) $\text{SO}_4^{2-}$ in the NaAc-HAc buffer (10 mM NaAc, pH=4.0).
Figure S4. Direct observation and corresponding absorption spectra measurement of cysteamine-AuNPs in the presence of \( \text{PO}_4^{3-}, \text{NO}_3^{-}, \text{CO}_3^{2-}, \text{S}^{2-}, \) and \( \text{SO}_4^{2-} \) in the NaAc-HAc buffer (10 mM NaAc, pH=4.0).

2. Investigation of sensing conditions for sulfate analysis

Prior to the experiments, the optimization sensing conditions, including reaction buffer, and the optimal pH value of buffer, were investigated.

Figure S5. (A) Real-time monitoring of the absorption behavior \( (A_{650}/A_{520}) \) of the nanoparticles at different conditions; (B) UV-vis absorption spectra of the nanoparticles at different conditions: cysteamine-AuNPs in H\(_2\)O and NaAc-HAc buffer or in the presence of 50 \( \mu \)M sulfate.
Figure S6. The plots of the ratio $A_{650}/A_{520}$ of cysteamine-AuNPs (or cysteamine-AuNPs + 50 µM sulfate) vs. the pH value of (A) NaAc/HAc buffer, (C) ammonium acetate buffer, (E) potassium formate/formic acid buffer and (G) KH$_2$PO$_4$/phosphoric acid, respectively. Investigation of the influence of pH of (B) NaAc/HAc buffer, (D) ammonium acetate buffer, (F) potassium formate/formic acid buffer and (H) KH$_2$PO$_4$/phosphoric acid on the ratio $A_{650}/A_{520}$ of cysteamine-AuNPs towards sulfate, respectively. Defined as $\Delta D = (A_{650}/A_{520})_{\text{sulfate}} - (A_{650}/A_{520})_{\text{blank}}$. 
3. **Real samples analysis**

In order to test the feasibility of our proposed method in real samples, we studied the possible applicability of cysteamine-AuNPs probe for the direct measuring of $\text{SO}_4^{2-}$ in real samples. The unknown concentrations of $\text{SO}_4^{2-}$ in different samples were measured using both cysteamine-AuNPs and ion chromatography method. The results were listed in Table S1.

### Table S1. Determination of $\text{SO}_4^{2-}$ in water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Detected (ppm)*</th>
<th>Added (ppm)</th>
<th>Found (ppm)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>35.777 (34.866)</td>
<td>25.000</td>
<td>59.045</td>
<td>97.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.000</td>
<td>82.903</td>
<td>96.65</td>
</tr>
<tr>
<td>River water</td>
<td>80.355 (78.288)</td>
<td>25.000</td>
<td>103.258</td>
<td>98.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.000</td>
<td>132.115</td>
<td>101.35</td>
</tr>
</tbody>
</table>

*The numbers in bracket with red color are the detected concentration of water samples measured by ion chromatography.*