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

Min Zhang, Yu-Qiang Liu and Bang-Ce Ye\*

Lab of Biosystem and Microanalysis, State Key Laboratory of Bioreactor Engineering, East China University of Science & Technology, Meilong RD 130, Shanghai, 200237, China.

## **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

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<sup>-1</sup>.



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)  $PO_4^{3-}$ , (C)  $CO_3^{2-}$ , (D)  $NO_3^{-}$  or  $S^{2-}$ , (E)  $SO_4^{2-}$  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  $PO_4^{3-}$ ,  $NO_3^{-}$ ,  $CO_3^{2-}$ ,  $S^{2-}$ , and  $SO_4^{-2}$  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<sub>2</sub>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  $\mu$ M sulfate) vs. the pH value of (A) NaAc/HAc buffer, (C) ammonium acetate buffer, (E) potassium formate/formic acid buffer and (G) KH<sub>2</sub>PO<sub>4</sub>/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<sub>2</sub>PO<sub>4</sub>/phosphoric acid on the ratio  $A_{650}/A_{520}$  of cysteamine-AuNPs towards sulfate, respectively. Defined as  $\Delta D = (A_{650}/A_{520})_{sulfate} - (A_{650}/A_{520})_{Blank}$ .

### 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  $SO_4^{2-}$  in real samples. The unknown concentrations of  $SO_4^{2-}$  in different samples were measured using both cysteamine-AuNPs and ion chromatography method. The results were listed in Table S1.

Sample	Detected (ppm)*		Added (ppm)	Found (ppm)	Recovery (%)
Tap water	35.777	(34.866)	25.000	59.045	97.15
			50.000	82.903	96.65
River water	80.355	(78.288)	25.000	103.258	98.01
			50.000	132.115	101.35

**Table S1.** Determination of  $SO_4^{2-}$  in water samples

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