Supporting Information

Electrochemical Identification of Metallic and Semiconducting Single-Walled Carbon Nanotubes

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Part 1: Ultra-long SWNTs growth1, 2.

Ultra-long SWNTs were grown by chemical vapor deposition using solution of 0.01M FeCl₃ in ethanol as catalyst precursors. The catalysts were stamped on the marked Si/SiO₂ substrate with patterned Pt microelectrodes using a piece of PDMS as a soft stamp. The catalysts were calcined at 700 °C for 45min. Then the substrate was put in a quartz tube with inner radius of 3 cm. A mixture of 500 sccm Ar and 100 sccm H₂ was loaded in as a carrier gas. After calcining the catalysts at 950 °C for 20min in the mixed gas, ethanol bubbled by Ar was added as a carbon source for 30min and then the quartz tube was cooled down under hydrogen and argon. Note that higher growth temperature and longer growth time will severely damage Pt microelectrodes.

Part 2: Preparation of Pt microelectrodes and electrical measurements3.

Fig S1a shows schematic illustrations of experimental details for preparation of Pt microelectrodes, electrical measurements, and electrodeposition. Sixteen groups of Pt microelectrodes (sputtered 80nm Pt with 20nm Ti adhesive layer) were patterned on the Si/SiO₂ substrate using a standard photolithography and lift-off process before carbon nanotubes growth. After SWNTs growth, an SWNT crossed over the Pt microelectrodes (Fig S1b), and the distance between catalysts and Pt microelectrodes is 3-5mm, so we have SWNTs with enough length for electrodeposition. Using these Pt microelectrodes, electrical transport characteristics of as-grown SWNTs (Fig S1c and d) were measured using a low-current measurement system Keithley 4200 coupled with a TMC four-probe station before electrodeposition. Note that before electrical measurements, we scratched
down the SWNTs around Pt microelectrode using very thin metal probes to avoid current leakage. We used well-aligned SWNTs array with low density, coupled with the marks on the substrate, to make sure we did electrical measurements and electrodeposition on the same SWNT.

**a)**

**Patterning Pt microelectrode**

**Growing SWNTs**

**Electrodeposition**

**Electrical measurement**

**b)**

*Image of patterned Pt microelectrode and SWNTs growth with marks on the substrate.*

*Image of patterned Pt microelectrode array with SWNTs growth, scale 200μm.*
Figure S1. a) Schematic illustrations of patterning Pt microelectrodes, growing carbon nanotubes, and electrical measurements on marked substrate. b) Typical SEM image of an SWNT crossing over a group of Pt microelectrodes. c) Typical electrical transport characteristics of an m-SWNT with ON/OFF ratio \(\approx 6\). d) Typical electrical transport characteristics of an s-SWNT with ON/OFF ratio \(> 10^3\).
Part 3: Electrodeposition and Cyclic voltammetry on SWNTs\textsuperscript{4,5}.

Macroscopic Au electrode (85nm Au with 15nm Ti adhesive layer) were thermally evaporated around the catalysts region using a clean silicon wafer as shadow mask. The samples were annealed at 600°C for 30min in argon to improve the contact between SWNTs and electrodes. The long and aligned SWNTs electrically connected to Au electrode were used as the working electrodes and immersed into electrolyte solution containing 1mM AgNO\textsubscript{3} and 0.2M KNO\textsubscript{3} so that part of Au electrode was placed into the solution, which showed little effect on metal deposition on SWNTs. The electrodeposition was carried out with a commercial potentiostat (CHI 660B) in a three-electrode mode using a Pt foil as counter electrode and a Ag/AgCl wire as reference electrode. All potentials are given versus Ag/AgCl. Various deposition conditions were tested using many different samples with similar fabrication procedures. Cyclic voltammetry (CV) of Ag deposition on several long, aligned SWNTs in a “droplet cell” were shown in Figure S2. Note that the droplet we used did not cover Au electrode due to the length of SWNTs. Compared with a control test with only 0.2M KNO\textsubscript{3} in the solution (solid black line in Figure S2a), CV response indeed represented Ag nucleation and growth on SWNTs.

![Cyclic voltammogram of Ag redox reaction on SWNTs electrodes in the aqueous solution containing 1mM AgNO\textsubscript{3} and 0.2M KNO\textsubscript{3} (red line). A control test in 0.2M KNO\textsubscript{3} solution is also shown (black line). The scan rate is 100mV/s. The arrows indicate the scan direction.](image)

*Figure S2.* Cyclic voltammogram of Ag redox reaction on SWNTs electrodes in the aqueous solution containing 1mM AgNO\textsubscript{3} and 0.2M KNO\textsubscript{3} (red line). A control test in 0.2M KNO\textsubscript{3} solution is also shown (black line). The scan rate is 100mV/s. The arrows indicate the scan direction.
Part 4: Typical AFM images and Raman spectrum of sampled SWNTs.

Tapping mode AFM (Nanoscope III) was used to determine the diameters of carbon nanotubes before electrodeposition, and according to the AFM height profile scan, we can confirm whether they are single-walled (Figure S3a). Raman spectra were obtained with a Renishaw confocal imaging Raman microscope. The excitation energy is 1.96 eV (632.8nm) with a 1 μm spot size. For all carbon nanotubes, we observed the G-mode splitting profiles and for some SWNTs, the radial breathing mode (RBM) was observed (Figure S3b), and their diameters could be derived from the expression $d = \frac{248 \text{ cm}^{-1}}{\omega_{\text{RBM}}}$. For other SWNTs, however, we could not observe their RBM because of the limitation of laser energy.

![AFM image and Raman spectrum](image)

**Figure S3.** a) Typical AFM images and height profile scan of an SWNT on the substrate. b) Typical Raman spectra of an SWNT.
Part 5: Typical AFM images of Ag-decorated m- and s-SWNT.

Figure S4. Tapping mode AFM images of an m-SWNT (left) and an s-SWNT (right) after Ag electrodeposition at -0.6V for 80ms. The particle sizes are denoted.

Part 6: 62 combined SEM images of m-SWNT (down) and s-SWNT (up) after electrodeposition on the same substrate.

Typically, to view the two carbon nanotubes decorated with silver from Au macroelectrode to Pt microelectrode, 62 SEM images was divided into 11 segments (numbered 1 to 11). Most of SEM images were photographed with the same magnification, but when the interval between two SWNTs increased, we used lower magnification to put them in one SEM images. Images of different magnification were seamlessly obtained using electron beam-induced deposition (EBID), so 62 SEM images showed complete silver nanoparticles distribution along two SWNTs, although they overlapped over short distances around Au electrode (see segment 1 to 3). Note that the diameters of the two SWNTs in SEM images cannot represent the actual values obtained by AFM, because charge accumulation along the tubes made them brighter and wider7.
References