

[Supporting material]

Towards full carbon interconnects: high conductivity of individual carbon nanotube to carbon nanotube regrowth junctions

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I. FABRICATION OF PRIMARY MWNTS

MWNT were produced by aerosol-assisted CCVD. The method is based on the catalytic decomposition of liquid hydrocarbons by pyrolysing mixed aerosols containing both the hydrocarbon and the metallic source which simultaneously and continuously fill the reactor^{1,2}. A solution composed of ferrocene dissolved in toluene (2.5 wt.%) was used to synthesize the nanotube sample at 850°C during 15 min. The sample, formed of aligned nanotube carpets covering the reactor walls, was collected by scratching the reactor walls. The carpet pieces were observed by Scanning Electron Microscopy (SEM). They contain almost no by-products such as amorphous carbon or encapsulated metal particles outside nanotubes. The tube length was about 1050 μm (see Fig.A1a). SEM and Transmission Electron Microscopy (TEM), as well as X-ray diffraction analysis, showed that nanotubes contained iron-based particles at their basis (catalyst particles) and inside their hollow core¹⁻³. We performed thermogravimetric analysis (TGA) under flowing air up to 1000°C (SETARAM apparatus) to determine the iron content in samples by measuring the remaining weight corresponding to iron oxide after oxidative treatment. TGA analysis showed that Fe content is of about 2.9 wt%. TEM observations of individual nanotubes showed that their diameter is in the [10-120] nm range with most of the tubes in the [30-70] nm range (see Fig.A1b).

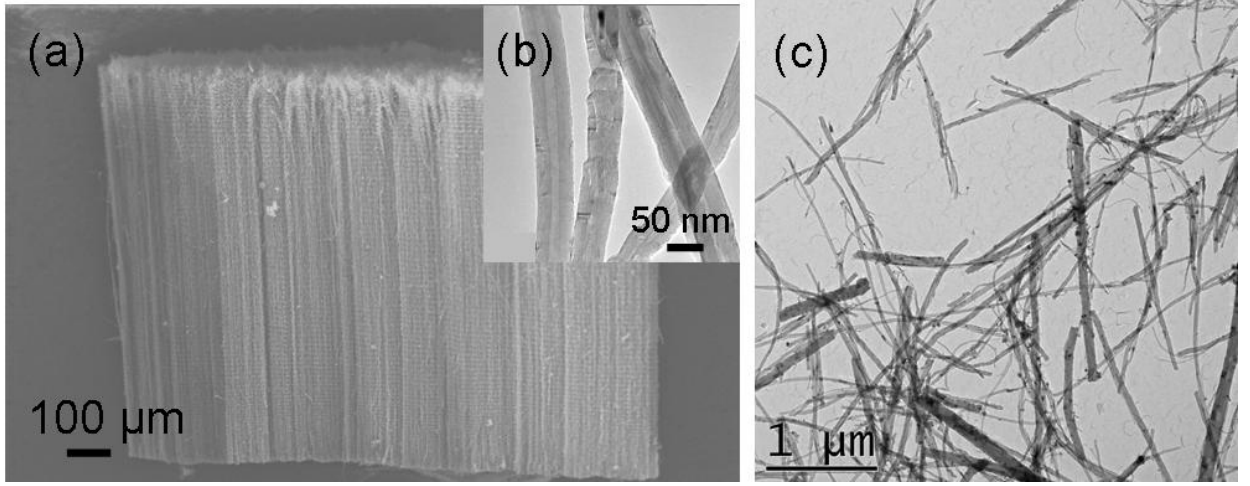


Figure A1: (a) SEM image of the aligned MWNT carpet obtained from a toluene + ferrocene (2.5 wt.%) solution after 15 min synthesis duration time at 850°C. (b) TEM image of the same MWNT after dispersion on the TEM grid. (c) TEM image of the MWNTs after acid treatment.

In order to chemically attach the ferritin on the surface of MWNT, carboxyl moieties were generated to the MWNTs using acid treatment. After the acid treatment for 8h in a $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1) solution in an ultrasonic bath, MWNT final length range distribution has been measured from several TEM pictures (more than 100 nanotubes). MWNT length is in the [1-6] μm range with a mean length of 3 μm . Final dry sample is obtained by evaporating water in a hood. Moreover, from TEM pictures analyses, acid treated MWNT exhibit a larger amount of structural defects than the pristine ones (see Fig.A1c).

II. SAMPLE CHARACTERIZATION

TEM analysis has been performed using a TOPCON 002B model from AKASHI equipped with a LaB6 filament. It is a 200kV ultra-high resolution TEM with a point-to-point resolution of 0.18-0.20 nm. SEM imaging was done using Hitachi Scanning Electron Microscope. Atomic Force Microscope (AFM) characterization of the sample was with Veeco Dimension 3100 instrument in Tapping-mode using NanoSensors cantilevers.

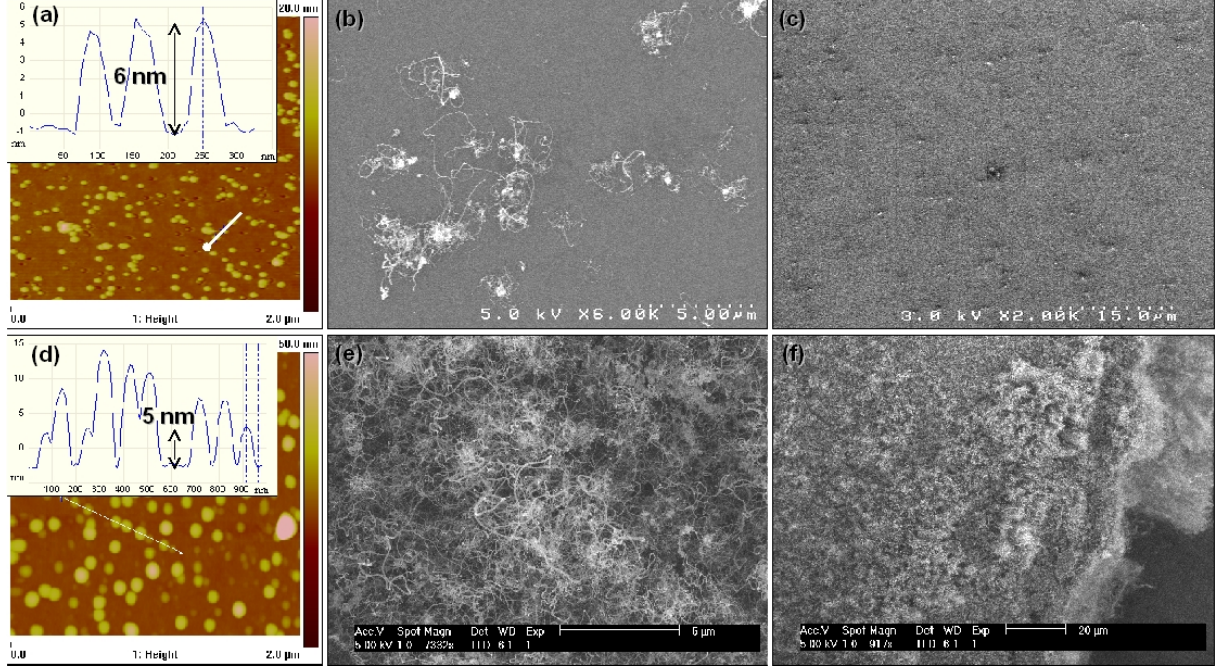


Figure A2: CVD-growth from the catalyst particles on the oxidised silicon substrate. AFM images and height profiles of (a) ferritin and (d) Fe-particles deposited on the substrate. SEM-images of the (b-c) ferritin and (e-f) Fe-particle samples after CVD growth.

III. FABRICATION OF MWNT-FERRITIN COMPLEXES

MWNT-ferritin conjugates were fabricated using covalent EDC/NHS chemistry. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) were purchased from Sigma. Acid treated MWNT tubes were first dispersed (0.1 g/l) in 100 mM Hepes by sonicating for 1 min (80 W 45 kHz bath) and then for 20 min with 40 % power. 0.5 mM solutions of each EDC and NHS were mixed in 1:1:1 with the MWNT dispersion (NHS/EDC ratio of 1:1). Obtained solution was stirred for 30 min at 16°C. EDC/NHS functionalized MWNTs were mixed with the Horse spleen ferritin solution (Sigma F4503, diluted to 50 nM in 25 mM Hepes) in volume ratio 3:2. The mixture was then stirred for 2 h at 20°C. The final concentrations were 0.02 g/l MWNTs, 100 μ M EDC, 100 μ M NHS, 20 nM Ferritin and 25 mM Hepes. The ferritin/MWNT mass ratio was 3:2. The final product was stored at 6°C. MWNT-ferritin conjugates were characterized using TEM and from the images the MWNTs were estimated to contain about 10 ferritins per 100 nm length of nanotube (See Fig. 1a in the main paper).

IV. FABRICATION OF FE-NANOPARTICLES

Iron nanoparticles were fabricated using the protocol obtained from Park *et al*⁴. Particles were stored in toluene at concentration of about 30 g/l. Prior to the AFM characterization the particles (diluted to 1.5 g/l) were deposited on thermally oxidised (150 nm SiO₂) highly phosphorus-doped silicon substrate by placing a drop of Fe-particle solution on the substrate and flushing it right away with acetone followed by drying with nitrogen flush. AFM characterisation showed that the Fe-particle solution contains different size particles with diameter from ~ 5 to ~ 30 nm (see Fig. A2d). The Fe-particles on SiO₂ were used in 700°C CVD-process and a lot of CNT-growth was obtained as can be seen from the picture (see Fig. A2e-f).

V. FABRICATION OF MWNT-FE PARTICLE CONJUGATES

MWNT-Fe-particle conjugates were fabricated by simple mixing and stirring method. The MWNTs (10 mg/l) dispersed in N-methylpyrrolidone (NMP) were mixed with the Fe-particles (6 g/l) in toluene in volume ratio 10:1. The mixture was then stirred for 2 hours in room temperature. Resulting solution contained 10 mg/l MWNT and 0.6 g/l Fe-particles. The Fe-particle/MWNT mass ration was 60:1. Solution was then filtered using 0.45 μ m filter and finally dispersed in DMF using a few second sonication with 60 % power.

VI. FABRICATION OF METAL-STRUCTURE

Prefabricated metal-structure on substrate was used for (1) the localization of the MWNTs before and after CVD-growth, (2) the alignment in e-beam lithography to make the metallic contacts to the primary and secondary MWNTs and (3) for dielectrophoretic trapping of the MWNTs and Fe-particles. Conventional UV-lithography was used to fabricate the metal-structure on the substrate. Metallization was done in UHV-chamber using e-beam evaporation of 5 nm layer of Pd was deposited as a adhesion layer, followed by the deposition of 20 nm layer of Au.

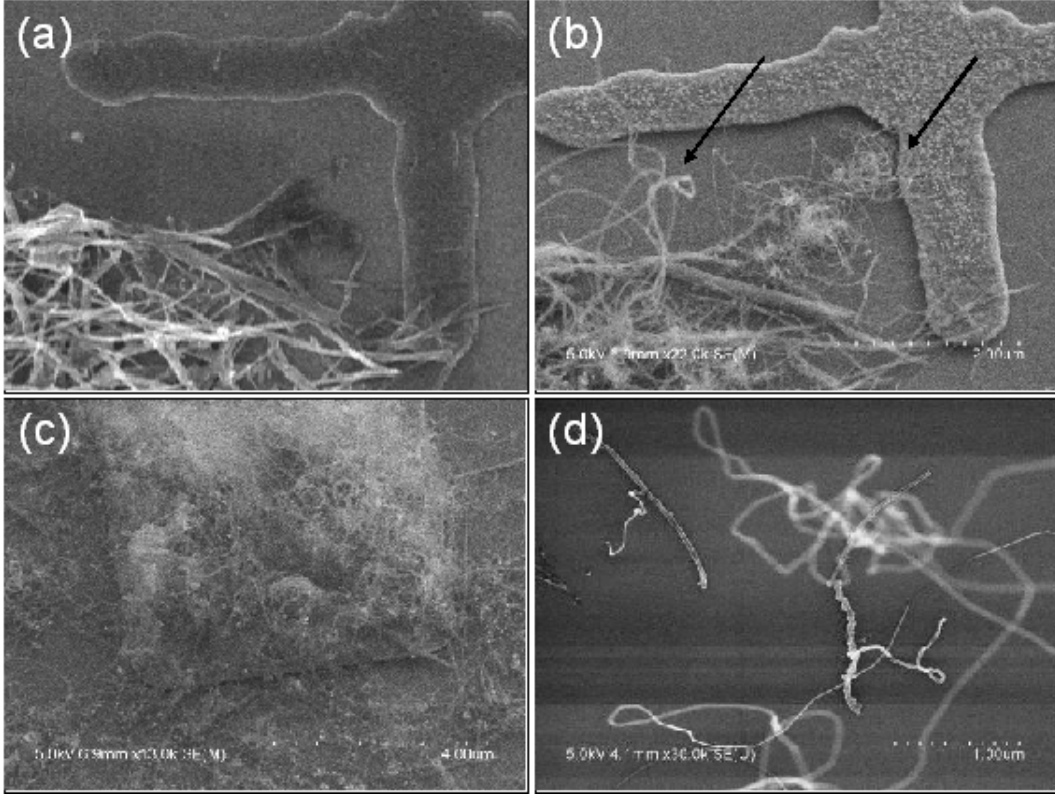


Figure A3: MWNT-Fe-particle conjugates on the substrate (a) before and (b) after CVD re-growth. The SEM-images of re-growth tubes protruding from the substrate are shown in (c) and (d).

VII. PREPARATION OF SAMPLES FOR CVD-GROWTH

The MWNT-catalyst solution was deposited on the oxidized silicon substrates containing prefabricated metal-structure using spin-coating. Spinner parameters were 800 rpm for 20 s followed by 3000 rpm for 20 s. After spin-coating the sample was baked on hot-plate at 100°C in order to evaporate the solution residues from the substrate and also increase the binding of the tubes to the substrate surface. Spin-coating and baking step was repeated 4 to 6 times depending on the solvent and MWNT concentration. In some cases, MWNT-catalyst conjugates were deposited using dielectrophoresis (DEP) by applying AC signal (1-5 MHz, 10 V_{p-p}) onto 10 μ m separated parallel electrodes for 30-60 s.

VIII. SUBSEQUENT DEP OF MWNTS AND FE-PARTICLES

In addition to the MWNT-catalyst conjugates fabricated by coupling the MWNTs and catalyst particles in solution, we also used subsequential trapping of MWNTs and Fe-particles using DEP. Parameters used for DEP of MWNTs (10 mg/l tubes in IPA) were 5 MHz and 10 V_{p-p} (for about 30 s) and for DEP of Fe-particles (1.5 g/l particles in toluene) 5 MHz and 10 V_{p-p} (for about 1 min.)

IX. CVD-GROWTH

CNT growth was performed in a acetylene CVD reactor⁵. The reduction of the iron oxide catalysts into Fe(0) was performed in situ just before CVD growth ($H_2:N_2$ in ratio 100:250 sccm, 700°C, 2 mbar, 20 min), followed by a growth step ($C_2H_2:N_2$ in ratio 50:250 sccm, 2 mbar, 10 min). 1 min hot-filament activation was used in the beginning of the reduction step to activate the reduction process.

X. TESTING OF THE CATALYST

Both catalysts, namely ferritin⁶ and Fe-particles⁷, were first deposited on SiO₂ substrate in order to test how well they work as a catalyst for growth of carbon nanotubes in our acetylene based 700°C CVD process. AFM images and height profiles for the ferritins and Fe-particles on the substrate are shown in Fig. A2a and A2d, respectively. After this the samples underwent the subsequent calcination at 550°C in air, H_2 reduction and the CVD growth. SEM images of the ferritin and Fe-particle samples after the CVD growth are shown in Fig. A2b-c and Fig. A2e-f, respectively.

XI. GROWTH FROM LARGE MWNT-CATALYST NETWORK

The CVD regrowth process was first tested and optimised using a high amount of MWNT-catalyst conjugates deposited on the substrate. The metallic alignment marks were prefabricated on the oxidised silicon substrate to be able to localise the same MWNTs before and after CVD growth. Examples of SEM-images of the MWNT-Fe-particle conjugate network before and after CVD growth is presented in Fig. A3a and b, respectively.

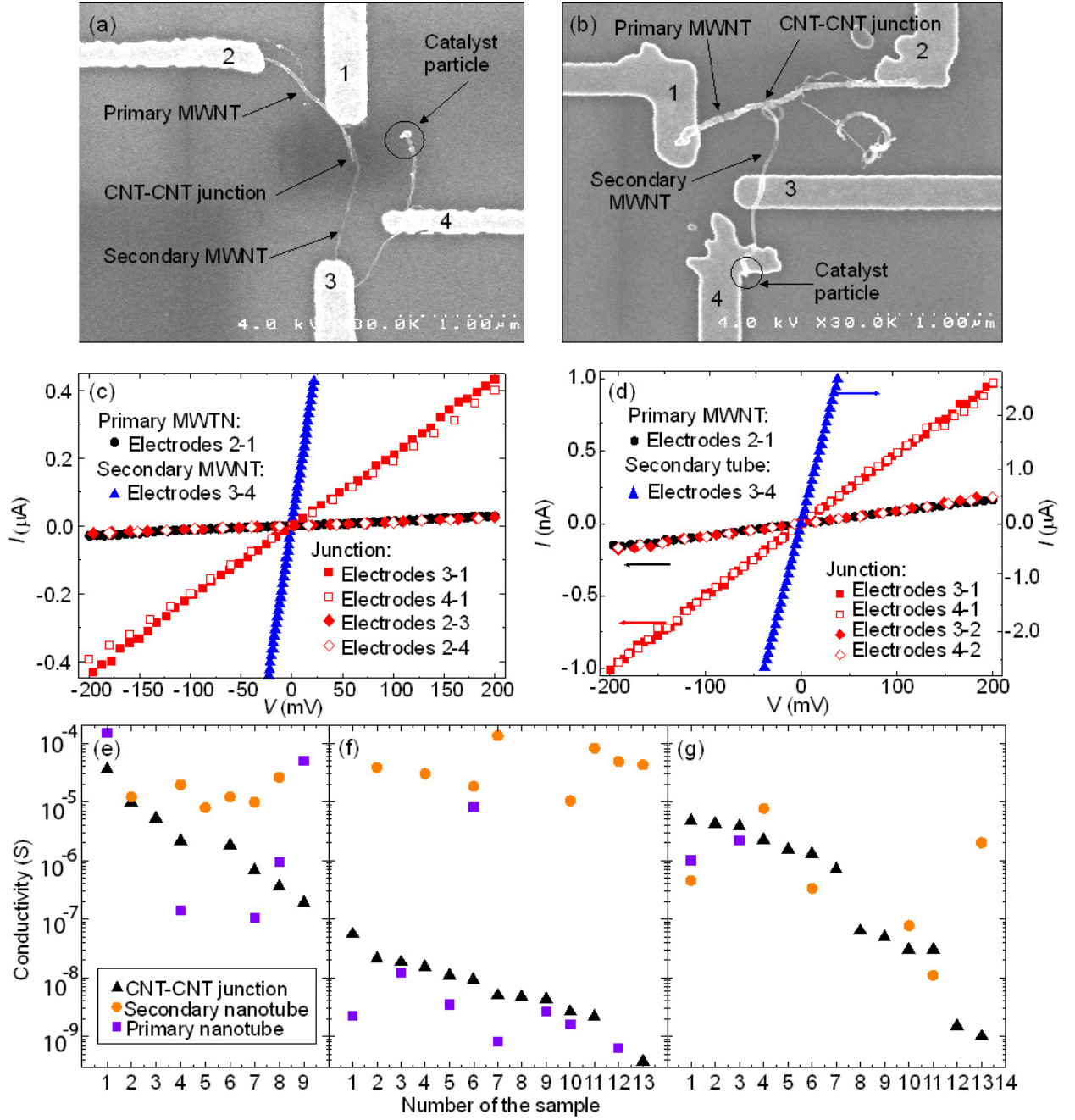


Figure A4: Examples of the connected CNT-CNT junction structures with the different electrode configurations, where contacts to the primary MWNT are made (a) on the same or (b) opposite sides of the CNT-CNT junction. All measured I-V curves (c) for the sample shown in image a, and (d) for the sample shown in image b. Obtained conductances in the cases of (e) MWNT-ferritin conjugate, (f) MWNT-Fe-particle conjugate and (g) subsequent MWNT and Fe-particle DEP samples.

In Fig. A3c and d one can observe that the re-grown nanotubes which grow out from the MWNT-Fe-particle network are protruding from the substrate. In Fig. A3c one can see that growth yield is higher from the MWNT-Fe-particle conjugates which lay on top of the micron-size gold electrode. In Fig. A3c, the re-grown tubes which appear more bright in the image, are not in focus as the conjugates lying on the substrate. To avoid detachment of the tubes during the e-beam lithography step (spin-coating and lift-off), the samples were dipped in acetone and N₂ dried in order to obtain a combing-effect which enforces the protruding tubes in contact with the substrate.

XII. E-BEAM LITHOGRAPHY

Deposition of PMMA/MMA-MAA double-layer resist. EL10 (MMA-MAA) using 5000 rpm for 60 min and 1 min baking at 175°C, followed by deposition of A2 (PMMA) resist using 4000 rpm for 60 min and 1 min baking at 175°C. JEOL SEM equipped with ELPHY software which was used for e-beam patterning. Samples were developed by immersing them for 45 s in MIKP:IPA solution and then for 30 s in IPA. Metallization was done using e-beam metal evaporation in UHV-chamber. A 7 nm layer Pd was deposited order to act as an adhesion layer and also to decrease the CNT-metal contact resistance. This was followed by the deposition of a 50 nm layer of Au. After the e-beam lithography, the samples were annealed for 15-30 min at 400°C in a vacuum furnace to decrease the CNT-metal contact resistance.

Depending on the location of the CNT-CNT junction on the primary MWNT, the connections 1 and 2 to the primary MWNT were made on the same side (Fig. A4a) or different side (Fig. A4b) of the junction, due to the resolution limit of the e-beam lithography.

XIII. *I-V* MEASUREMENTS

Agilent 4156C Parameter Analyzer was used to capture the current-voltage (*I-V*) curves (two-probe measurement). To verify that all four electrodes are properly connected to the MWNTs, the *I-V* curves were recorded using all different two-electrode configurations; 1-2 for the primary MWNT, 3-4 for the secondary MWNT and 1-3, 1-4, 2-3 and 2-4 for the junction. It can be observed from the *I-V* curves shown in Fig. A4c and d that current

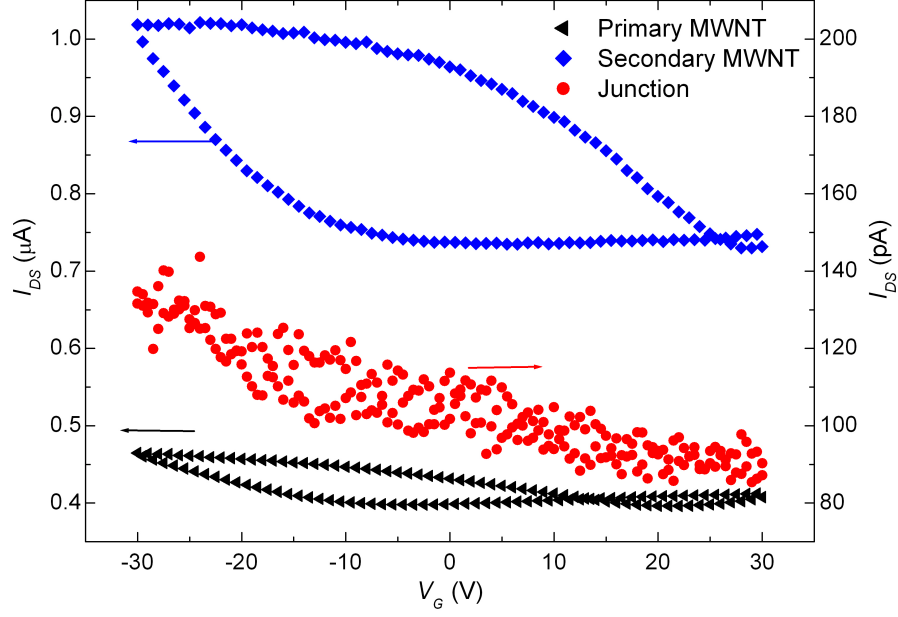


Figure A5: The largest observed gating effect in the CNT-CNT junction and the primary and secondary MWNTs using silicon back-gate. Bias voltage $V_{DS} = -50$ mV for the secondary tube and $V_{DS} = -200$ mV for the junction and the primary tube.

mediated through the junction is mostly determined by the electrode connected to the primary MWNT (electrode 1 or 2). From all four I-V curves recorded for the junction we use the one showing the highest current to determine the junction conductance. However, this way one can obtain only the lower limit for the real junction conductance, since the primary MWNT or the metal-primary MWNT contact is the conductance bottleneck. Obtained conductances for all measured samples are summarised in the Fig. A4e-g. The bulk silicon below the oxide-layer was electrically floating during the I-V measurements.

XIV. GATING EFFECT

the possible effect of gating on the conductivity of the MWNTs or to the junction was studied by applying a ± 30 V voltage to the silicon back-gate. We found only a slight change in the current as can be observed from Fig. A5) where we present the V_{DS} vs. V_G for the

samples showing the maximum gating effects observed in the MWNTs and in the junction.

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