

Supporting Information

Single Particle Detection by Area Amplification – Single Wall Carbon Nanotube Attachment to a Nanoelectrode

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Experimental Details

Reagents

Hydrogen tetrachloroaurate (HAuCl_4) was obtained from Alfa Aesar (Ward Hill, MA). Potassium nitrate (KNO_3) was obtained from Fisher Scientific (Pittsburgh, PA). Ferrocenemethanol (97%) and trisodium citrate dihydrate (99%) were obtained from Sigma-Aldrich. Single wall carbon nanotubes (Pure tubes) were obtained from Nanointegris (Skokie, IL). According to the manufacturer, SWCNTs have diameters in the range of 1.2 to 1.7 nm (mean 1.4 nm) and length in the range of 100 nm to 4 μm (mean $\sim 1 \mu\text{m}$). All chemicals were used as received. Millipore water ($>18 \text{ M}\Omega\text{-cm}$) was used in all experiments.

Preparation of ultramicroelectrodes (UME)

Carbon fiber UMEs were prepared following the general procedure developed in our lab. Briefly, a 10 micron carbon fiber was sealed in glass after rinsing with ethanol and water. The electrode was then polished with alumina powder water suspension to a mirror finish. The surface area was checked with standard redox electrochemistry of ferrocene methanol.

Preparation of Pt nanoelectrodes

Platinum nanoelectrodes were prepared according to a procedure reported elsewhere.¹ Briefly, a 25- μm diameter Pt microwire (99.99%, Alfa-Aesar) was inserted in a 7-cm piece of quartz capillary tubing (1.0 mm o.d., 0.3 mm i.d., Sutter). The Pt wire was then tightly sealed in quartz by heating the quartz tubing with a CO_2 laser under vacuum. A laser puller (Sutter) was used to pull the Pt/quartz ensemble into two ultrasharp tips. A nanometer-sized Pt disk was then exposed by first sealing the sharp quartz tip into a borosilicate glass capillary and then polishing with sand paper and with alumina powder water suspension on a wet polishing cloth. The size of the Pt nanodisk was checked with steady-state cyclic voltammetry in a 5 mM ferrocene solution. A Pt disk electrode with the Pt surface flush with the silica insulation was ensured by polishing the Pt disk and rechecking the CV response until a constant CV response was obtained.

Instrumentation

The electrochemical experiments were performed using a CHI model 920c potentiostat (CH Instruments, Austin, TX) with the three-electrode cell placed in a Faraday cage. A 3 mm diameter carbon rod was used as counter electrode. The reference electrode was Ag/AgCl in a saturated KCl solution. TEM images were

obtained using a FEI Tecnai transmission electron microscope and JEOL 20100F transmission electron microscope. Galaxy 16D (VWR, Westchester, PA) is used for particle purification.

Preparation of carbon nanotube conjugated gold nanoparticles (Au-SWCNT)

The Au-SWCNT was prepared by dispersing 0.15 mg of carbon nanotubes in 50 mL water. After 1 min, 6 mL of a solution containing 34 mM trisodium citrate was added, followed by addition of HAuCl_4 (25 mM, 1 mL) under stirring. The temperature was slowly increased to the boiling point ($\sim 5^\circ\text{C}/\text{min}$). The solution was kept boiling for another 30 min.

Preparation of metal nanoparticles (NPs)

The platinum nanoparticle (diameter 4 nm) solution was prepared by dissolving 1 mM H_2PtCl_6 and 1.2 mM sodium citrate in 40 mL water. Then 2.7 mL of 60 mM freshly-made NaBH_4 solution was added drop wise under vigorous stirring. The reaction was stopped after 30 min.

The Pt NP (diameter 32 ± 3 nm) solution was prepared according to the procedure reported previously.² A seed-mediated growth procedure was used to prepare stable citrate-capped large Pt NPs. Seed particles were prepared as follows. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (3.8 mM, 7 mL) was added to boiling water (90 mL) with stirring. After 1 min, 2.2 mL of solution containing 34 mM trisodium citrate and 2.6 mM citric acid was added, followed by a quick addition of freshly prepared sodium borohydride (21 mM, 1.1 mL). After 10 min, the solution was cooled to room temperature. For 32 nm particles, 1 mL of Pt seed solution was added to 29 mL of water with stirring. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (0.4 M, 0.045 mL) was added, followed by addition of 0.5 mL solution containing 34 mM trisodium citrate and 71 mM ascorbic acid. The temperature was slowly increased to the boiling point ($\sim 5^\circ\text{C}/\text{min}$). The reaction time was 1 h with the reflux condenser. NPs were washed two times by precipitation in a centrifuge at 14000 rpm for 10 min.

The gold seed NP (diameter ~ 10 nm) solution was prepared by first boiling 150 mL of a 2.2 mM trisodium citrate in aqueous solution. HAuCl_4 (25 mM, 1 mL) was then injected under stirring. The solution was kept boiling for another 15 min. The solution obtained appeared ruby colored. The resulting Au NPs are well dispersed in water.

The gold NP (diameter $\sim 18, 22, 31, 36, 42,$ and 54 nm) solution was prepared according to the procedure reported previously.³

A seed-mediated growth procedure was used to prepare stable citrate-capped large Au NPs. After the synthesis of the Au seeds and in the same reaction vessel, the solution was cooled to 90°C . Then, HAuCl_4 solution (25 mM, 1 mL) was injected. After 30 min, the reaction was finished. This process was repeated twice. After that, the sample was diluted by extracting 55 mL of sample and adding 53 mL of water and 2 mL of trisodium citrate (60 mM). This solution was then used as a seed solution, and the process was repeated again.

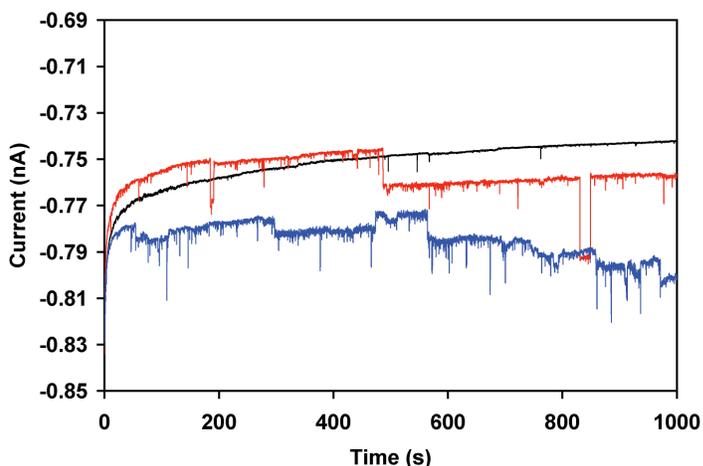


Figure S1. Chronoamperograms recorded for a 2 μm diameter Pt UME in 2.5 mM FcMeOH with 1 mM KCl and either 2.5 ng/mL SWCNTs (black line), 13 ng/mL SWCNTs (red line), or 38 ng/mL SWCNTs (blue line). Additions of SWCNTs were performed at an open circuit and without removing the UME from the electrolyte solution. The applied potential was +0.5 V vs. Ag/AgCl and the sample time was 100 ms.

Simulation model

The simulation was performed using COMSOL Multiphysics software v4.3 for a 2-D space with axial symmetry represented through variables r and z . **Figure S2** shows the geometry used for this study. A nm to μm -scale geometry was tested for making a dimensionless plot.

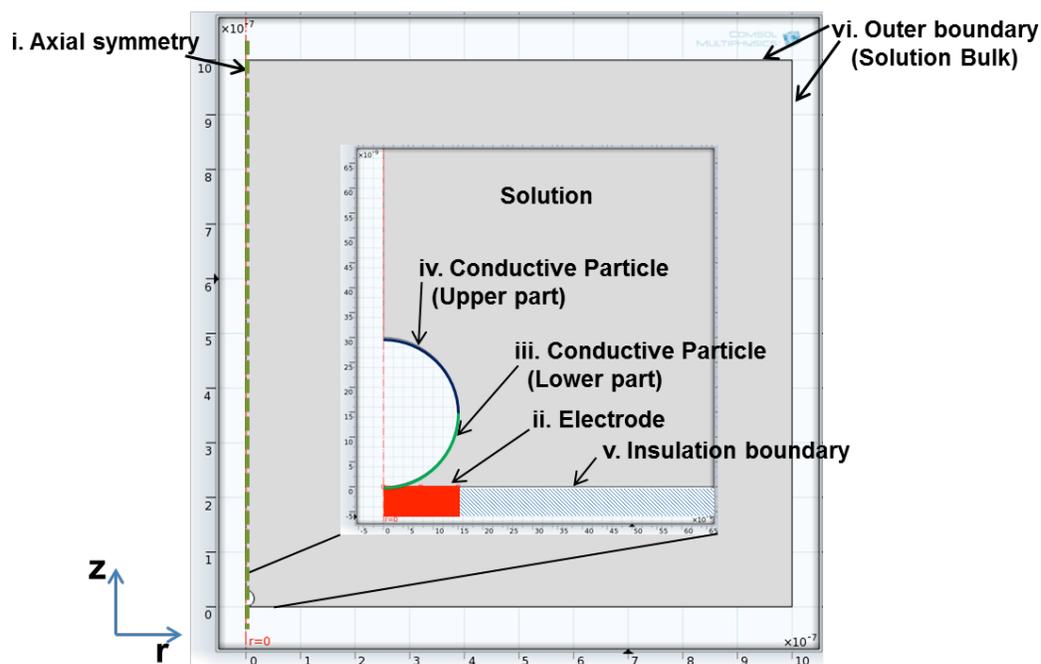
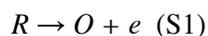


Figure S2. Geometry of the model used in simulations. Pt nanoelectrode disk (15 nm radius) embedded in a glass sheath. Size of conductive particle varies (radius of 1.00 nm, 4.22 nm, 7.44 nm, 10.7 nm, 13.9 nm, 17.1 nm, 20.3 nm, 23.6 nm, 26.8 nm, and 30.0 nm), while fixing an electrode size.

Table 1. Boundary conditions used in **Figure S2**.

Boundary selection	Boundary conditions	Quantity	Note
i	Axial symmetry	$r = 0$	symmetry axis
ii	Concentration	$C_R = 0, C_O = 4 \text{ mM}$	electrode surface
iii	Concentration	$C_R = 0, C_O = 4 \text{ mM}$	electrode surface
iv	Concentration	$C_R = 0, C_O = 4 \text{ mM}$	electrode surface
v	Insulation/Symmetry	$n \cdot J_i = 0$	Insulator
vi	Concentration	$C_R = 4 \text{ mM}, C_O = 0 \text{ mM}$	simulation space limit

Ferrocenemethanol (R) oxidation reaction is simply expressed as:



In the model considered, the concentration of redox species are denoted as $C_i(r, z)$ and described by the diffusion equation S2.

$$J_i(r, z) = -D_i \nabla C_i(r, z) \quad (\text{S2})$$

where J_i is the flux of each species, D_i is the diffusion coefficient, C_i is the concentration, every species are indicated by the subscript. Diffusion coefficient of FcMeOH is $7.8 \times 10^{-6} \text{ cm}^2/\text{s}$.

The current of the disk electrode is obtained according to equation S3:

$$i_{\text{Disk}} = \int_0^{r_D} 2\pi r \frac{\partial C_R}{\partial n} dr \quad (\text{S3})$$

where r_D is a radius of disk electrode.

The current of the conducting sphere (upper part) is obtained according to equation S4:

$$i_{\text{S1}} = \int_0^{r_S} 2\pi r \frac{\partial C_R}{\partial n} dr \quad (\text{S4})$$

where r_S is a radius of conductive sphere.

The current of the conducting sphere (lower part) is obtained according to equation S5:

$$i_{S2} = \int_0^{r_s} 2\pi r \frac{\partial C_R}{\partial n} dr \quad (S5)$$

Finally, total current is obtained from sum of each current.

$$i_T = i_{\text{Disk}} + i_{S1} + i_{S2} \quad (S6)$$

Diffusion coefficient calculation

Diffusion coefficient (D) of NP is obtained from Einstein-Stokes relation ($D=kT/(6\pi\eta r)$) where k is the Boltzmann constant, T is absolute temperature, η is viscosity of solution, and r is the radius of NP. For a 20 nm diameter NP, diffusion coefficient is $2.45 \times 10^{-7} \text{ cm}^2/\text{s}$ at 293 K.

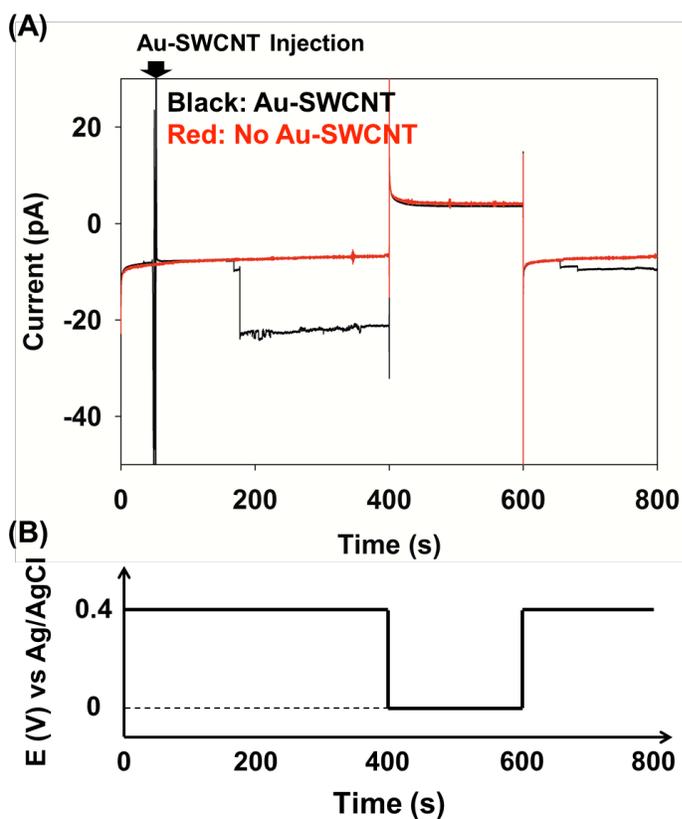


Figure S3. (A) Current-time curves for single Au-SWCNT attachment and detachment at the Pt nanoelectrode by controlling the electrode potential in the presence of 4 mM FcMeOH and 100 μM KNO_3 with Au-SWCNT (85 ng/mL, black line) and without Au-SWCNT (red line). (B) Applied electrode potential is plotted vs. time. Data acquisition time is 50 ms. Pt nanoelectrode (diameter ~ 15 nm) was used.

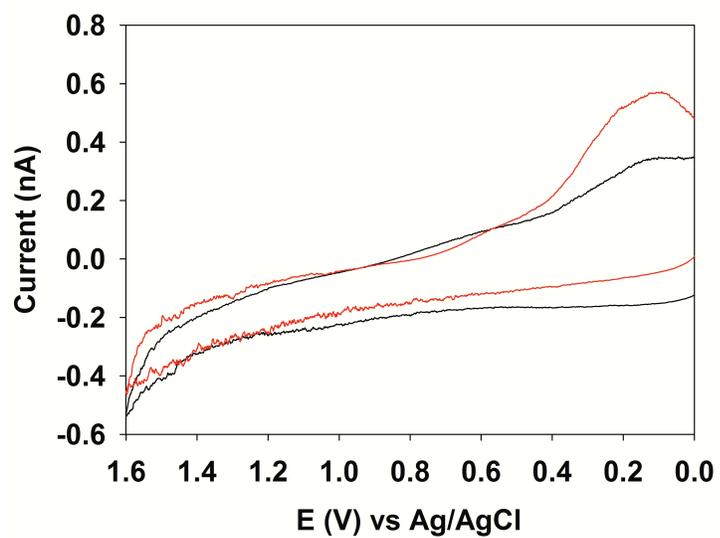


Figure S4. Cyclic voltammograms for AuNP (citrate, ~18 nm diameter) attached to carbon UME (red line), and carbon UME (black line) immersed in 0.1 M H_2SO_4 . AuNP attached carbon UME is prepared by applying 0.4 V (vs Ag/AgCl) for 400 s in 4 mM FcMeOH and 100 μM KNO_3 with 90 pM of AuNPs. Diameter of carbon UME was 10 μm .

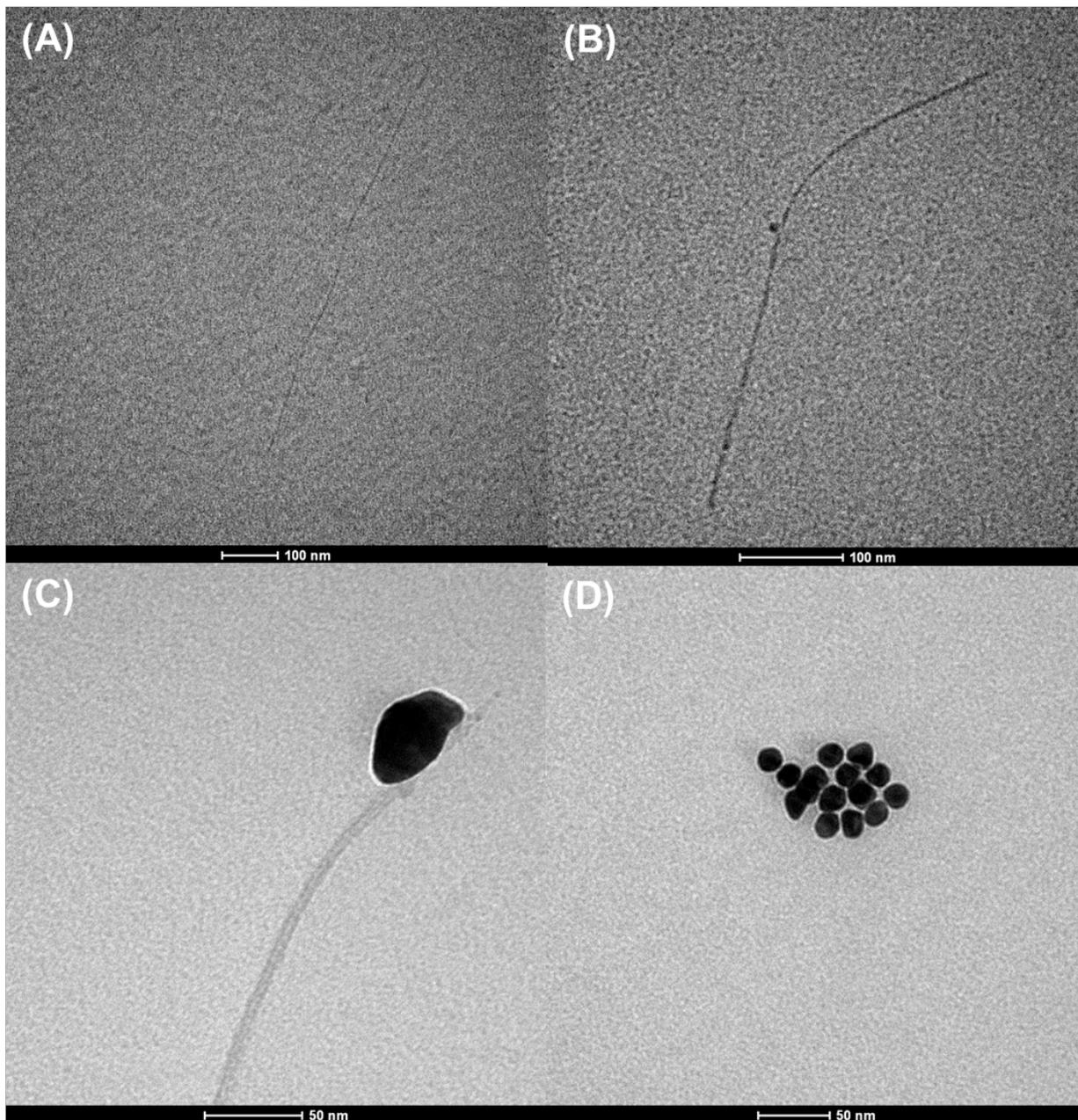


Figure S5. TEM images obtained from Au-SWCNT solution which include (A) SWCNT, (B,C) Au-SWCNT, and (D) AuNPs.

¹ Li, Y.; Bergman, D.; Zhang, B. *Anal. Chem.* **2009**, *81*, 5496-5502.

² Zhou, H.; Park, J. H.; Fan, F.-R. F.; Bard, A. J. *J. Am. Chem. Soc.* **2012**, *134*, 13212-13215.

³ Bastus, N. G.; Comenge, J.; Puntès, V. *Langmuir* **2011**, *27*, 11098-11105.