

# **An improvement in scanning electrochemical microscopy based on plasmon-accelerated electrochemical reaction**

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## 1. Experimental Section

**Chemicals and reagents.** Hydroxymethylferrocene ( $C_{11}H_{12}FeO$ , >95%), sodium dihydrogen phosphate dohydrate ( $NaH_2PO_4 \cdot 2H_2O$ ,  $\geq 99.0\%$ ), disodium hydrogen phosphate-decahydrate ( $Na_2HPO_4 \cdot 12H_2O$ ,  $\geq 99.0\%$ ), potassium ferrocyanide trihydrate ( $K_4Fe(CN)_6$ ,  $\geq 99.5\%$ ), tripropylamine (>99%), auricchloridedihydrate ( $HAuCl_4$  Au $\geq 47.8\%$ ) were purchased from Sigma-Aldrich. All aqueous solutions were prepared with doubly distilled water produced by a Milli-Q (resistivity of 18.2 M $\Omega$  cm) system.

**Apparatus.** The capillary was pulled by P-2000 (Sutter Instrument Co). JSM-7800F scanning electron microscope (JEOL Ltd., Japan) was applied to characterize the UME tip. A CHI 750C bipotentiostat (CH Instruments, Shanghai, China) was used for electrodeposition of AuNPs and test the chemical properties of UME tip with a three electrodes setup, where Ag/AgCl and Pt electrodes were used as the reference and counter electrodes, respectively. The laser was purchased from Changchun New Industries Optoelectronics Tech. Co., Ltd (MGL-FN-532nm-300mW-17100294). The current of the laser can be read directly. But the power should be calculated from the P-I curve provided by the company.

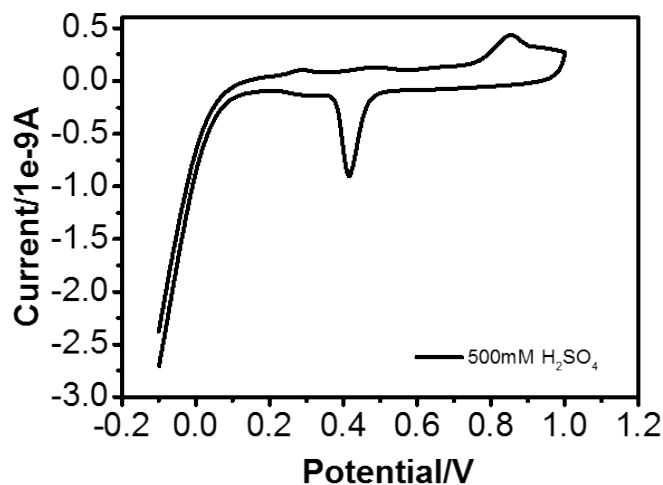
All feedback curves were measured by a homemade SECM setup. The homemade SECM instrument comprises a signal acquisition system (multiclamp 700B from Molecular Devices, LLC), an E518 piezoelectric micro-positioning device (with a minimum step size of 0.1nm) and a C884 mechanical micro-positioning device (with a minimum step size of 50nm) as shown in Figure S6. The two micro-positioning devices were purchased from Physik Instrument (PI) GmbH & Co. KG. The signal acquisition system was operated by a LabView program to control the voltage between the two electrodes as well as record the tip current simultaneously. The position of the tip could be controlled in a programmed mode according to the recorded current as a function of the tip-substrate distance. A Faraday cage was used to protect the equipment from external radio frequency interference during testing. A two-electrode system was used where Ag/AgCl acts as the counter electrode. The Faraday cage and the laser were put on a vibration prevention platform. A plane mirror was set 45° to the table in order to ensure the vertical illumination of the probe.

**Fabrication and characterization of gold nanoparticles microelectrodes.** Glass capillaries (1.5

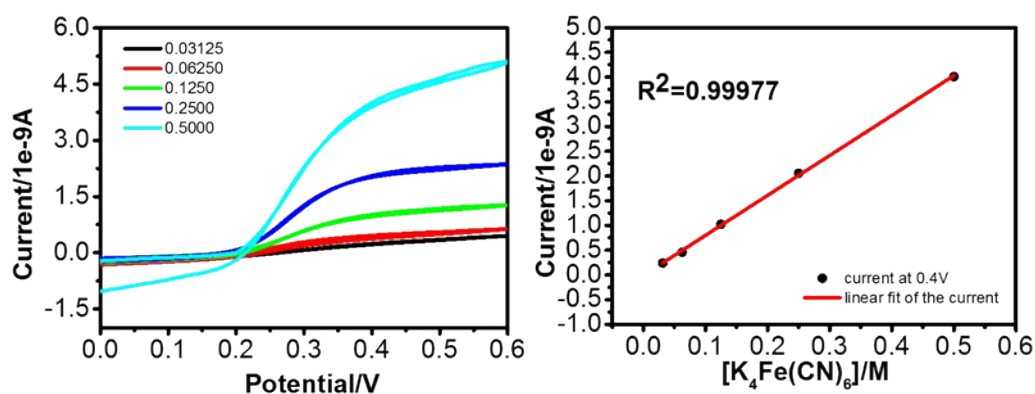
mm outside diameter, 0.5 mm inside diameter) were obtained from Sutter Instrument Company (USA). The quartz capillary was pulled using a double row parameters (Heat=710, Fil=4, Vel=35, Del=115, Pul=50; Heat=710, Fil=4, Vel=35, Del=115, Pul=50). Pyrolysis of butane under argon atmosphere was used to fill the quartz capillary with solid carbon [1]. Then the electrode was modified with AuNPs by electrodeposition in 1.0 mM H<sub>AuCl<sub>4</sub></sub> solution (-0.3 V, 400 s).

**Finite-difference time-domain simulation.** Three-dimensional full-field finite-difference time domain (FDTD) (the package of Lumerical FDTD Solutions 8.15) was used to simulate the EM field variation with the nanoparticle-substrate distance. The model was designed with one AuNP (50 nm diameter) and SiO<sub>2</sub> substrate (100 $\mu$ m $\times$ 100 $\mu$ m $\times$ 200nm) underneath the particle with distance from 500 to 2000 nm. Light (x-polarized) source ranging from 400 to 600 nm was introduced from z-direction. An x-y mesh plane was applied to the model which is always tangent to the gold sphere. When the simulation runs over, we recorded the electric field on the x=0, y=0 under 532nm excitation.

## 2. Characterization of AuNPs deposited carbon UME

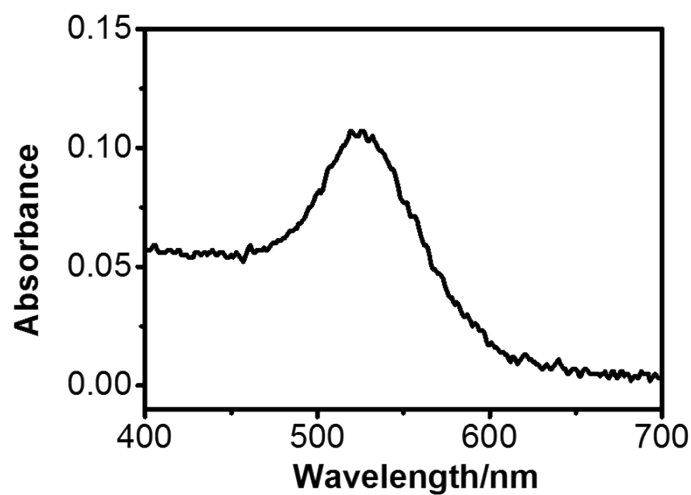


**Fig.S1** CV of AuNPs deposited carbon UME in 0.5 M H<sub>2</sub>SO<sub>4</sub>. The stripping peak of gold indicated the formation of Au on the carbon UME.



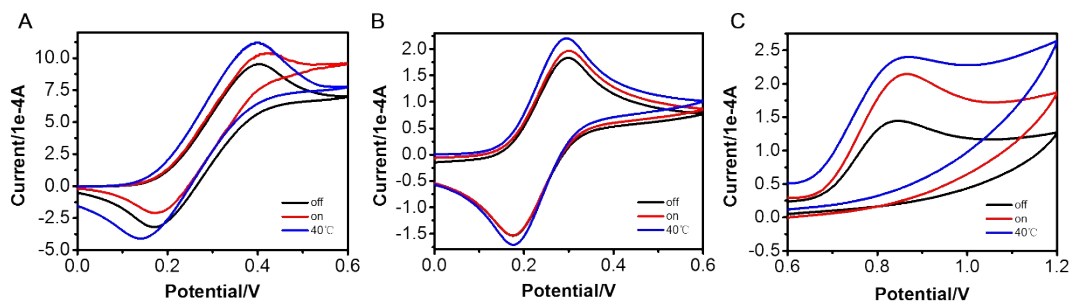
**Fig. S2** CV scans for carbon UME after AuNPs deposition in  $K_4Fe(CN)_6$  solution with concentration of 0.031 M, 0.062 M, 0.12 M, 0.25 M and 0.50 M.

### 3. UV-vis absorption of electrodeposited AuNPs



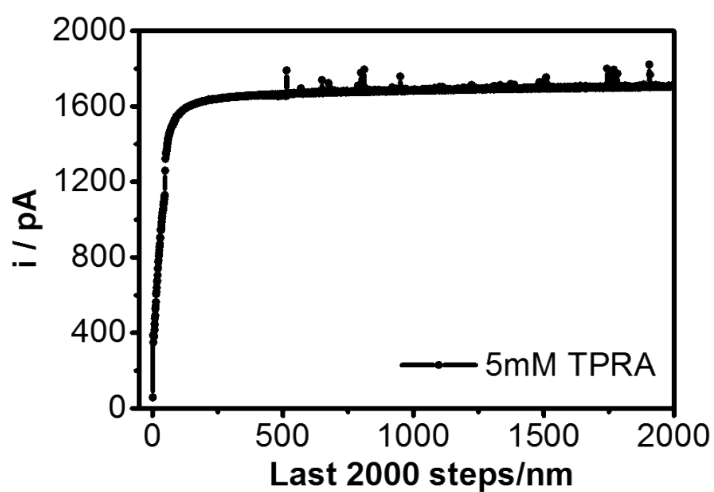
**Fig.S3** UV-vis spectrum of AuNPs modified ITO electrodes after electrochemical deposition in 1.0 mM  $HAuCl_4$  solution at -0.3 V vs. SCE for 400 s.

### 4. PAER on AuNPs modified GC with different species



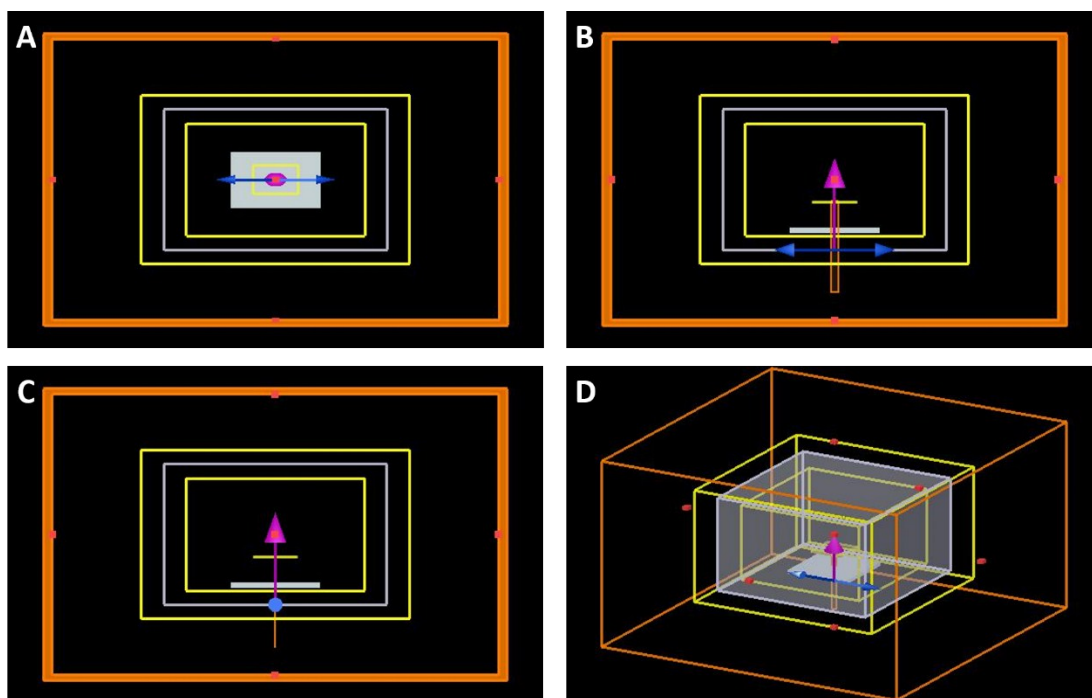
**Fig.S4** CV scans with (red) and without illumination (black) at room temperature, and at 40 °C (blue) in 0.2 M pH 7.4 PBS containing (A) 0.1M  $K_4Fe(CN)_6$ , (B) saturated ferrocene, (C) 5 mM tripropylamine (scan rate: 100 mV/s). The intensity of the 532 nm laser is 498 mW/cm<sup>2</sup>.

## 5. Approach curve with tip touching the substrate



**Fig.S5** SECM tip currents vs tip distances (approach curve) obtained in 5 mM tripropylamine ( $E_T = 1.0$  V vs Ag/AgCl). The intensity of the 532 nm laser is 498 mW/cm<sup>2</sup>.

## 6. FDTD model



**Fig.S6** (A)  $x$ - $y$  plane, (B)  $y$ - $z$  plane, (C)  $x$ - $z$  plane, and (D) the perspective view of the simulation model.

## 7. Reference

- [1] Y. Takahashi, A. I. Shevchuk, P. Novak, Y. Zhang, N. Ebejer, J. V. Macpherson, P. R. Unwin, A. J. Pollard, D. Roy, C. A. Clifford, H. Shiku, T. Matsue, D. Klenerman and Y. E. Korchev, *Angew. Chem. Int. Ed.*, 2011, **50**, 9638.