Supporting Information for

Regiospecific Synthesis of Au-Nanorod/SWCNT/Au-Nanorod Heterojunctions

Yossi Weizmann, Jeewoo Lim, David M. Chenoweth and Timothy M. Swager*

*To whom correspondence should be addressed. E-mail: tswager@mit.edu

Department of Chemistry and Institute for Soldier Nanotechnologies Massachusetts Institute of Technology 77 Massachusetts Avenue, Cambridge, MA 02139 (USA).

This PDF file includes:

Materials and Methods
Fig. S1-S3
References

Materials and Methods

Materials

Unless otherwise noted, all the starting materials were obtained from commercial suppliers and used without further purification. Purified HiPco Single-Wall Carbon Nanotubes were purchased from Unidym, Inc. Purified MWCNT; hexadecyltrimethylammonium bromide, 99% (CTAB); *N*-hydroxysulfosuccinimide sodium salt (sulfo-NHS); Triton X-100 and polyethylene glycol (PEG) with average mol wt 10,000 were purchased from Sigma-Aldrich. Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \times XH_2O$), 99.999%; L-(+)-ascorbic acid, 99+% and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 98+% (EDC) were purchased from Alfa Aesar. HEPES and hydrogen peroxide 30% were purchased from EMD Biosciences, Inc. Monoamino gold nanoparticles were obtained from Nanoprobes, Inc. Centricon separation devices

and 0.6 μm polycarbonate membrane filters were purchased from Millipore. Ultrapure water from a NANOpure Diamond (Barnstead) source was used throughout all of the experiments.

General Methods

Transmission electron microscopy (TEM) images were taken on JEOL 2010 and JEOL 200CX instruments (acceleration voltage 200 KV) using 200-mesh carbon-coated copper grid (Electron Microscopy Sciences). All atomic force microscopy (AFM) imaging measurements were performed at room temperature by using a Multimode scanning probe microscope with a Nanoscope 3A controller (Digital Instruments/Veeco Probes). AFM topographical images were taken on samples deposited on freshly cleaved grade v-4 mica surfaces (Structure Probe, Inc.) that were first passivated with a 5 mM $MgCl_2$ solution for 1 min followed by drop casting the solution of interest. Images were taken with Ultrasharp SiN AFM tips (MikroMasch) in tapping mode at their resonant frequency, and these images were analyzed with WsXM SPIP software (Nanotec).[1] Confocal Raman microscopy was performed using a Horiba Jobin Yvon Raman confocal microscope (model LabRAM-HR) with a 784.4 nm (1.58 eV) laser as the excitation light source. A x50 objective was used for imaging with a pin hole size of 300 microns. All sonication procedures were conducted with an ultrasonic bath (Branson Ultrasonics Corporation, model 3510). SEM images were taken with a cold field-emission gun scanning electron microscope (FEG-SEM).

Cutting and oxidation of SWCNT

Commercial HiPco SWCNTs were cut and etched according to a reported procedure[2] with some modification, to give shortened SWCNTs bearing carboxylic groups at their ends (SWCNT-COOH) and also as defect sites on the sidewalls. Specifically, 50 mg pristine pure HiPco SWCNTs were place in oxidative reaction of 24 mL suspension contains a 3:1 H_2SO_4 (98%)/HNO_3 (70%) solution at 40 ^oC and under sonication at 42 kHz. Sonication during the cutting protocol was reduced to 35 min. The solution was filtered using a 0.6 μm polycarbonate membrane filter and then etched for 30 minutes with a 20 mL of a 4:1 H_2SO_4 (98%)/H_2O_2 30% solution to remove all carbon particles

produced by the first reaction. The resulting diluted nanotube-acid mixture was then filtered using a 0.6 μm polycarbonate membrane filter leaving a SWCNT filter cake. The nanotubes were then rinsed with water until a pH above 5 was obtained. Final rinsing was done using ethanol and the resulting filter cake dried in a vacuum desiccator.

Shielding SWCNT-COOH sidewall surface

Typically, 0.1% SWCNTs-COOH (wt/v) were place in water solution contains 0.25% Triton x-100 (v/v) and 0.25% PEG (10,000 M_r) (wt/v) in a final volume of 1 mL, and sonicated for 4 hrs at 42 kHz in ice bath, followed by centrifugation at 14,000 r.p.m for 1 hour. Next, the supernatant was collected; leaving a small residual amount of unwanted aggregated SWCNTs behind.

Tethering AU-NPs to the shielding SWCNT-COOH terminus sites

Generally, 0.02% SWCNT-COOH (wt/v) were place in a HEPES buffer solution 0.1 M, pH 7.4 consisting of 0.05% Triton X-100 (v/v), 0.05% PEG (10,000 M_r) (wt/v), 0.6×10^{-9} mol 1.4 nm monoamino gold nanoparticles, 2 mM EDC and 5 mM sulfo-NHS in a final volume of 1 mL, and stirred gently overnight in the dark at room temperature. The reaction mix was then purified and separated from the excess Au-nanoparticles using a Centricon filtration device (100,000 cutoff), and concentrated to a final volume of 500 μL.

Synthesis of Gold Nanorods

Gold nanorods were synthesized by the three-step seeding protocol as described by Murphy et al.[3] Specifically, two 20 mL flasks and one 100 mL conical flask (labeled A, B, and C, respectively) were used. To these flasks were added 9 mL (in flasks A and B) and 45 mL (in flask C) of growth solution containing a mixture of 2.5×10^{-4} M $HAuCl_4$ and 0.1 M CTAB solutions and kept at 27 ^{o}C. Then, 50 μL of 0.1 M freshly prepared ascorbic acid (flasks A and B) and 250 μL (flask C) were added and hand shaken, the solutions became colorless. Next, 200 μL of seed solution (Au-NP/SWCNT/Au-NP) was added to flask A (step 1) and gently mixed. Immediately after 15 seconds 1 mL of the resulting mixture was transferred quickly from flask A to flask B and gently mixed (step 2). This

was followed by transferring 5 mL portion of flask B into flask C after 30 seconds and mixing gently by hand shaking (step 3). The color of the resulting solution slowly changed to purple. Flask C was then kept undisturbed for additional 16 h at 27 ^{o}C. High aspect ratio nanorods along with other shapes (triangles, hexagons, and small rods) precipitate from the solution and form a thin barely noticeable film at the bottom of the flask. The resulting supernatant, which contained mostly spherical nanoparticles, was carefully removed and the film on the bottom was carefully rinsed with a small portion of pure water to remove the residual amount of the supernatant. The same procedure was used for the SWCNTs.

References

1. Horcas, I. et al. *Rev. Sci. Instr.* **2007**, *78*, 013705.
2. Liu, J., Rinzler, A. G., Dai, H., Hafner, J. H., et al. *Science* **1998**, *280*, 1253.
3. Jana, N. R., Gearheart, L. & Murphy, C. J. *J. Phys. Chem. B* **2001**, *105*, 4065-4067.

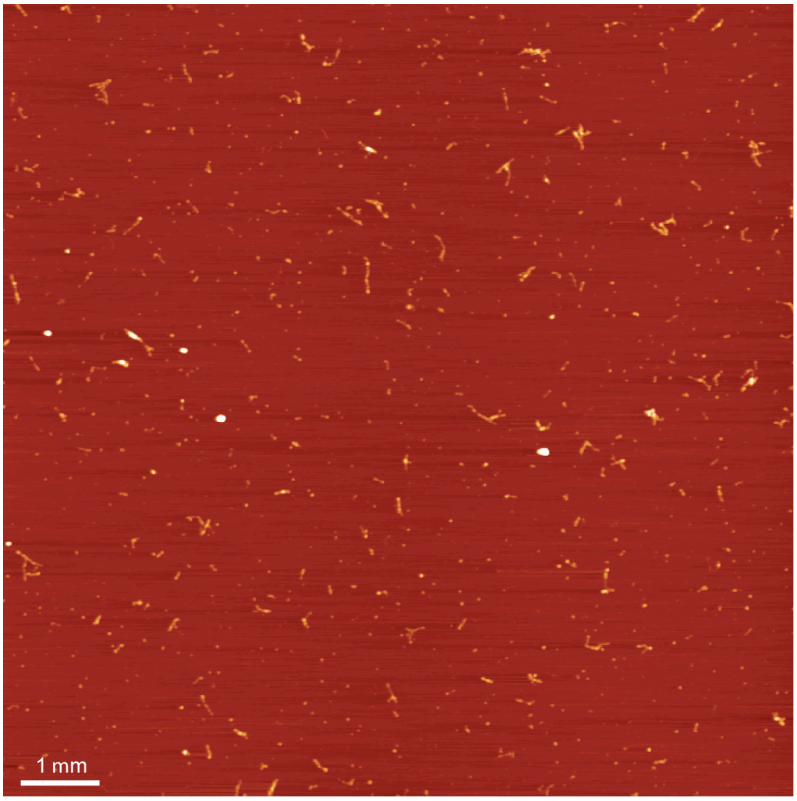

Figure S1. AFM image of oxidized shielded carbon nanotubes. Oxidized nanotubes were incubated with Triton X-100/PEG (M_r = 10,000) in an aqueous solution and sonicated for 4 h in an ice bath. This process results in a stable dispersion of SWCNTs wrapped with surfactant and polymer.

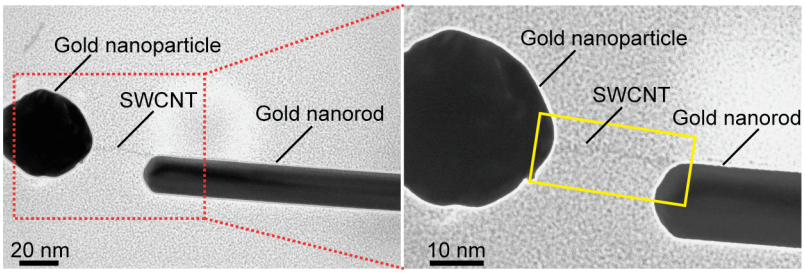

Figure S2. TEM image of Au-nanorod/SWCNT/Au-nanoparticle nanostructure. TEM image showing a 30 nm long SWCNT between a Au-nanorod and a Au-nanoparticle. Right image displays an enlarged view of the heterojunction from the image on the left. All images are shown with their respective scale bars.

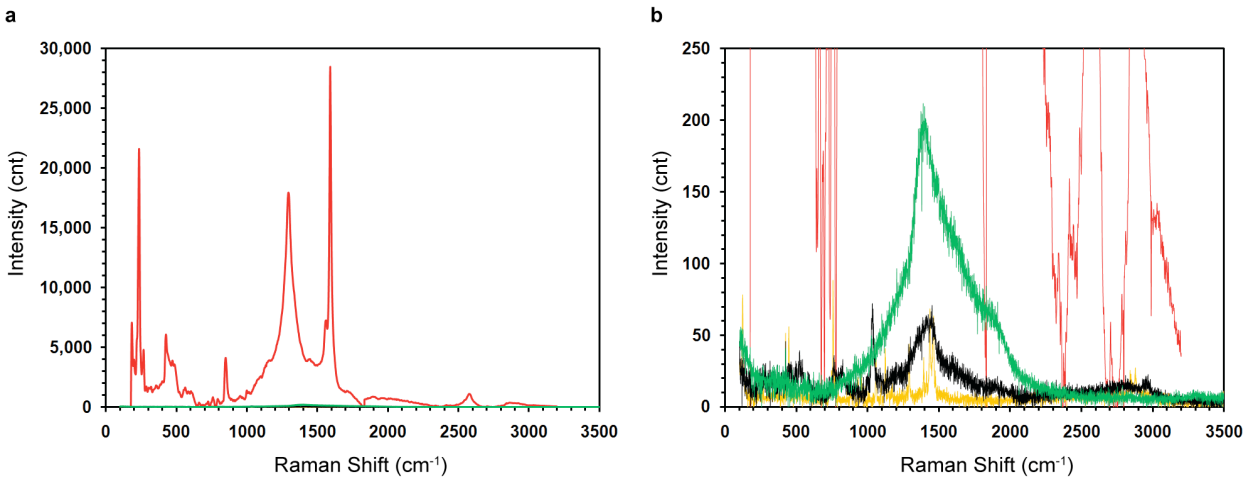

Figure S3. Confocal Raman spectra of Au-nanorod/SWCNT/Au-nanorods (red, top spectrum), Au-nanorods (green), 1.4 nm Au-nanoparticles (black), CTAB (yellow) using a laser excitation wavelength of 784.4 nm (1.58 eV). (a) Full scale spectrum. (b) Expanded view of y-axis intensity from 0-250 counts showing the Au-nanorods (green), 1.4 nm Au-nanoparticles (black), and CTAB spectra in the baseline.