Electronic Supplementary Material (ESI) for Analytical Methods.

Direct Imaging of Single Gold Nanoparticle Etching: Sensitive Detection of Lead Ions

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EXPERINMENTAL SECTION

Chemicals and materials. $HAuCl_4$, 2-Mercaptoethanol (2-ME), sodium thiosulfate, glycine and all metallic salts used in this experiment were obtained from Sinophorarm (Shanghai, China). Trisodium citrates were purchased from Sigma-Aldrich. Ultrapure water with an electric resistance of 18.2 MΩ was supplied through a Milli-Q water purification system.

Synthesis of 50 nm spherical AuNPs. The 50 nm AuNPs used in this study were prepared by a seed-mediate approach by using 18 nm AuNPs as the seeds.[1] First, 18 nm AuNPs were prepared via reducing $HAuCl_4$ by using trisodium citrate. In brief, 1.03 mL of 24.28 mM $HAuCl_4$ solution was gently mixed with 98.97 mL DI water, and then heated to boil while stirring vigorously; 588 μL of 0.2 M sodium citrate solution was then rapidly added into the boiling solution, the mixture was vigorously stirred and refluxed for 20 min, and the color of the solution gradually changed from light yellow to wine red. When the color change was completed, the solution was boiled for another 5 min. And the solution was cooled to room temperature with continuous stirring. The LSPR spectral maximum of the AuNP seed solution was 518 nm as monitored by using UV-Vis spectroscopy. Next, 10 mL of the as-prepared seed solution was diluted to 80.0 mL DI water and 300 μL 0.013 M trisodium citrate solution was added into the solution with vigorous stirring. After the mixture was heated to boil, 1 mL of

$HAuCl_4$ (2.428 mM) was gently added into the solution every 2 min for ten times. Then the mixture was vigorously stirred and refluxed for 5 min. The color of the solution changed from light yellow to pale red, and finally to wine red. When the color change was completed, the colloidal solution was kept stirring for another 15 min. The size of the AuNPs prepared by this procedure was ~ 50 nm.

Pb^{2+} detection in bulk solutions. For UV-Vis measurement, 300 μL of the as-synthesized 50 nm AuNPs, 50 μL 5 mM glycine buffer of pH 10, and 50 μL 1 mM $Na_2S_2O_3$ solution were first mixed together with continuous shaking at room temperature for 15 min to allow stable absorption of $S_2O_3^{2-}$ onto the AuNP surface. Then into this $S_2O_3^{2-}$/AuNP probe solution, 500 μL Pb^{2+} solution with various concentrations was added. After shaking for another 15 min, 100 μL 10 mM 2-ME was added in order to make the solution go sufficiently. The solution was then gently equilibrated for another 1.5 h and the UV-Vis spectra were taken.

Coverslip silanization. The coverslips (Corning, NY) were cleaned using chromic acid lotion to remove organic residues, followed by sonication in ultrapure water for at least 3 times to remove excess dusts. Then, the cleaned coverslips were dried in an oven for 5 ~ 6 h at 80 ℃. After that, the coverslips were modified with thiol groups by incubating them in 0.1% 3-mercaptopropyl trimethoxysilane ethanol solution for 3 h and then were rinsed with ethanol several times. Finally, they were dried under a stream of nitrogen.

Sample preparation and DFM measurement. For single AuNP experiments, the $S_2O_3^{2-}$-AuNPs were then immobilized onto the salinized coverslip via the Au-S chemistry by dropping the solution mixture onto the glass surface for 3 min. The non-adsorbed AuNPs were rinsed away with water and the slide was dried under a stream of N_2 prior to DFM observation. The coverslip was put on top of a glass-slide with a concavity filled with 40 μL of Pb^{2+} solution that

was diluted by 2-ME. To prevent evaporation of the solution during long-time observation, the micro solution chamber was sealed with nail polish.

Apparatus. UV-Vis spectra of NPs were acquired using a UV-1800 spectrometer. Dark field imaging was performed on an upright Nikon 80i microscope (Japan). White light from the halogen lamp was focused onto the sample obliquely via an oil immersion dark field condenser (NA 1.43-1.20). Scattered light from the NPs was collected using a 40× objective and then captured using a DP72 color CCD camera (Olympus). Morphology characterization of the freshly synthesized NPs was performed using TEM (JEM 1230, JEOL). The optical setup is shown in Figure 1.Computer simulation of the AuNP color images was performed using Matlab 7.5. All DFM and TEM images were processed using Image J.

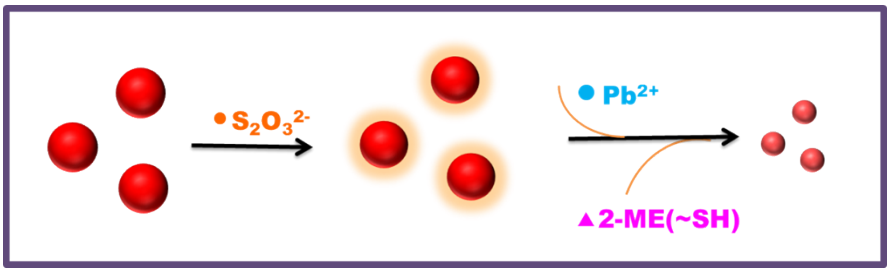

Figure S1. Schematic diagram of the sensing principle of Pb^{2+} by the 2-ME/$S_2O_3^{2-}$-AuNPs probes.

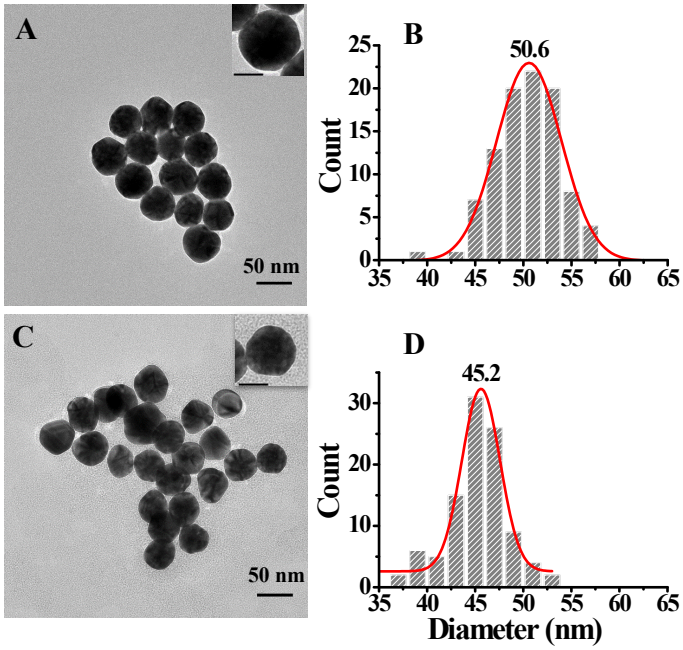

Figure S2. (A, C) TEM images of the AuNPs samples (A) before and (C) after the etching reaction. (B, D) The corresponding distribution of AuNP diameters (B) before and (D) after the etching reaction. Over 100 particles were counted in each case.

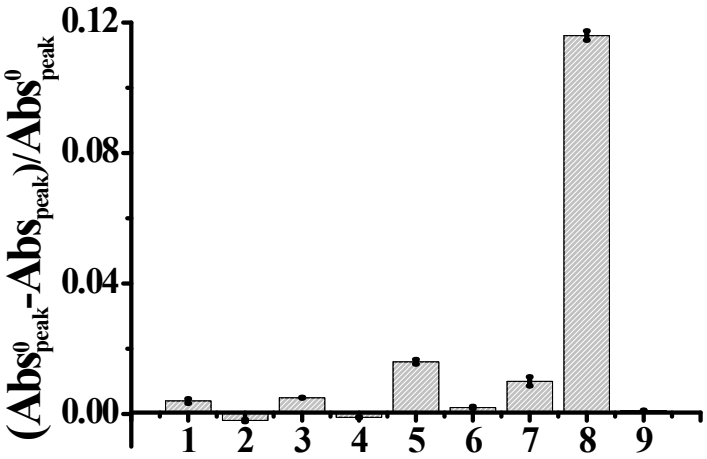

Figure S3. Selectivity of the 2-ME/$S_2O_3^{2-}$-AuNP probes for Pb^{2+} ions. Legend: 1. Cd^{2+}; 2. Cr^{3+}; 3. Fe^{3+}; 4. K^{+}; 5. Mn^{2}; 5. Na^{+}; 6. Ni^{2+}; 7. Pb^{2+}; 8. Pb^{2+} (5 nM); 9. Zn^{2+}. The concentrations of these anions are all 5 μM unless indicated otherwise.

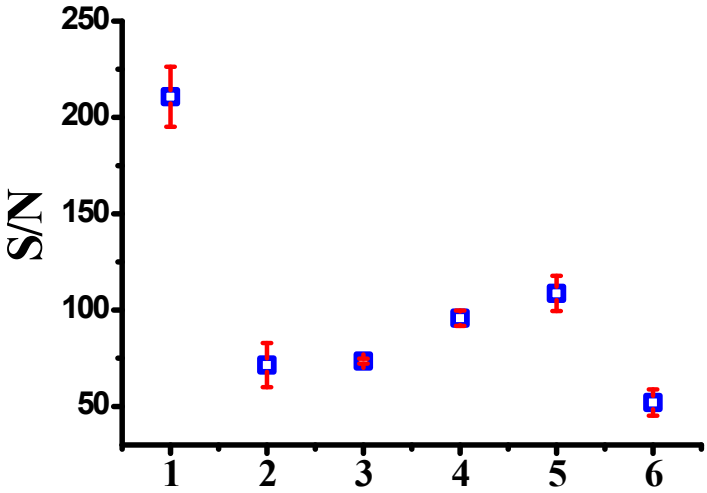

Figure S4. Signal-to-noise ratio (S/N) of the detection system with different camera settings. 1. ISO 200, exposure time 3 s; 2. ISO 400, exposure time 0.8 s; 3. ISO 400, exposure time 1 s; 4. ISO 400, exposure time 2 s; 5. ISO 400, exposure time 3 s; 6. ISO 800, exposure time 0.8s.

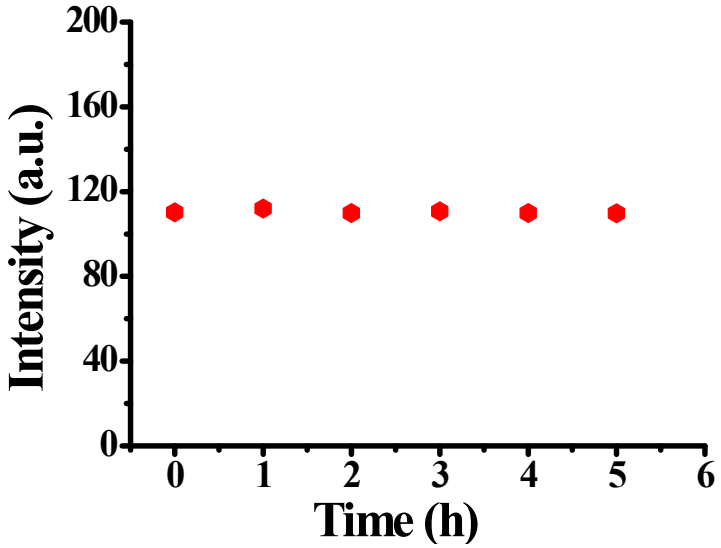

Figure S5. The experimentally measured scattering intensity of 2-ME/$S_2O_3^{2-}$—AuNPs probes in the absence of Pb^{2+} as a function of time.

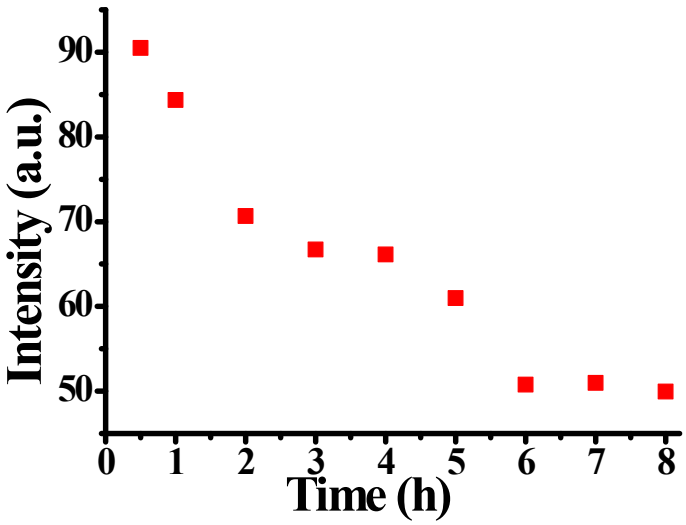

Figure S6. The time dependent variation of the scattering intensity change of 2-ME/$S_2O_3^{2-}$-AuNPs probes immobilized on a glass surface during an etching reaction. The concentration of Pb^{2+} is 2 nM.

Reference 1. Z. Yuan, J. Cheng, X. Cheng, Y. He and E. S. Yeung, *Analyst.*, 2012, **137**, 2930-2932.