Electronic Supporting Information (ESI) for

A "light-on" colorimetric assay for anions detection using the inhibitory effect of anions on the catalytic activity of metal nanoparticles for the degradation of methyl orange

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1. Experimental

1.1 Reagents

Hydrogen tetrachloroaurate (Ⅲ) trihydrate ($HAuCl_4·3H_2O$) and Hydrochloroplatinic acid were purchased from Sinopharm Group Chemical Regent Co. Ltd. (Beijing, China), Silver nitrate ($AgNO_3$) was purchased from Alfa Aesar. Methyl orange (MO) was purchased from Sangon Biotechnology Co. Ltd. (Shanghai, China). Urea, uric acid (UA) and sodium borohydride ($NaBH_4$) were all purchased from Sigma-Aldrich Chemical Company. Other inorganic salts and glucose (Glc) were obtained from Beijing Chemical Reagent Company. All the chemicals were analytical grade and used without further purification. Ultrapure water (18.2 MΩ·cm) was employed in the work. The room temperature at which the experimental was conducted was 25 ℃. Phosphate buffer (PB) of 100 mM concentration with different pH were prepared by mixing 100 mM Na_2HPO_4 and KH_2PO_4 stock solution with different ratios. Sodium borohydride solution was freshly prepared before the experiment every time. 96-wells ELISA plates were purchased from Sangon Biotechnology Co. Ltd. (Shanghai, China).

1.2 Apparatus

UV/vis absorption spectra were recorded with a Cary 50 Scan UV/vis spectrophotometer (Varian, Harbor City, CA, USA). The absorbance of MO was measured on a EL808 microplate reader (Bio Tek Instruments, Inc. USA). TEM images were acquired by using the Hitachi

H-800 (Hitachi) transmission electron microscope operated at 200 kV. A filter paper was put under the carbon-coated copper grip when preparing samples to preclude the possibility of particle aggregation during drying.

1.3 Synthesis of metal nanoparticles

Gold, silver and platinum nanoparticles were all protected by citrate.

The 4 nm AuNPs was prepared as follows [1]. 0.5 mL of 0.01 M $HAuCl_4$ and 0.5 mL of 0.01 M trisodium citrate were added to 18 mL water under stirring. Then 0.5 mL newly prepared $NaBH_4$ was added, thereupon, the color of the solution turned from colorless to orange. Stop stirring and let the solution stand and activate for 2-6 hours before use.

The AgNPs was prepared according to the previous report with minor modification [2]. In brief, 250 μL of 100 mM $AgNO_3$ and 250 μL of 100 mM trisodium citrate were added into 100 mL of water under stirring. Then a freshly prepared aqueous solution of $NaBH_4$ (6 mL, 25 mM) was added quickly with vigorous stirring at room temperature. The stirring was stopped after 30 min, and the resulting bright yellow colloidal silver solution was stored at 4 ℃ before use.

Platinum particles [3] were prepared by heating 100 mL of a 1 mM $PtCl_6^-$ solution to reflux and adding 10 mL of 38.8 mM aqueous sodiumcitrate, followed by boiling of the mixture for an additional time interval of 30 min at which point the solution turned from clear to black. The heat was then turned off, and the solution was stirred for an additional 10 min. Finally, the solution was allowed to cool to room temperature

1.4 Procedure for the determination of anions

Taking the detection of SCN^- as an example, typically, 10 μL PB (pH 8.04, 100 mM), 3 μL PtNPs nanoparticles and 5 μL various concentrations of anions were added into 96-well microplate containing 65 μL water. After homogenous mixing and incubations for 2 min, 5 μL MO (1 mM) and 15 μL $NaBH_4$ (1 g/L) were added successively and homogenous mixed. After the solution was equilibrated for 2 min, UV-vis absorbance was measured via Microplate Spectrophotometer Power PowerWave XS2 endpoint mode at wavelength 450 nm. For AuNPs and AgNPs, 5 μL HCl (2 M) was added and then UV-vis absorbance was measured at wavelength 490 nm.

1.5 Anions detection in real samples.

Tap water was tested as received. Human urine sample was processed with a C18 solid phase extraction (SPE) column (100 mg/3 mL, Aumi, Tianjin, China). Prior to use, the C18 SPE column was pretreated in sequence by 2 mL of methanol and 2 mL of water. First 3 mL of eluent was discarded and 1 mL of remaining solution was collected for test.

5 μL processed sample was added to the system for the detection of corresponding anion. For standard addition method, known amounts of standard anion solution were added to the samples prior to dilution, and the recovery was measured.

2. Figures

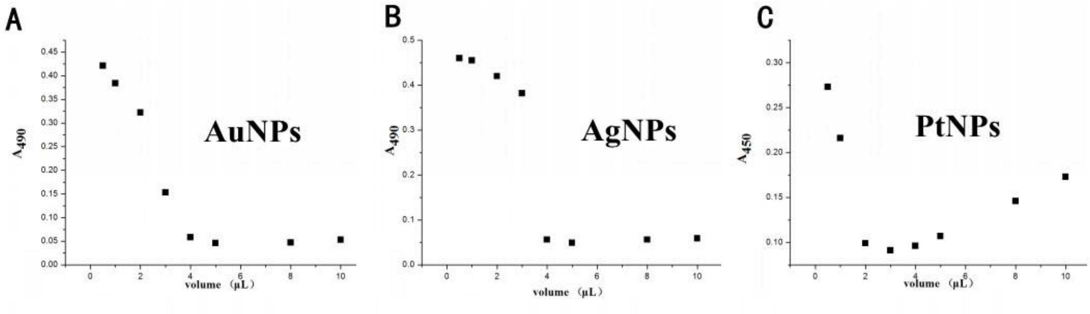


Fig. S1. The absorbance of MO with the increase of the concentration of AuNPs, AgNPs and PtNPs respectively. MO: 50 μM, $NaBH_4$: 0.15 g/L.

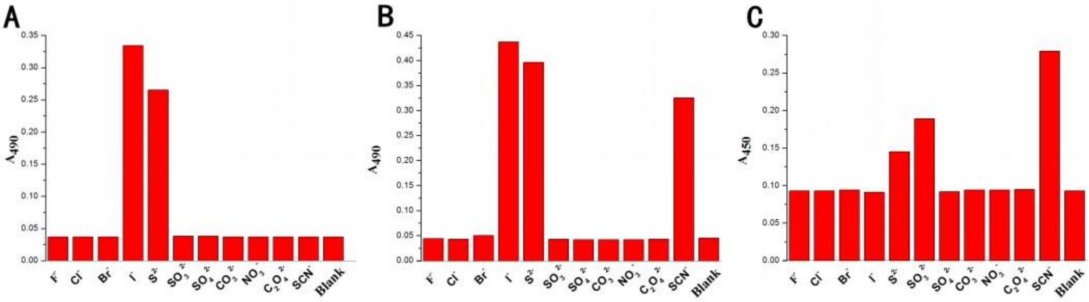


Fig. S2. The absorbance of MO in the presence of $NaBH_4$ and different anions with the catalysis of (A) AuNPs, (B) AgNPs or (C) PtNPs. MO: 50 μM, $NaBH_4$: 0.15 g/L; the incubation time: 2 min. The concentration of anions: 100 μM; pH: 8.04.

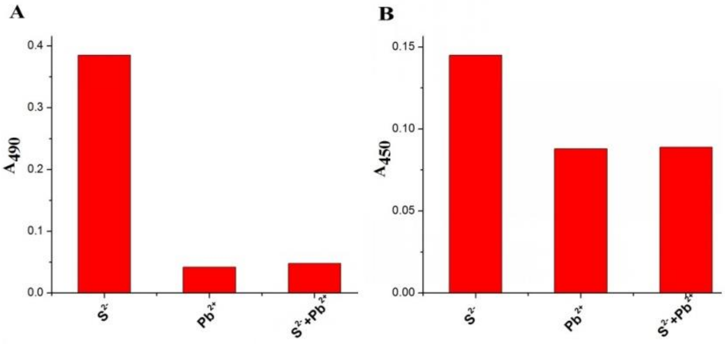


Fig. S3. The absorbance of MO in the presence of S^{2-}, Pb^{2+} and ($S^{2-}+Pb^{2+}$) with the catalysis of (A) AgNPs, (B) PtNPs. pH: (A) 7.17, (B) 8.04; the concentration of ions: 100 μM S^{2-}, 100 μM Pb^{2+}.

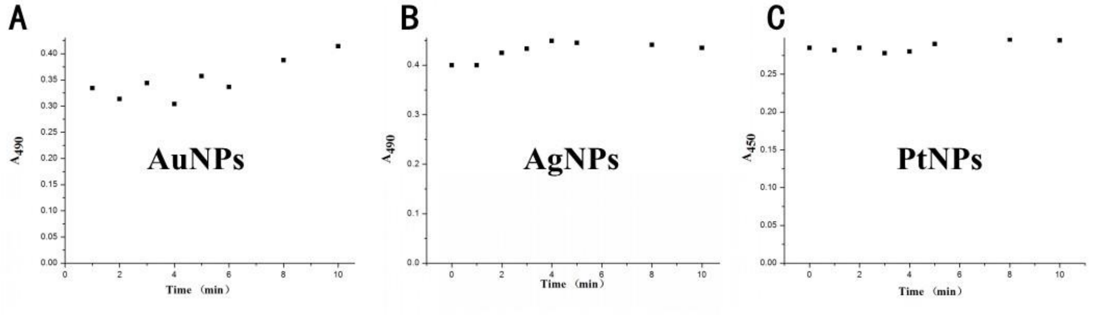


Fig. S4. The effects of the incubation time of anions with nanoparticles on the absorbance of MO. (A) S^{2-} and AuNPs; (B) I^- and AgNPs; (C) SCN^- and PtNPs. The concentration of anions: 5 μM.

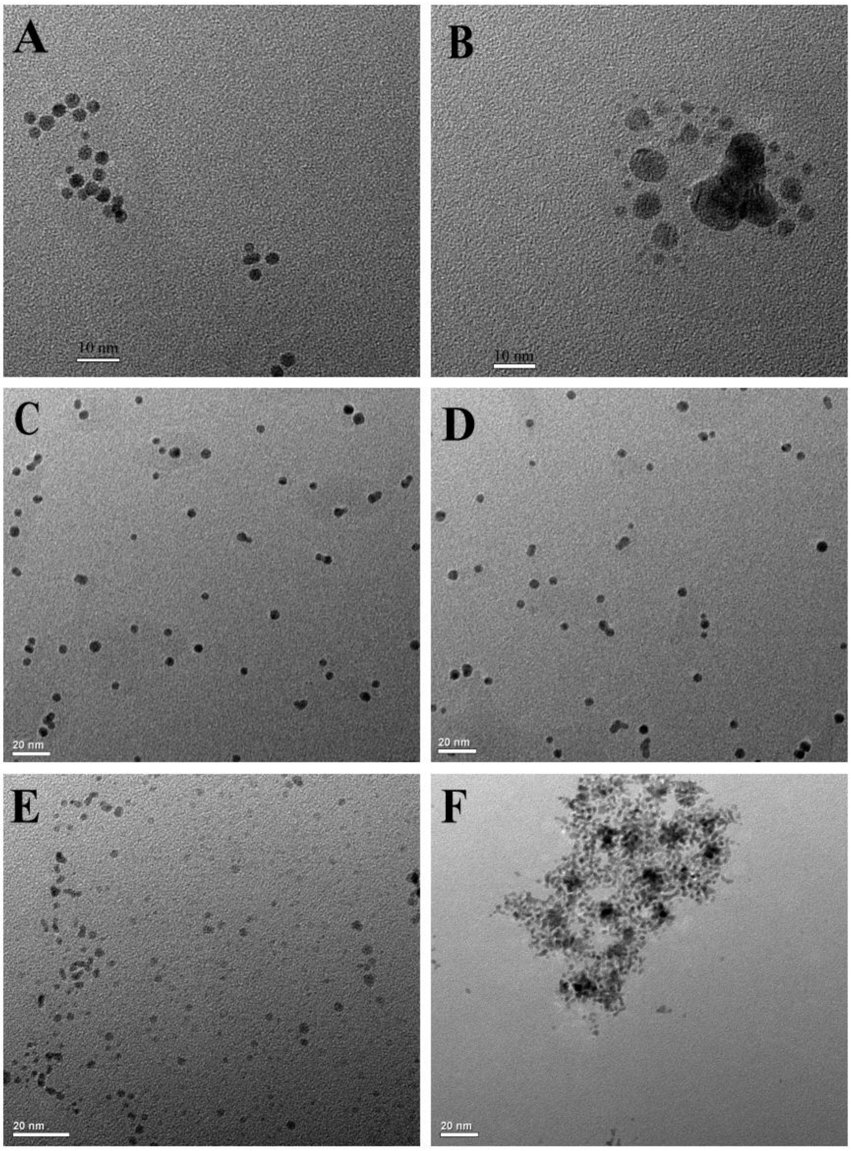
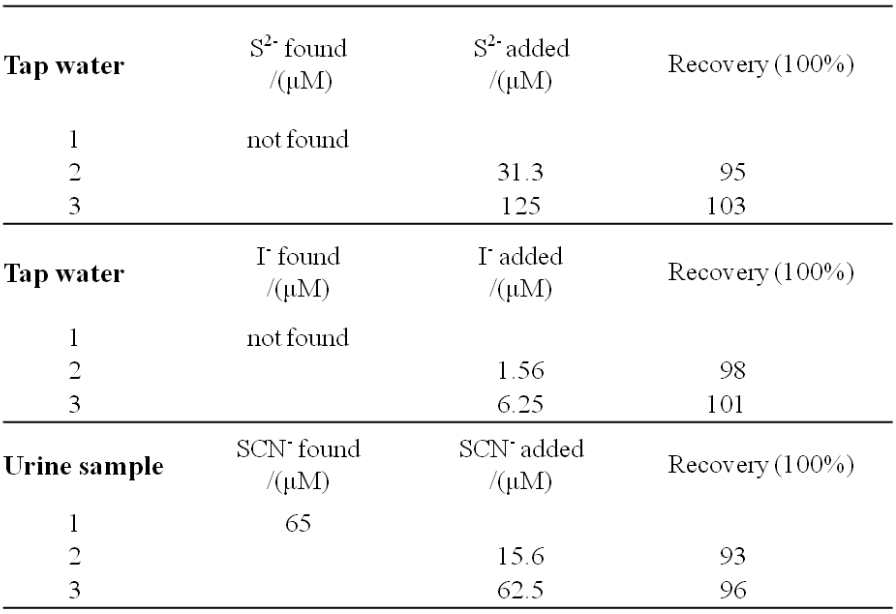


Fig. S5. TEM images of the metal nanoparticles. AuNPs (A) before and (B) after the addition of S^{2-}, AgNPs (C) before and (D) after the addition of I^-, PtNPs (E) before and (F) after the addition of SCN^-



Tap water	S^{2-} found /(μM)	S^{2-} added /(μM)	Recovery (100%)
1	not found		
2		31.3	95
3		125	103

Tap water	I^- found /(μM)	I^- added /(μM)	Recovery (100%)
1	not found		
2		1.56	98
3		6.25	101

Urine sample	SCN^- found /(μM)	SCN^- added /(μM)	Recovery (100%)
1	65		
2		15.6	93
3		62.5	96

Table S1. Determination of S^{2-}, I^- and SCN^- in real samples.

References

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2. H. Wei, C. G. Chen, B. Y. Han and E. K. Wang, *Anal. Chem.*, 2008, **80**, 7051.

3. R. Polsky, R. Gill, L. Kaganovsky and I. Willner, *Anal. Chem.*, 2006, **78**, 2268.