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Supporting Information

Multifunctional Nanopipette for Metal Ion Recognition and Ultra-trace Analysis

Kang Wang[1], Gongming Qian[2], Yunchuan Li[1], Ruixia Wang[1], Jing Guo[1*]

[1]The State Key Laboratory of Refractories and Metallurgy, and Institute of Advanced Materials and Nanotechnology, Wuhan University of Science and Technology, Wuhan 430081, China

[2]College of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

*E-mail: jguo008@outlook.com

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S1. Au nanoelectrode characterization

The fabricated Au nanoelectrodes were characterized by cyclic voltammetry (CV). We estimated the exposed areas of insulated Au nanoelectrodes based on CVs (Figure S1). The steady-state CVs of the Au nanoelectrodes were recorded in 1 M KCl solution containing 100 mM using an electrochemical workstation (CHI760E, CHI Instruments, Inc., USA). The diffusion-limited current i_d is calculated using equation S1,

$i_d = \mathrm{mFDC}\sqrt{2\pi A_{eff}}$, (equation S1)

where A_{eff} is the exposed area, m is a geometry factor, F is the Faraday constant (96485 C/mol), D and C is the diffusion constant (7.4×10^{-6} cm^2/s) and bulk concentration (100 mM) of Ferrocyanide ions, respectively. We used m=1 for the calculation. Figure S1 shows the range of i_d is from 1.0 to 3.3 nA. According to equation S1 and i_d, and the exposed area of the Au nanoelectrodes is between 0.003 and 0.03 μm^2.

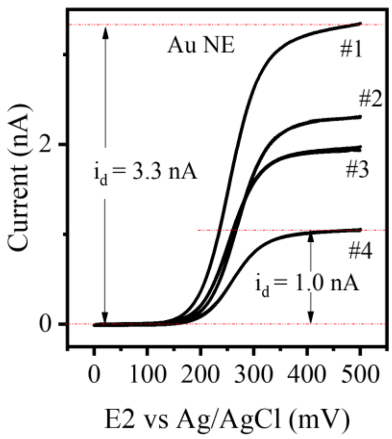

Figure S1. The CVs of four different Au NE/NP nanopipettes in 1M KCl with 100mM $Fe(CN)_6^{4-}$ and the sweep rate is 100 mV/s.

S2. TA modification of Au NE/NP

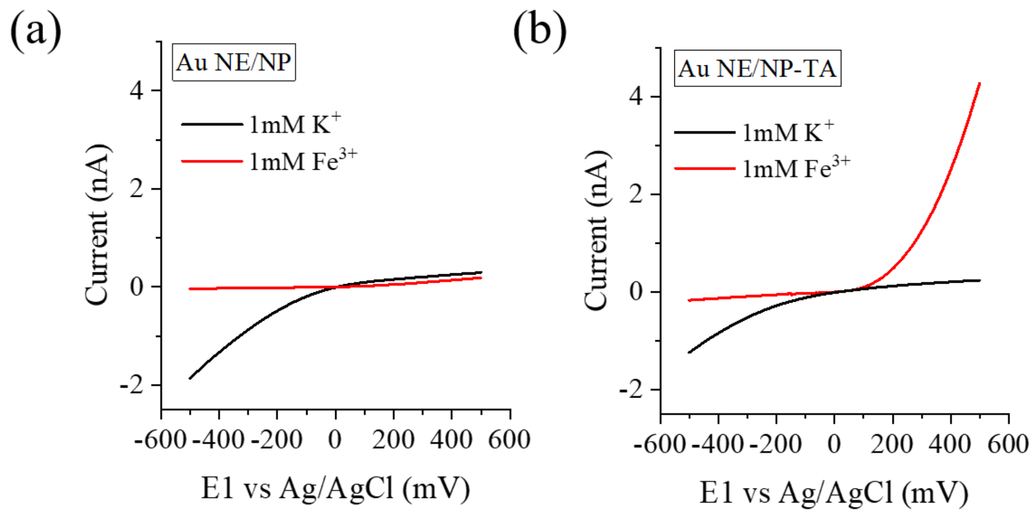

Figure S2. (a) *I-V* curves of Au NE/NP in the 1 mM K^+ and 1 mM Fe^{3+}. (b) *I-V* curves of Au NE/NP-TA in the 1 mM K^+ and 1 mM Fe^{3+}.

S3. I-V curves of Au NE/NP-TA in the same valent metal ions

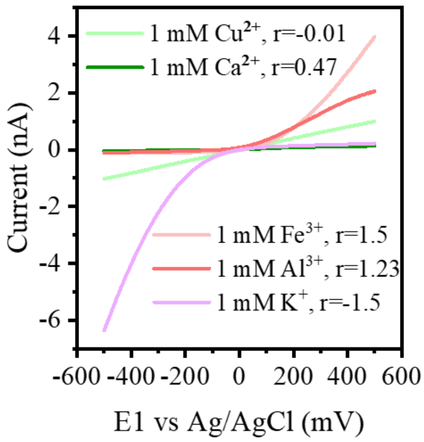

Figure S3. *I-V* curves of Au NE/NP-TA in metal ions with different valent.

S4. CV curves of different metal ions

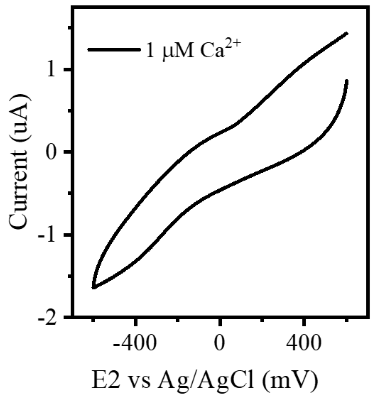

Figure S4. CV curves of Au NE/NP-TA in 1 μM Ca^{2+}.

S5. I-V curves of different valent metal ions

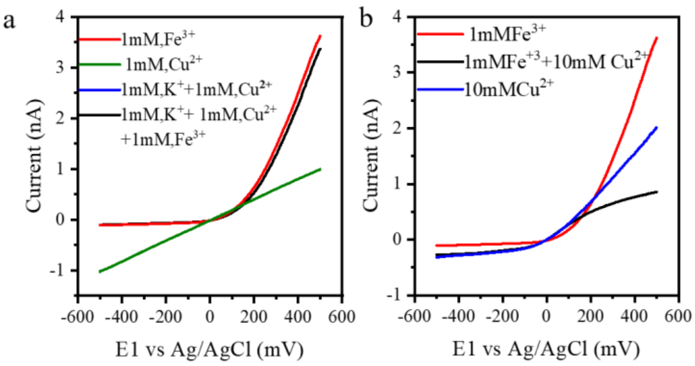

Figure S5. (a) *I-V* curves of Au NE/NP-TA in the solution of Fe^{3+}(red line), a mixture of K^{+} + Cu^{2+} + Fe^{3+} (black line), and a mixture of K^+ + Cu^{2+} (blue line), respectively. Note the blue and green lines are overlapped. (b) *I-V* curves of Au NE/NP-TA in the 1 mM Fe^{3+} (red line), 1 mM Fe^{3+} +10 mM Cu^{2+} (black line), and 10 mM Cu^{2+} (blue line). Note that, all the metal ion concentration is 1 mM and the bath solution pH is 4.

S6. Regeneration of Au NE/NP-TA

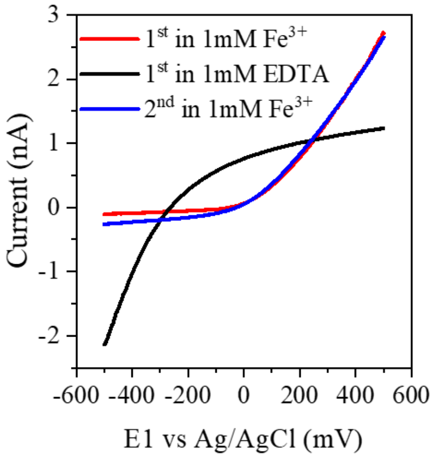

Figure S6. *I-V* curves of Au NE/NP-TA in the 1 mM Fe^{3+} and EDTA, alternatively.

S7. Stability of Au NE/NP-TA

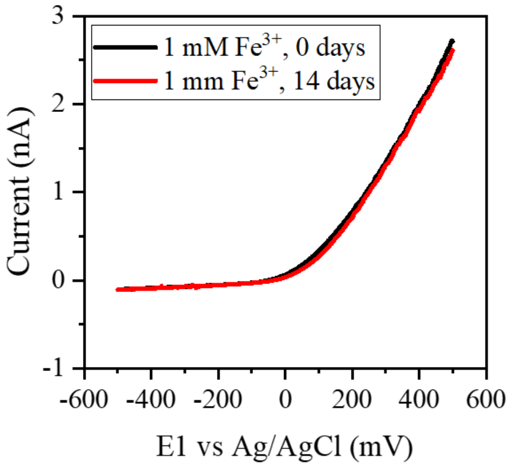

Figure S7. *I-V* curves of Au NE/NP-TA in the 1 mM Fe^{3+} with a storage time of 0 and 14 days. The tip of Au NE/NP-TA was stored in 10 mM PBS.