Supporting Information

Stabilizing Nanometer Scale Tip-to-Substrate Gaps in Scanning Electrochemical Microscopy Using Isothermal Chamber for Thermal Drift Suppression

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Experimental Section

Chemicals. Tetradodecylammonium (TDDA) bromide, tetraethylammonium chloride (TEACl), 1,2-dichloroethane (DCE), potassium chloride, ferrocenemethanol, and *N*-dimethyltrimethyl silylamine were purchased from Sigma-Aldrich (Saint Louis, MO). Potassium tetrakis(pentafluorophenyl)borate (TFAB) was obtained from Boulder Scientific Company (Mead, CO). All reagents were used as received except that ferrocenemethanol was recrystallized twice from hexane prior to use. The TFAB salt of TDDA was prepared by metathesis.[S-1] 10 mM TEACl was dissolved in 18.3 MΩ cm deionized water (Nanopure, Barnstead, Dubuque, IA) containing 0.3M KCl. The aqueous solution was filtered with a 0.2 μm filter (Fisher Scientific, Hanover Park, IL).

Nanopipet Fabrication. A quartz capillary (O.D. 1 mm, I.D. 0.7 mm, 10 cm long, Sutter Instrument, Novato, CA) was air blow cleaned before pulling and was pulled in a CO_2-laser puller (Model P-2000, Sutter Instrument) by running the line of a program with parameters of heat = 710, filament = 4, velocity = 30, delay = 120, and pull = 182. The pulled capillary was checked under optical microscope (BX-41, Olympus America Inc., Melville, NY) to select a pipet with a fainted tapered end of 1.2 ± 0.2 μm, which corresponds to a real tip radius of 10–15 nm as determined by field-emission SEM (model XL-30, Philips Electron Optics, Eindhoven, Netherlands) and also electrochemically (see the main text). The pulled nanopipets were dried for >1 hour under vacuum in Mini-Vacuum Desiccator (Bel-Art Products, Pequannock, NJ) and then silanized by introducing 50 μL of *N*-dimethyltrimethyl silylamine (Selectophore grade, Sigma-Aldrich) into the desiccator. Silanization was performed in the sealed desiccator for 50 ± 10 min, which was adjusted depending on the temperature and humidity of the atmosphere. After silanization, a vacuum was applied to the desiccator for ~1 min to remove the extra silanization

agent, then nitrogen gas was introduced to the desiccator before it is opened to take away the silanized pipets. The silanized nanopipets were filled with 4 μL of a DCE solution containing 0.1 M TDDATFAB. It took ~2 minutes or longer to fill a region of 250 μm from the tip of a well silanized nanopipet with the DCE solution by gently tapping the outer pipet wall using a tweezers. In contrast, a region of >1 mm from the tip of an inadequately silanized nanopipet was filled within 30 s. An electrochemically etched Pt wire (99.99 %, 50 μm diameter, Goodfellow, Oakdale, PA) was inserted into a DCE-filled nanopipet as an organic reference/counter electrode. A modeling clay (Sargent Art, Inc., Hazleton, PA) was used to fix the position of the Pt wire. The nanopipet electrode was used immediately for SECM experiments.

SECM Measurements. A *z*-axis piezoelectric positioner with a capacitive position sensor (P-621.ZCD, PI, Auburn, MA) was operated in the closed-loop mode using an amplifier/servo controller (E-665.CR, PI) for tip positioning. A Labview program or PIMikroMove (PI) was used to control the positioner in the drift compensation mode, which eliminates drift in the digital-analog converters on the E-816 submodule that plugs into the main board of the controller. An *x*, *y*-axes piezoelectric positioner (P-620.2CD, PI) was also mounted on the SECM stage (M-462, Newport, Irvine, CA) with micrometers (SM-25 for *z*-axis and AJS100-1 for *x*, *y*-axes, Newport). The amperometric tip current was measured using the potentiostat of CHI 900 (CH Instruments, Austin, TX). Inchworm motors of CHI 900 were also used for tip positioning without an isothermal chamber. The SECM stages were placed on a vibration isolation table with a faraday cage (model 63-533, TMC, Peabody, MA). A SiO_2/Si wafer (W-1P-300, Graphene Supermarket, Calverton, NY) was used as a substrate.

Isothermal Chamber. The isothermal chamber in Figure 2 is based on the box of VIPs (200VIP-UPS, ThermoSafe Brands, Arlington Heights, IL) and extruded aluminum heat sinks (68C6958, HS Marston Aerospace, Wolverhampton, England). In the chamber, an SECM cell was sealed with a rubber cap (Figure S-1a) to prevent solvent evaporation, which cools down the solution. The isothermal chamber was closed with a VIP and then with an aluminum plate (panels b and c, respectively). A high-resolution thermometer (Model 1504 and 5641, Fluke Electronics, American Fork, UT) is seen at the left-hand side of the SECM stage in Figure 2. The detailed scheme of the home-built isothermal chamber is available upon request.

Some care was taken to avoid the heating of the chamber air by an operator and an illumination. An operator wore cryogenic shoulder glove and apron (Tempshield, Mount Desert, ME) to minimize the temperature raise during the setup of tip and cell. Also, operator's hands were kept outside of the chamber when the *z*-axis micrometer of the SECM stage was rotated using a hexagonal wrench to approach the tip to the substrate within the maximum 100 μm travel distance of the *z*-axis piezoelectric positioner. The SECM cell was illuminated using a small LED lamp (MR-WN120-20S, Quadica Developments, Brantford, Ontario, Canada) to minimize heat generation in the chamber when the tip approach was monitored using a high magnification video microscope (VZ-400 and VAR-20, CALTEX Scientific, Irvine, CA) equipped with a CCD camera (INFINITY 2-1, Lumenera, Ottawa, Ontario, Canada).

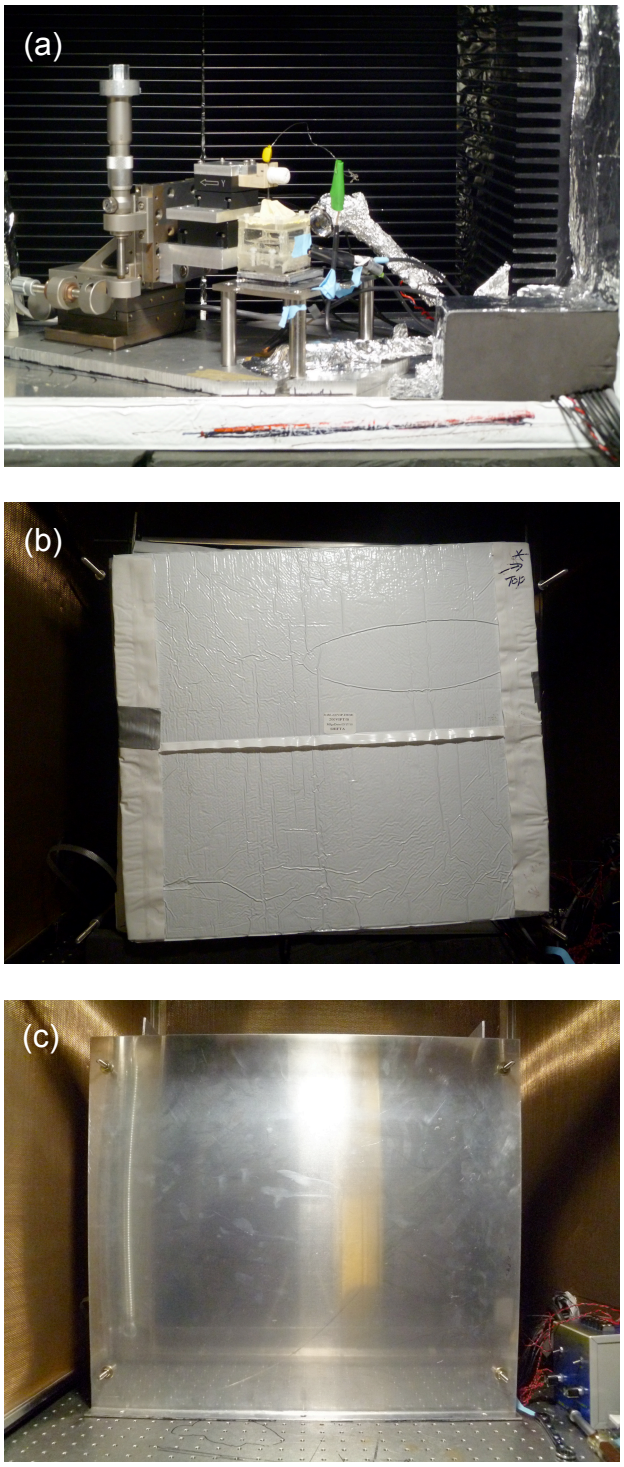

Figure S-1. Images of (a) SECM stage, tip, and cell, and the isothermal chamber closed (b) with (b) a VIP and then (c) with an aluminum plate.

Fluctuation of Piezoelectric Positioner. Changes in the position of the *z*-axis piezoelectric positioner was read from the capacitive sensor (Figure S-2) to demonstrate the fluctuation of piezo position during the measurement of feedback tip current in Figure 4. The relative piezo position was defined against the position where the tip approach was stopped. The standard deviation of the relative piezo position was 0.4 nm.

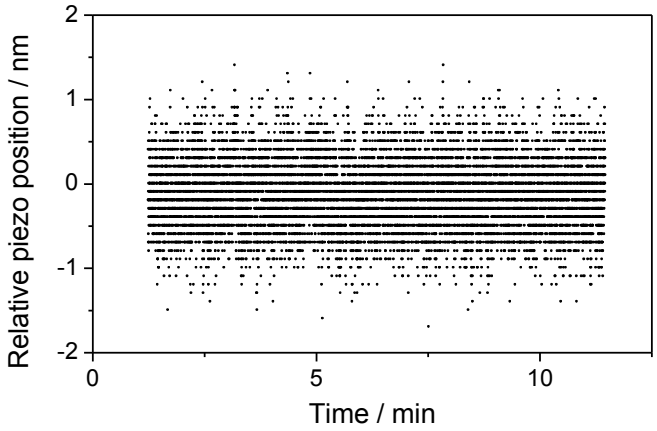

Figure S-2. Plot of relative piezo position read from the capacitive sensor of the positioner. The zero position corresponds to the position where the tip approach was stopped.

REFERENCES

(S-1) Guo, J.; Amemiya, S. *Anal. Chem.* **2006**, *78*, 6893.