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Preferential growth of single-walled carbon nanotubes with metallic conductivity

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SUPPORTING ONLINE MATERIAL

MATERIALS AND METHODS

Synthesis of SWNT growth

SWCNTs were grown from Fe nanocatalysts deposited onto silicon support. The silica layer (~120-300 nm) was thermally grown on a highly doped p-type Si wafer. The catalyst particles were obtained by immersing the substrate into 0.04-0.07 mg $Fe(NO_3)_3$ dissolved in a 1 ml isopropanol solution (from 1-12 minutes) followed by dipping the substrate in hexane (10 sec.) and drying under flowing air. Methane was used as the carbon source. Before SWCNT growth, the catalyst particles were reduced at 450 ºC. The temperature was then increased to 860 ºC with He or with Ar flowing through the reactor (700 cm^3/min) with various amount of H_2/H_2O or H_2 with following annealing up to 10 min. Then, CH_4 was introduced in the system for 10 min at a flow rate of 300 cm^3/min, terminating the other gases streams.

Raman measurements

The RBMs of these samples (S#1 $\rightarrow$ S#8) associated with the 532 nm laser excitation show a similar tendency as those for 632.8 nm, although one should consider that for the diameter range of grown tubes the abundance of semiconducting tubes that are under resonance with this excitation is higher (*S1, S2*). For the 785 nm laser excitation, the samples with high metallic content show weak signals, which is expected due to the diameter range of grown metallic SWCNTs (170-230 cm^{-1}).

We also studied the dependence of met./sem ratio on the H_2 concentration without presence of H_2O (7.6×10^{-4} mTorr) in the ambient. An increase of the H_2 from 10% to 20%

results in a slight variation of the percentage of metallic tubes from the range of ~27%-50% to ~35%-54%. One of the possible scenarios for this slight variation could be the in situ modification of tubes electronic structure by reductive species (H_2). Although chemisorption of atomic hydrogen (H) in SWCNTs is possible at appropriate conditions (*S3*) hydrogen was shown to reduce the conductivity of initial tubes (due to the sp^2-sp^3 reconstruction) and has not significant impact on Raman spectra (changes in the D-band). Even if we assume the formation of atomic H during the nanotube growth, still in situ chemisorption is not likely as desorption temperature of hydrogen was found ~200 ºC-300 ºC (*S3*), which is much lower than the synthesis temperature. The molecular hydrogen (H_2) has very small effect on the electrical response of nanotube films (*S4*, *S5*).

CNTFET device preparation

Prior to SWCNT growth, four grid patterns were defined using E-beam lithography in the region confined by the four alignment marks. This grid allowed us to locate SWCNTs and define the contact on them. First, the substrate with the alignment marks was cleaned by sonicating it in acetone, and then in isopropanol. Finally, it was dried in flowing N_2. Then Co-polymer resist Ethyl Lactate (EL 9) was spun at the rate of 6000 rpm on the cleaned substrate and soft baked at 180 ºC for 5 minutes. Next, E-beam resist Polymethylacrylate PMMA (A 8) was spun at the same rate and baked at 180 ºC for another 5 minutes. Then a second E-beam resist PMMA (A 5.5) was spun at the same rate and baked at 180 ºC for 15 minutes. Finally, the substrate was transferred inside the SEM chamber and the grid file was run and written by E-beam. The sample was developed using MIBK developer for 90 seconds and then washed with isopropanol, followed by etching using Buffer Oxide Etch solution (Hydrogen Fluoride) for 5-10 seconds. Finally, the E-beam resist and copolymer were removed by sonicating the sample in acetone.

Following growth, individual nanotubes were contacted by source and drain electrodes (Au/Ti) and the Si substrate was used as the back gate. The typical source-drain distance was 2 ~ 3 microns. Before transport property measurements all devices were annealed at 350 °C for 2 hours under flowing Ar to establish good ohmic contacts. The estimated contact resistance is about ~20-50 KΩ. Based on their source-drain current (I_{sd}) versus gate voltage (V_g) characteristics, the measured nanotubes can be classified into two categories: (1) semiconducting- those exhibiting FET behavior, where the current I_{sd} changed more than one order of magnitude when V_g changed from -20 to 20 V or (2) metallic-those exhibiting behavior, where the current I_{sd} was not sensitive to V_g (we define insensitivity to be less than 50% of I_{sd} variation during V_g changes from -20 to 20V. I_{sd}(max) was maintained at the level of micro-ampere range for all of our experiments in order to have I-V curves with high-quality signal-to-noise ratio. We used the same gate oxide thickness and gate voltage range (from -20 to 20V) in all of our measurements, although larger gate voltages were occasionally used in order to reach a convincing assignment of conductivity.

Photoluminescence measurements for the sample #6 reveal the presence of the semiconducting tubes of ~15.4 % (standard error 2.6) that is in reasonable agreement with metallic tube content ~80% based on Raman spectra estimation. (Table S1). More details on photoluminescence measurement and results can be find in (*S6*).

TEM measurements (FEI Titan 80/300 ETEM). TEM samples were prepared from (001) silicon wafers with a thermally grown 500 nm thick SiO_2 layer. The wafer was cut to a 3mm disk and the backside of the disk was hand-polished and dimpled down to about 5-10 um at the center of the disk. Then, the disk was Ar^+ ion-milled from the backside at a 4.5º angle and at 4.5 kV using a Gatan PIPS™ until the tiny hole at the center of the disk was made. Finally, the iron catalysts were deposited by the same method used for CNT synthesis, described above.

Figures

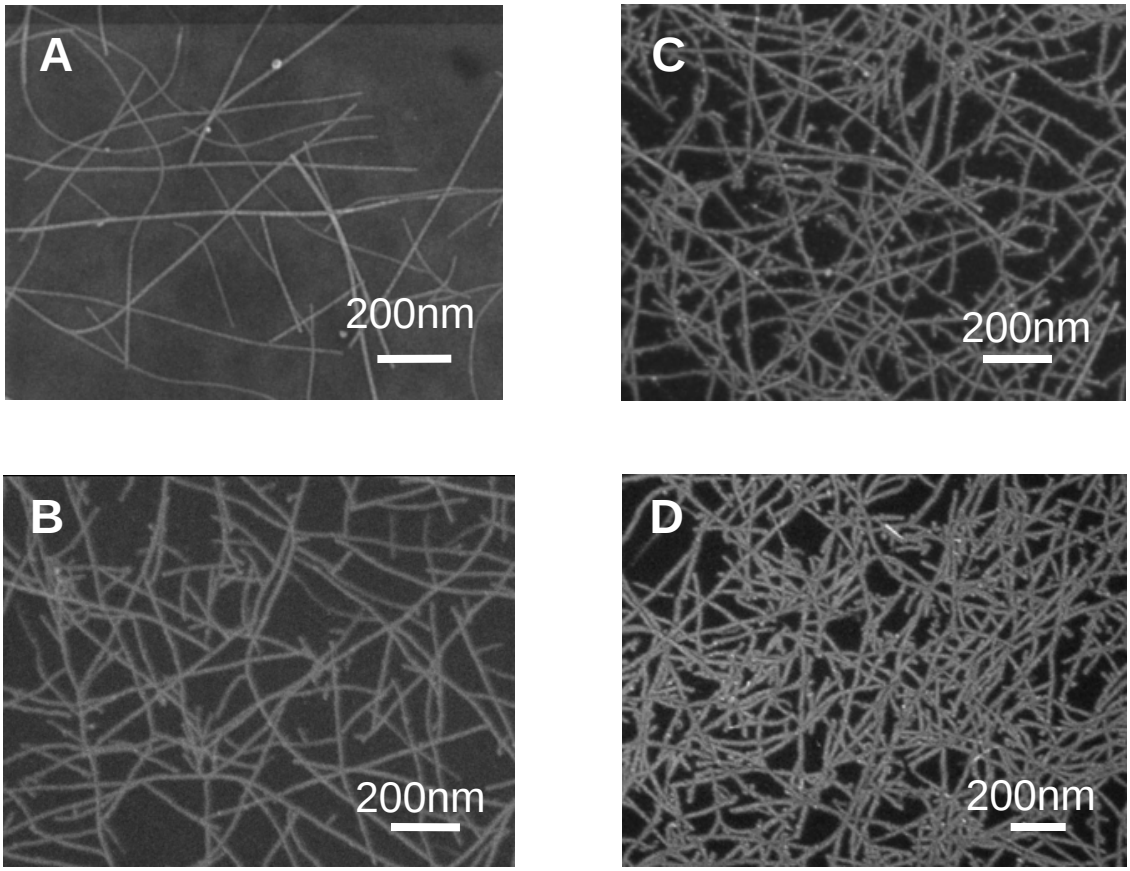

Fig. S1. Scanning electron microscope images of SWCNTs on silicon substrate grown from Fe particles preliminarily annealed in: **(A)** Ar:H_2 (9:1) ambient and **(B)** Ar:H_2 (8:2) **(C)** He:H_2 (9:1) and **(D)** He:H_2 (8:2) ambient in the presence of H_2O at 860 ºC.

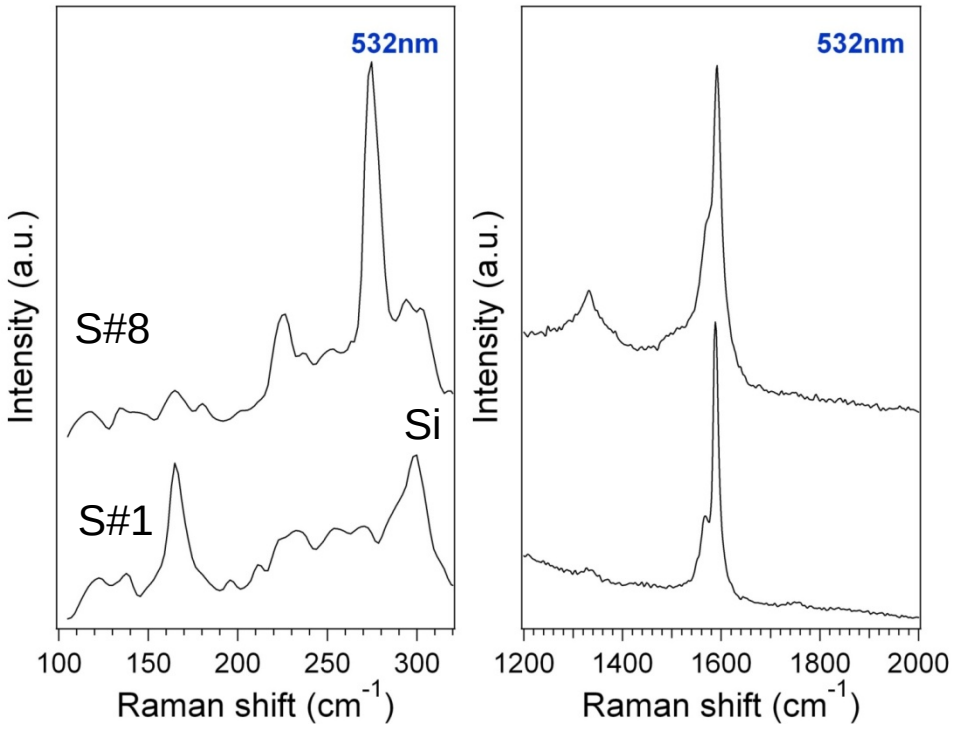

Fig. S2. Raman spectra of samples S#1 and S#8 for λ=532nm laser excitation wavelength.

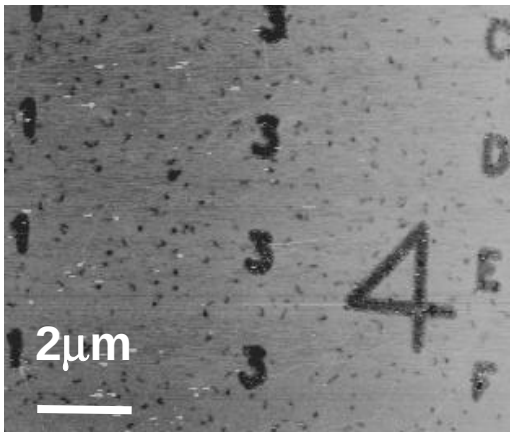

Fig. S3 The marks on the substrate for identification of individual SWCNTs**.**

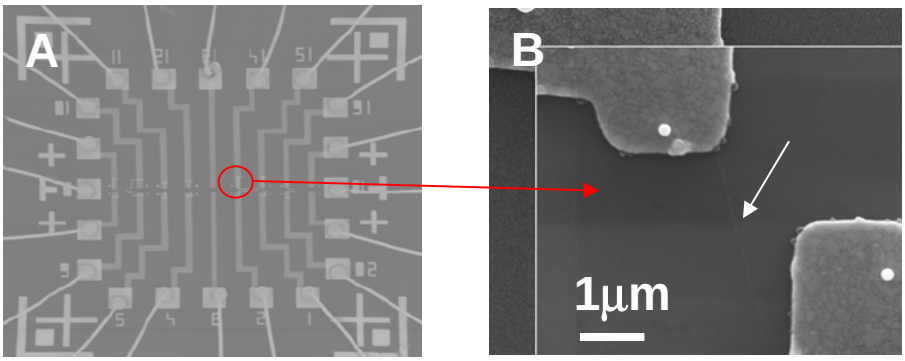

Fig. S4. Device fabrication and electrical characterization. (**A**) and (**B**) SEM images of the identification marks and contacts. In (B) the arrow indicates the position of the SWCNT incorporated in the device.

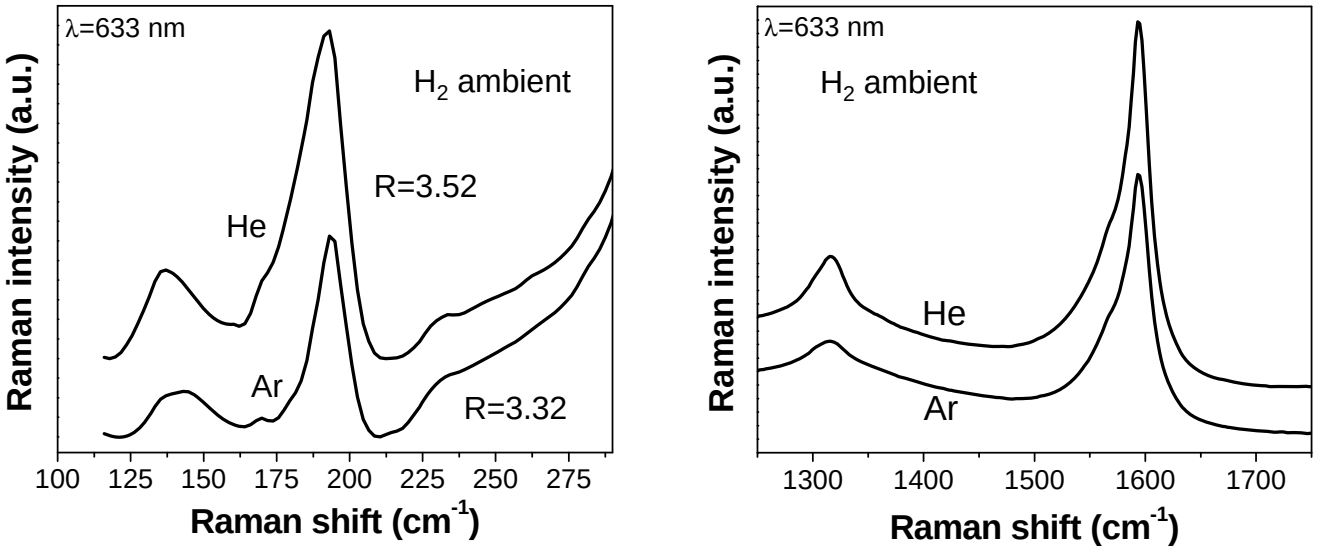

Fig. S5. The Raman spectra of SWCNTs obtained in H_2 ambient do not show significant dependence on the supported gas (He or Ar), while adding the H_2O in the He supported ambient results in an increase of the metallic/semiconducting ratio up to R=20.2.

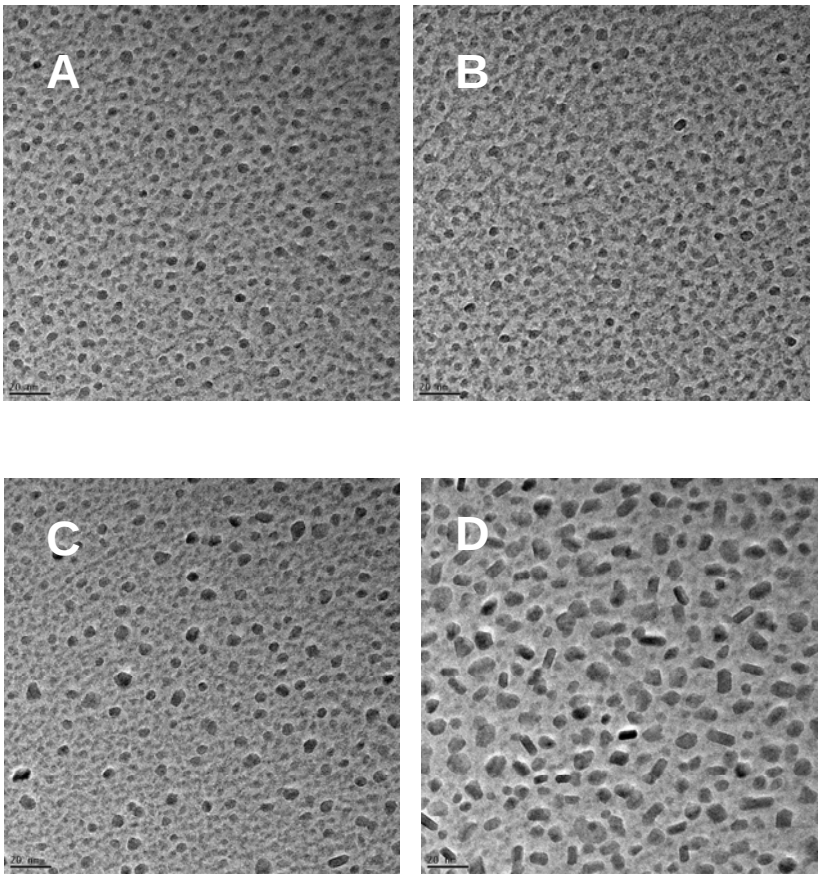

Fig. S6. In situ TEM micrographs of Fe catalyst size distribution evolution at 500 ºC for 15 min depending on ambient Ar/H_2O pressure for **(A)** 1.5 mTorr, **(B)** 22 mTorr, **(C)** 550 mTorr and **(D)** 1200 mTorr. Scale bar is 20 nm.

TABLES

Table S1. Compositions determined for as-produced or processed SWCNT samples (*S6*).

Sample	Source	% semiconducting	% metallic	% standard error
HiPco	Rice Univ.	62.9	37.1	0.5
CoMoCAT, standard grade	Univ. of Oklahoma	92.1	7.9	1.1
Laser ablation, low temperature method	NASA-JSC	54.7	45.3	1.4
HiPco, metallic-enriched by DGU	Northwestern Univ.	2.6	97.4	0.4
CVD preferential growth	Current work	15.4	84.6	2.6

REFERENCES

S1. H. Kataura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Duzuki, Y. Ohtsuka, Y. Achiba, *Synth. Metals* **103**, 2555 (1999).

S2. M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoa, G. G. Samsonidze, E. D. Semke, M. Usrey, D. J. Walls, *Science* **302**,1545 (2003).

S3. G. Zhang, P. Qi, X. Wang, Y. Lu, D. Mann, X. Li, H. Dai, *J. Am. Chem. Soc.* **128**, 6026 (2006).

S4. G. U. Sumanasekera C. K. Adu, B. K. Pradhan, G. Chen, H. E. Romero, P. C. Eklund, *Phys. Rev. B* **65**, 035408 (2001).

S5. J. Sippel-Oakley, H-T. Wang, B. S Kang, Z. Wu, F. Ren, A. G. Rinzler, S. J Pearton, *Nanotechn.* **16**, 2218 (2005).

S6. A. V. Naumov O. A. Kuznetsov, A. R. Harutyunyan, A. A. Green, M. C. Hersam, D. E. Resasco, P. N. Nikolaev, R. B. Weisman, *Nano Lett.* doi: 10.1021/nl9014342 (2009).