Supporting Information

Preparation, Electrochemical Responses and Sensing Application of Au Disk Nanoelectrodes Down to 5 nm

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AU NANOELECTRODE FABRICATION

The fabrication procedure of Au nanoelectrodes with somewhat improvement has been provided as follows, which was described in previous reports.[1-3]

In brief, the fabrication procedure involved four steps: 1) pre-sealing, 2) sealing, 3) pulling, 4) polishing. The first two steps involved the preparation of Au wire sealed in a silica capillary. In the last two steps, the ultra-sharp Au tip and Au nanoelectrodes were prepared by pulling the sealed Au wire and polishing sealed Au tips.

Step 1: Pre-sealing

a 25 μm Au wire was sealed into a 1-cm long piece of a silica capillary with an inner diameter of ~ 80 μm and an outer diameter of ~ 300 μm with the help of a stereo microscope. The small silica capillary/Au ensemble was then inserted into the center of a 7.5 cm long piece of a borosilicate glass capillary (*o.d.* = 1.0 mm; *i.d.* = 0.64 mm).

Step 2: Sealing

To prevent the Au/bi-layer silicate assembly from moving during the sealing procedure, a home-made aluminum clamp was used to secure the moving puller bars in place. A vacuum was connected to the capillary during the sealing process. The following parameters were used to obtain a complete seal between the Au wire and capillary walls. This program was applied for 3 cycles with each cycle consisted of a 40 s heating period followed by a 20 s cooling period. It must be pointed out that the parameters should be changed based on the instrument performance.

Heat	Filament	Velocity	Delay	Pull
540	1	75	120	0

Step 3: Pulling

The clamp was removed prior to the pulling step. The following parameters were used in the final pulling step:

Heat	Filament	Velocity	Delay	Pull
560	1	100	120	180

Step 4: Polishing

The Au/bi-layer capillary assembly was sealed and then pulled into two ultra-sharp tips. The ultra-sharp was sealed with care into borosilicate glass tubing using epoxy, which was then polished with sandpaper to expose the Au nanodisk under the control of a homemade ultrasensitive continuity tester to ensure the polishing stops when the very end of Au is exposed.

[1] B. B. Katemann, W. Schuhmann, Electroanal. 2002, 14, 22-28

[2] P. Sun, M. V. Mirkin, Anal. Chem. 2006, 78, 6526-6534.

[3] Y. Li, B. David, B. Zhang, Anal. Chem. 2009, 81, 5496-5502.

Table S1. Kinetic Parameters for the oxidation of Fc at Au nanoelectrodes in ACN/0.2 M $TBAPF_6$

r (nm)	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)	K^o (cm/s)	α
65.6	33.5	34.8	4.4	0.32
39.3	36.0	44.8	7.2	0.33
15.4	33.8	35.4	11.6	0.26
9.7	39.3	50.4	4.5	0.46
6.1	42.6	57.4	8.9	0.48
4.3	40.9	43.1	13.3	0.60

Table S2. Kinetic Parameters for the oxidation of $FcCH_2OH$ at Au nanoelectrodes in H_2O/0.1 M KCl

r (nm)	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)	K^o (cm/s)	α
58.4	31.0	32.0	3.5	0.28
47.3	38.0	41.5	4.6	0.37
19.0	39.0	48.5	12.2	0.42
16.8	36.0	41.0	5.9	0.62
8.1	40.0	54.0	17.1	0.37
8.0	39.0	57.0	9.7	0.60

Table S3. Kinetic Parameters for the oxidation of $Fe(CN)_6^{3-}$ at Au nanoelectrodes in H_2O/0.2M KCl

r (nm)	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)	K^o (cm/s)	α
64.6	44.0	50.0	0.5	0.58
24.4	32.2	37.8	4.9	0.39
20.6	41.5	44.0	1.6	0.58
11.8	36.5	42.0	9.1	0.62
10.7	42.8	46.7	5.4	0.60
6.3	40.0	45.0	9.3	0.62

Table S4. Kinetic Parameters for the oxidation of $Ru(NH_3)_6^{3+}$ at Au nanoelectrodes in H_2O/0.2M KCl

r (nm)	$\Delta E_{1/4}$ (mV)	$\Delta E_{3/4}$ (mV)	K° (cm/s)	α
73.4	48.0	46.0	7.4	0.58
40.1	68.0	42.0	11.3	0.60
23.6	47.0	43.5	9.8	0.62
10.5	38.6	32.5	15.0	0.56
6.2	43.1	40.0	12.2	0.58

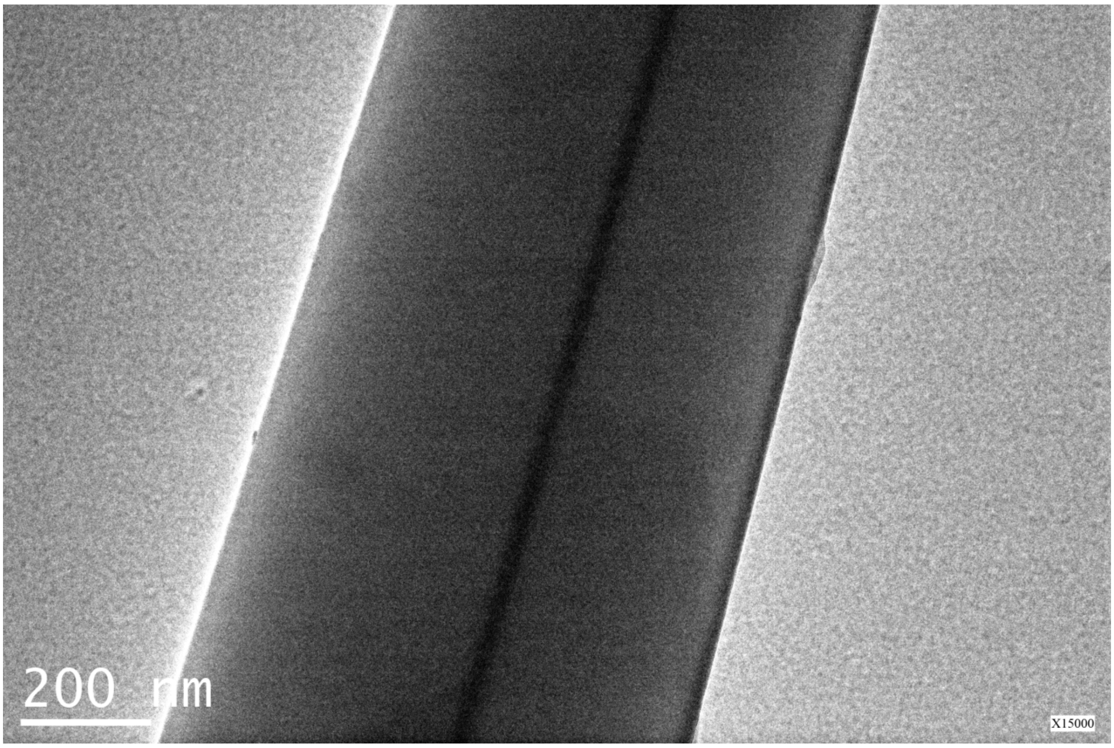

Figure S1. TEM image of single Au nanoelectrode sealed in SiO_2 with the radius of ~18 nm.

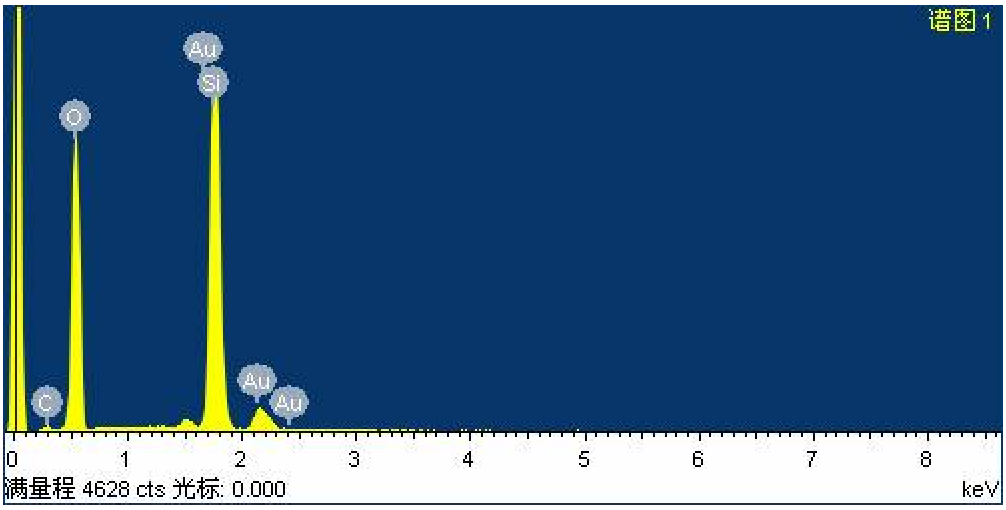

Figure S2. Energy dispersive X-ray spectroscopy (EDX) result of Au nanoelectrode.

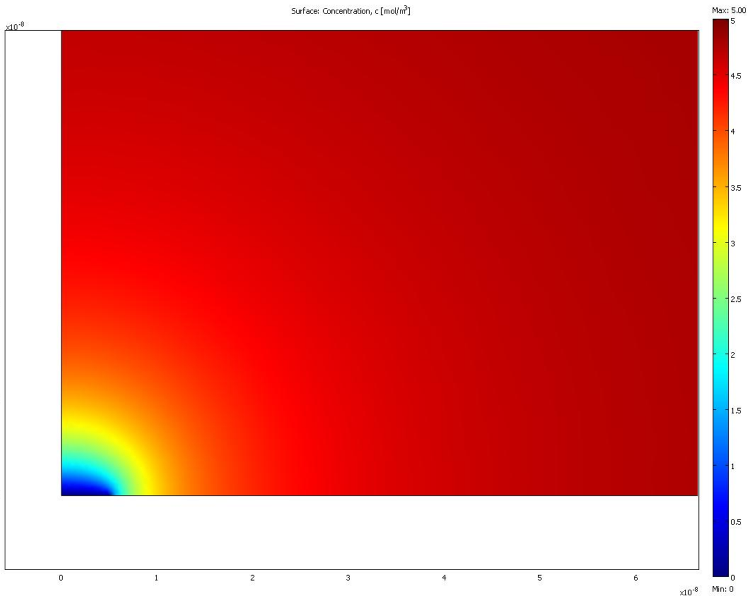

Figure S3. The simulation result of Fc diffusion on the surface of Au nanodisk electrode (radius: 5 nm).

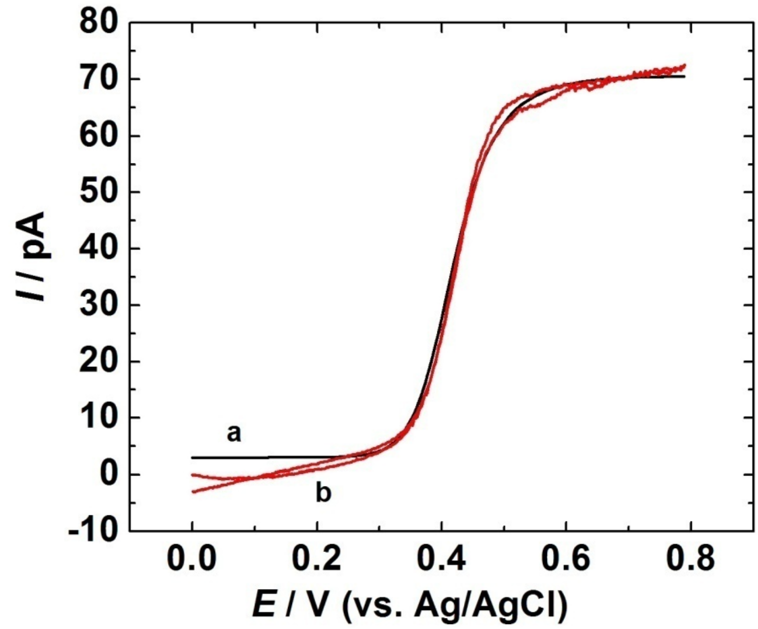

Figure S4. (a) The simulation result of Fc diffusion on the surface of Au nanodisk electrode. (b) Voltammetric responses of Au nanoelectrodes in a 5 mM Fc ACN solution containing 0.2 M $TBAPF_6$. Radius: 7.2 nm; Scan rate is 10 mV/s.

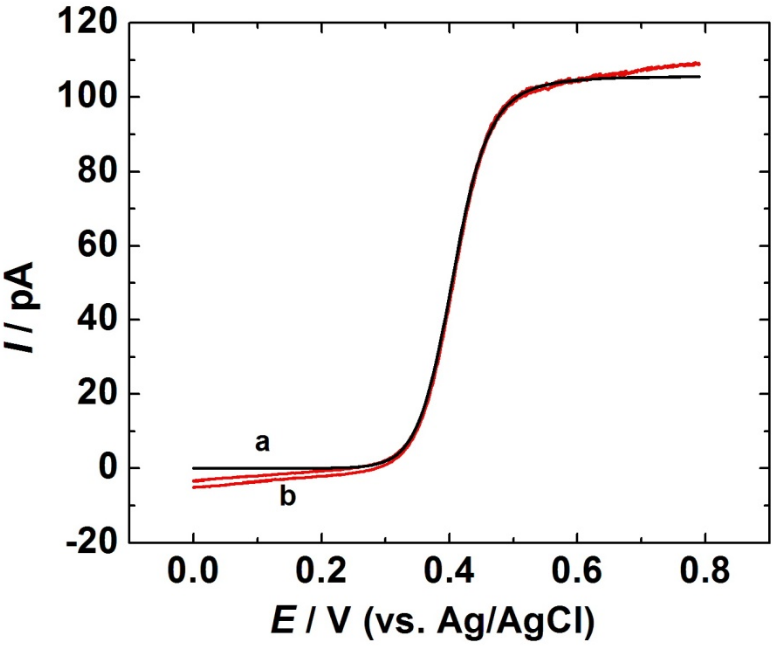

Figure S5. (a) The simulation result of Fc diffusion on the surface of Au nanodisk electrode. (b) Voltammetric responses of Au nanoelectrodes in a 5 mM Fc ACN solution containing 0.2 M $TBAPF_6$. Radius: 11.5 nm; Scan rate is 10 mV/s.

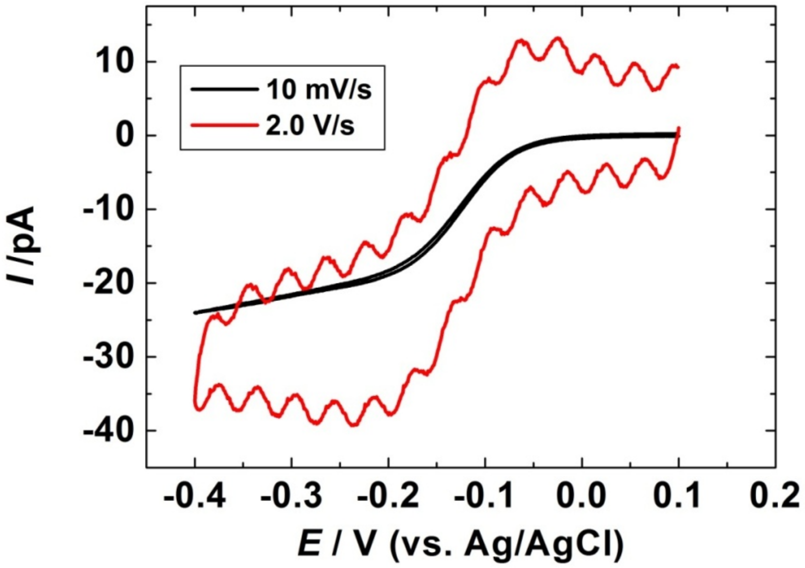

Figure S6. Voltammetric responses of a Au nanodisc electrode in an aqueous solution containing 5 mM $Ru(NH_3)_6Cl_3$ containing 0.2 M KCl at the can rate of 10 mV/s (black curve) and 2 V/s (red curve). Radius: 8.5 nm.

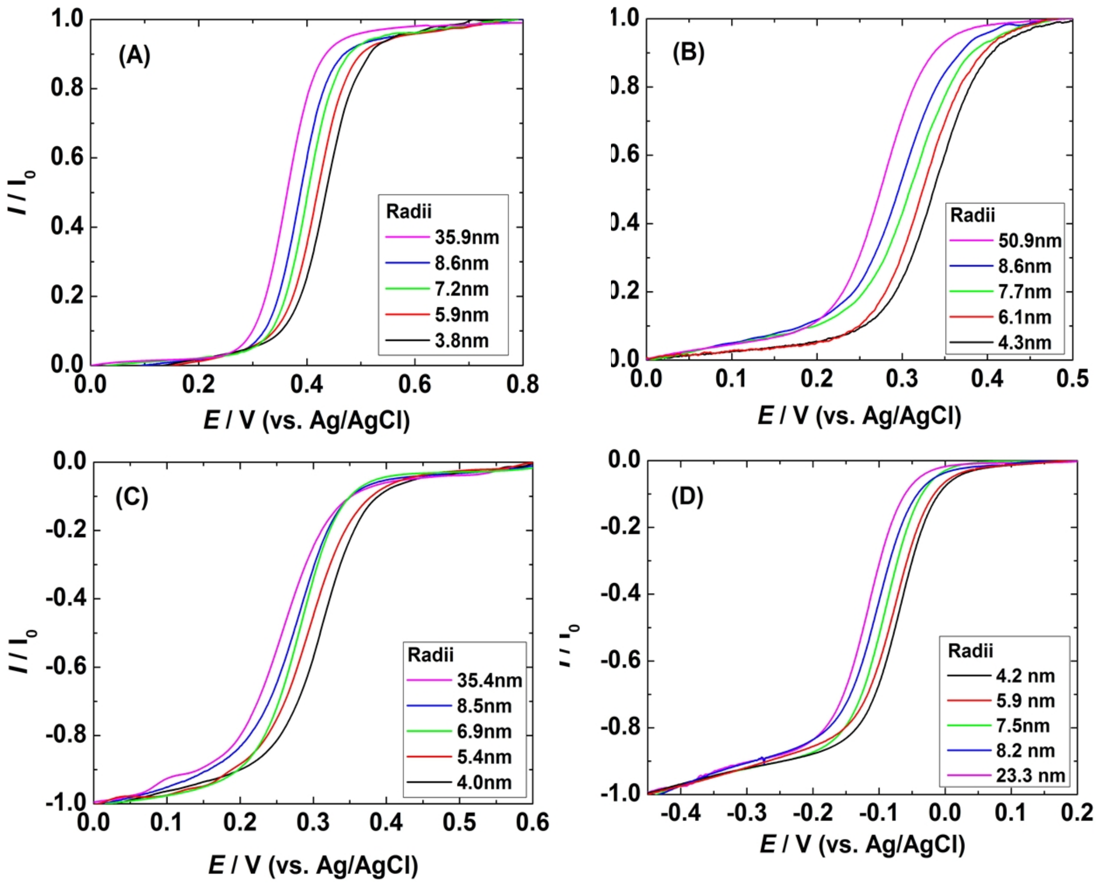

Figure S7. Normalized current to the limiting value of the voltammetric responses of Au nanoelectrodes in a 5 mM Fc ACN solution containing 0.1 M $TBAPF_6$ (A), 1 mM $FcCH_2OH$ containing 0.1 M KCl (B), 5 mM $K_3Fe(CN)_6$ containing 0.2 M KCl (C), and 5 mM $Ru(NH_3)_6Cl_3$ containing 0.2 M KCl (D). Scan rate is 10 mV/s.