High Aspect Ratio SiO_2-Coated SWNT Scanning Probe Nanoelectrodes

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Supporting Information

SiO_2 Film Characterization

Film thicknesses were determined using a Gaertner L116C ellipsometer operating at λ=632.8 nm. The complex refractive index for SiO2 was reported as n=1.46, and the substrate refractive indices for the model surfaces were: Si (n=3.85, k=0.2), Au (n=0.13, k=3.16) and HOPG (n=2.91, k=1.71).[1] Figure S1 shows Au and HOPG surfaces coated with SiO_2 that have a calculated RMS roughness of 1.5 and 0.9 nm.

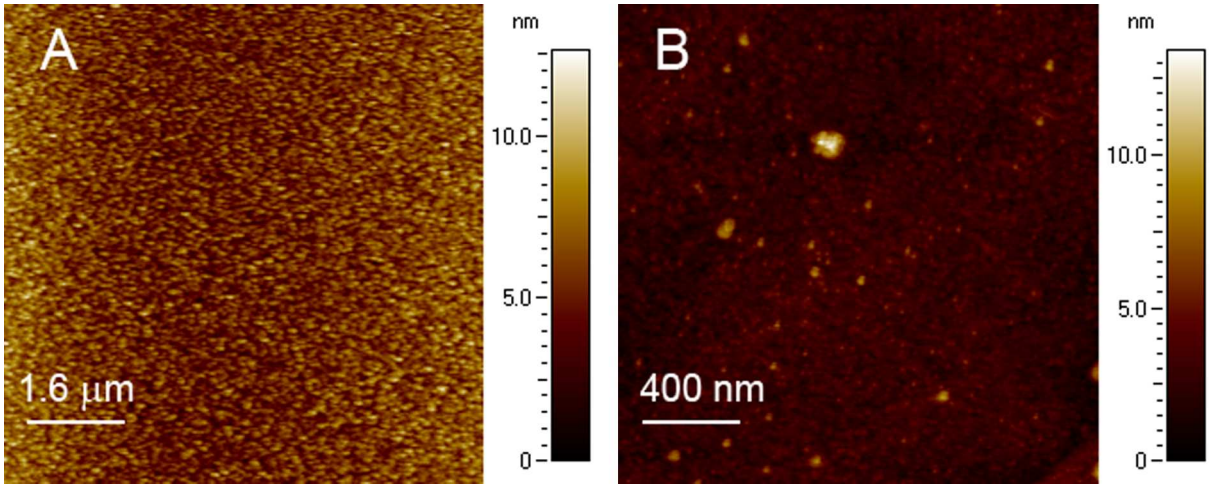

Figure S1. AFM images of gold (A) and HOPG surfaces (B) that were coated with 140 nm and 130 nm of SiO_2, respectively, after 2 min at 100 W in the plasma.

The electrochemical impedance spectra were collected with a Solartron impedance analyzer in the frequency range of 0.1 Hz to 50 kHz, with an amplitude of 40 mV and a potential of 0.2 V versus a platinum reference electrode. The electrolyte solution was 0.1 M KCl with 5 mM of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$.

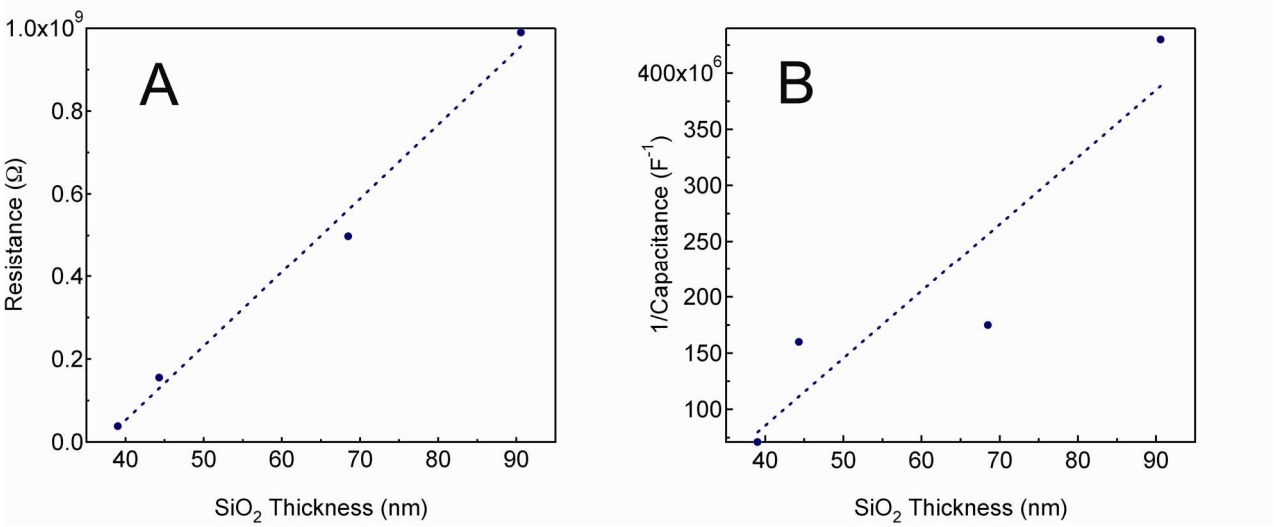

Figure S2. Resistance (A) and capacitance (B) values obtained from fitting of impedance spectra as a function of polymer thickness.

XPS Results

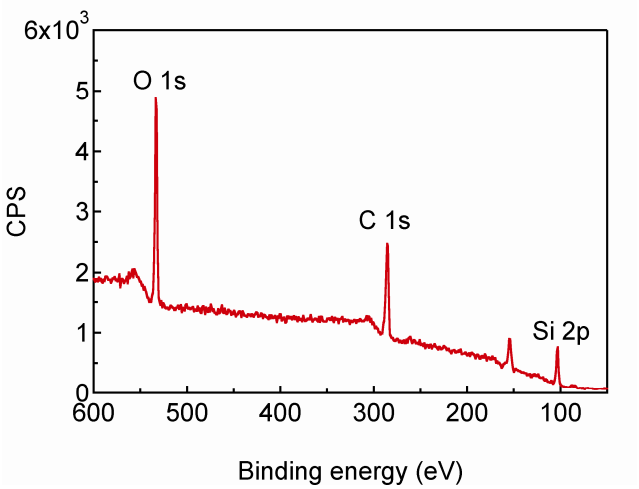

Figure S3. XPS results for a 12 nm SiO_2 film on a gold substrate

Preparation of Ferrocenylmethyl-trimethylammonium Hexafluorophosphate

The compound was prepared from 12.3 mg of FcTMAI (Strem) dissolved in 1 mL of Milli-Q water. After the addition of 100 µl of a 5 M solution of KPF_6 (Aldrich), a yellow precipitate was formed which was the less soluble PF_6^- salt of $FcTMA^+$. The product was pelleted at 13000 rpm and washed twice with 200 µl of 0.25 M solution of KPF_6. The compound was dried down overnight in a speed-vac. Finally, the $FcTMA^+$ PF_6^- was dissolved to make a 2 mM solution with 0.1 M KCl.

CVs of SiO_2 Passivated AFM Tip without Nanotube

Figure S4 shows CVs taken before and after TEM exposure of a SiO_2-coated AFM tip without an attached SWNT. The currents are due solely to charging effects before TEM imaging of the probe, while after TEM imaging the capacitive currents are overwhelmed by faradaic leakage currents. This behavior is also seen with attached SWNTs, as shown in Figure 3 of the manuscript.

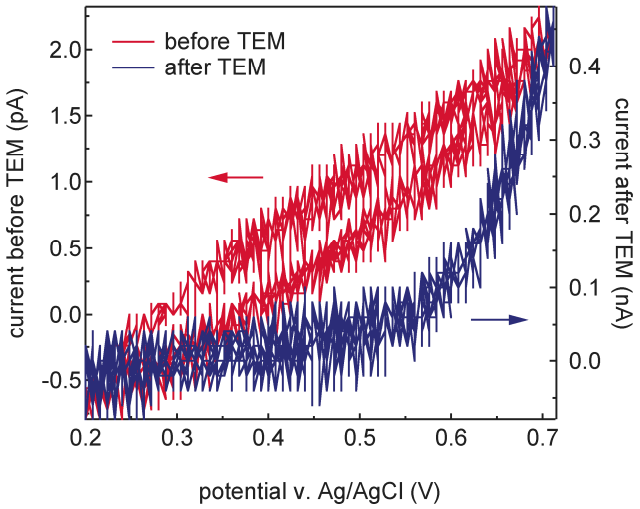

Figure S4. Cyclic voltammagram with $FcTMA^+$ of a gold coated AFM probe without nanotube passivated with 54 nm of SiO_2 before (left arrow) and after (right arrow) TEM imaging. The scan rate was 10 mV/sec.

Blind Experiments

Several SiO_2 coated probes were pulse etched and electrochemically deposited with gold before TEM imaging. The results from a typical probe are shown in figure S5. The amount of potential required for exposing the SWNT was much higher than for imaged tips. In addition, the area exposed by the pulse etching was often along the sidewalls of the nanotube and not the very end of the probe.

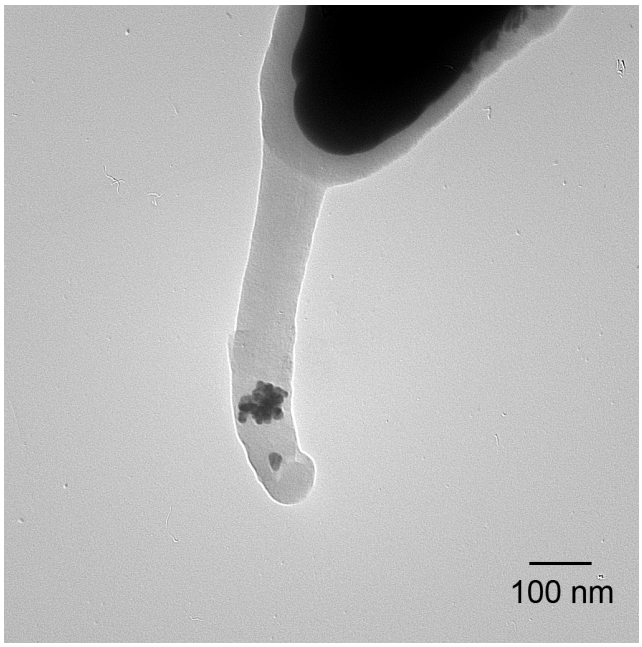

Figure S5. A SWNT nanoelectrode coated with 46 nm SiO_2 and pulse opened at +70.6 V. Gold was deposited electrochemically at -200 mV for 100 msec.

SiO_2 Film Breaking Due to Nanotube Buckling

When the attached SWNT was greater than 2 μm in length, and the deposited SiO_2 film was less than 30 nm thick, it was observed that the SiO_2 coating became brittle and cracked where the nanotube buckled. Figure S6 illustrates this behavior where it is clear that the nanotube was exposed between the gaps in the SiO_2 film.

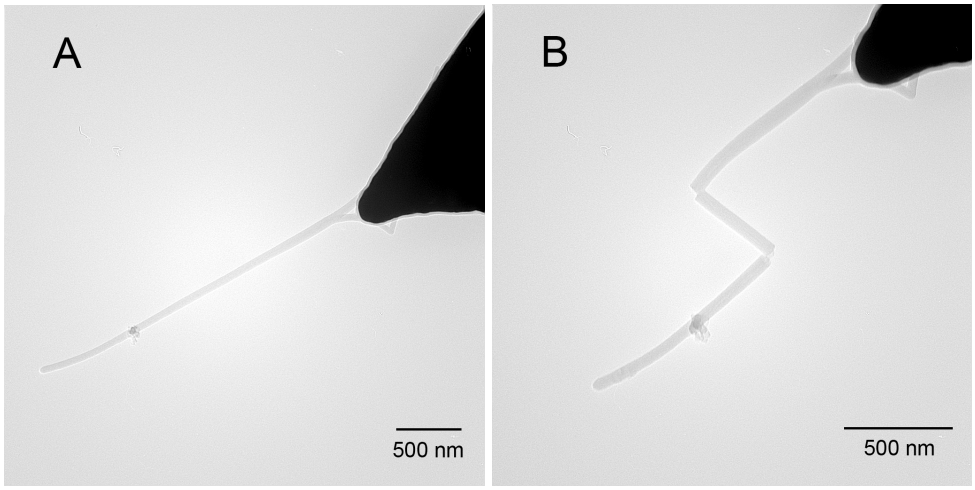

Figure S6. TEM images of a SWNT nanoelectrode coated with 26 nm of SiO_2 before (A) and after (B) the application of lateral force only (no pulsing).

1. Palik, E. D.; Ghosh, G., *Handbook of optical constants of solids*. Academic Press: Orlando, 1985.