Electronic Supplementary Information

Graphene Oxide as Multi-Functional p-Dopant of Transparent Single-Walled Carbon Nanotube Films for Optoelectronic Devices

Joong Tark Han,[†] *Jun Suk Kim,*[†] *Sae Byeok Jo,*[‡] *Sung Hun Kim,*[†] *Jong Soo Kim,* [§] *Boseok Kang,* [‡] *Hee Jin Jeong,*[†] *Seung Yol Jeong,*[†] *Geon-Woong Lee*[†,]* *and Kilwon Cho*[‡,]*

[†]Nano Carbon Materials Research Group, Korea Electrotechnology Research Institute, Changwon, 641-120 (Korea)

[‡]Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784 (Korea)

[§]Imperial College London (United Kingdom)

kwcho@postech.ac.kr; gwleephd@keri.re.kr

Experimental Methods

SWCNT film fabrication: In this study, the SWCNTs used (which were purchased from Nano Solutions Inc., Extube) were produced using the arc-discharge method, and were purified using a thermal treatment. The SWCNTs were dispersed in a 1 wt% sodium dodecylbenzenesulfonate solution at a concentration of 1 g/L, using bath sonication for 30 min and horn sonication for 1 hr. The sample was then submitted to two rounds of centrifugation at 10,000 rpm for 60 min, to remove impurities such as amorphous carbon and residual catalyst particles. The supernatant solution was deposited onto plastic substrates using an automatic spray coater (NCS Co. Ltd., NCS-400) with a 1.2 mm diameter nozzle and 400×400 mm^2 stage. The surfactant was removed by dipping in deionized water twice, for 10 min each time; this was followed by air drying at 70 °C for 5 min.

Preparation and sorting of GO nanosheets, and deposition on the SWCNT surfaces: GO sheets were prepared via the exfoliation of graphite oxide powder, which was produced from natural graphite (Alfa Aesar, 99.999% purity, –200 mesh) using a modified Hummers method. Briefly, 20 g of graphite and 460 mL of H_2SO_4 were mixed in a flask. Then, 60 g of $KMnO_4$ was added slowly, over a period of approximately 1 h. Stirring was continued for 2 h in an ice-water bath. After the mixture was stirred vigorously for 3 days at room temperature, 920 mL of deionized water were added, and stirring proceeded for 10 min in an ice-water bath. Fifty milliliters of H_2O_2 (30 wt % aqueous solution) was then added, and the mixture was stirred for 2 h at room temperature. The resulting mixture was precipitated and filtered to obtain the graphite oxide powder. The graphite powder was dispersed in water by magnetic stirring, and the highly functionalized graphite oxide with carboxylic acid groups was removed by the centrifugation of a 2 g/L aqueous GO solution. The sediment graphite oxide solution was diluted in water to a concentration of 400 mg/L, and was sonicated for 1 h to exfoliate the graphite oxide into GO nanosheets. The GO nanosheets were sorted using centrifugation at 10,000 rpm for 1 h, and the supernatant solution was then decanted. The sediment was redispersed in water to the same volume, and the centrifugation and decanting steps were repeated to prepare the size-sorted GO nanosheets. The supernatant solution was concentrated and freeze-dried to obtain a powder for characterization. Deposition of the GO supernatant solution onto the SWCNT films was performed directly, using air-spraying.

Characterization of the SWCNT films: Images of the resulting films were obtained using scanning electron microscopy (SEM, HITACHI S4800). The transmittance of each film was measured using a Varian Cary winRV spectrometer. The Raman spectra were measured to characterize the electronic structure of the film at room temperature, using a high-resolution Raman spectrometer (LabRAM HR800 UV) with an excitation wavelength λ of 633 nm. The Raman spectra were obtained by averaging the spectra collected from five points on each sample, to minimize errors in the data. The sheet resistance measurements were collected using a four-probe tester (Loresta, MCP-T610). Two-probe I-V measurements were performed to characterize the in situ electrical properties of the SWCNT films with the deposition of additional GO solution.

Organic photovoltaic device fabrication and electrical characterization: The GO-treated SWCNT electrodes prepared on PET substrates were patterned with reactive O_2 plasma, using appropriately designed metal masks. The patterned substrates were cleaned with warm ethanol, and this was followed by 30 seconds of UV-ozone treatment. After cleaning, PEDOT-PSS (Baytron P AI 4083, Bayer AG) was spin-coated to a thickness of 30–40 nm, and was baked at 120°C for 30 min. Regioregular P3HT (P100, Rieke Metals, Inc.) and PCBM (99.5%, Nano-C, Inc.) were used as the active materials in this study. A P3HT:PCBM blend solution was prepared in 1,2 dichlorobenzene, with a concentration of 20 mg/mL for each material, and the solution was blended at 55°C for 14 h, under severe agitation. The blend solution was then spin-cast onto the PEDOT-PSS-coated GO-SWCNT films and dried slowly in a closed jar, giving a total thickness of 220-240 nm. After drying, the active layer was thermally annealed at 120°C for 5 min. Al or LiF/Al cathodes were formed on top of these films, via thermal evaporation. ITO-based OPV devices were fabricated using exactly the same procedure, to exclude variables other than the electrode properties. The current–voltage (J-V) characteristics were measured using a Keithley 4200 power source, under AM 1.5G illumination at an intensity of 100 mW/cm2 (Oriel 1 kW solar simulator), with a PVM 132 reference cell certified by NREL. All electrical measurements and fabrication processes were performed in an inert N_2 environment.

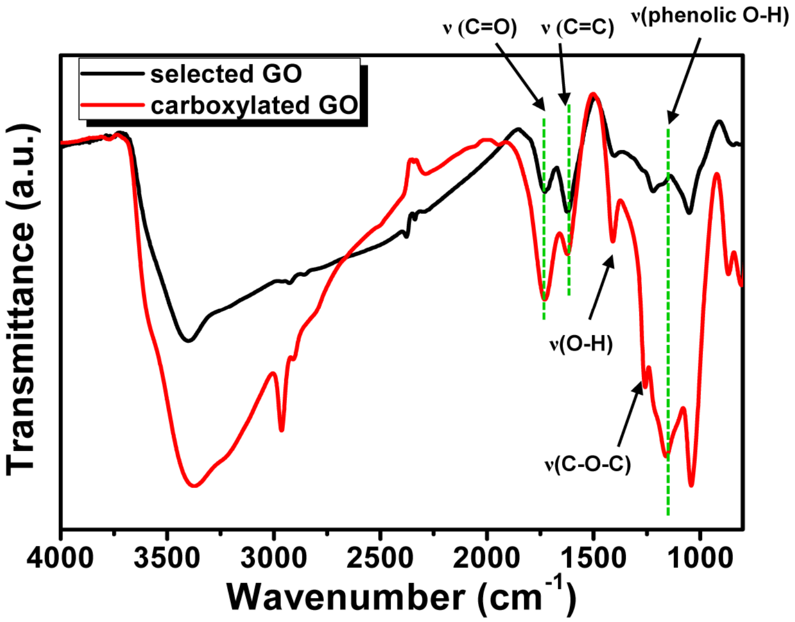

Figure S1. FTIR spectra of the carboxylated GO, and selected GO for the sorting experiments.

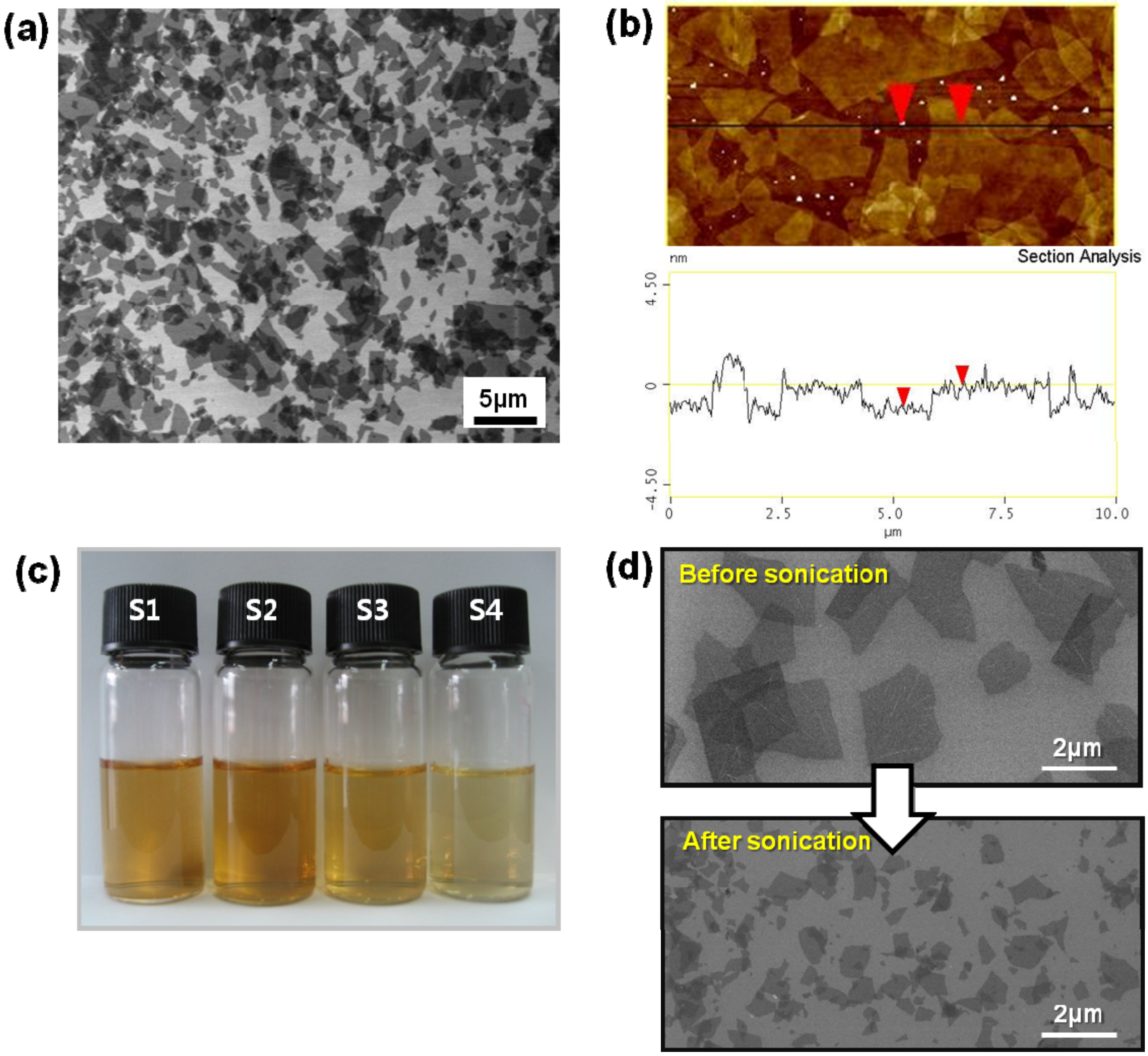

Figure S2. (a) SEM and (b) AFM images and height profile of single layered graphene oxide nanosheets. (c) Photographic images of the supernatant GO solutions from S1 to S4. (d) SEM image of S4-GO nanosheets before and after sonication.

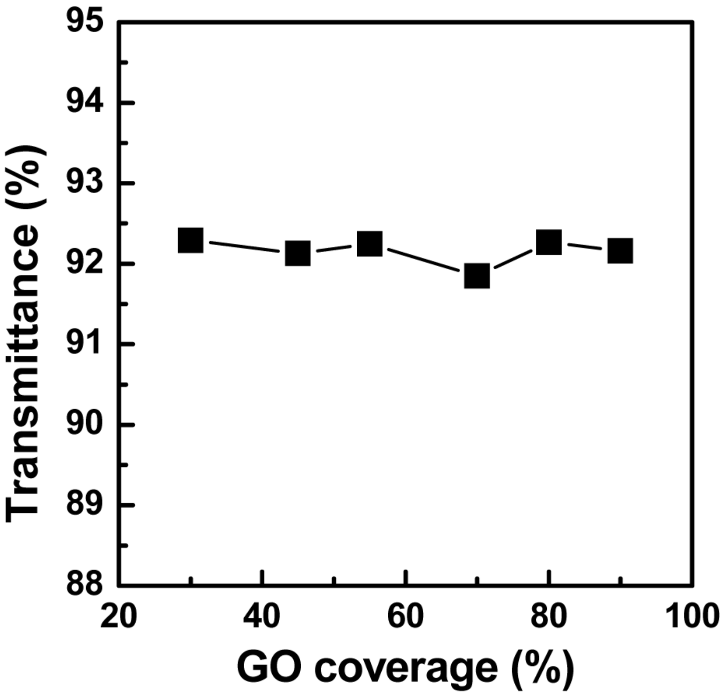

Figure S3. Transmittance of the SWCNT films as a function of GO coverage. The percentage of GO coverage was roughly estimated from the SEM images.

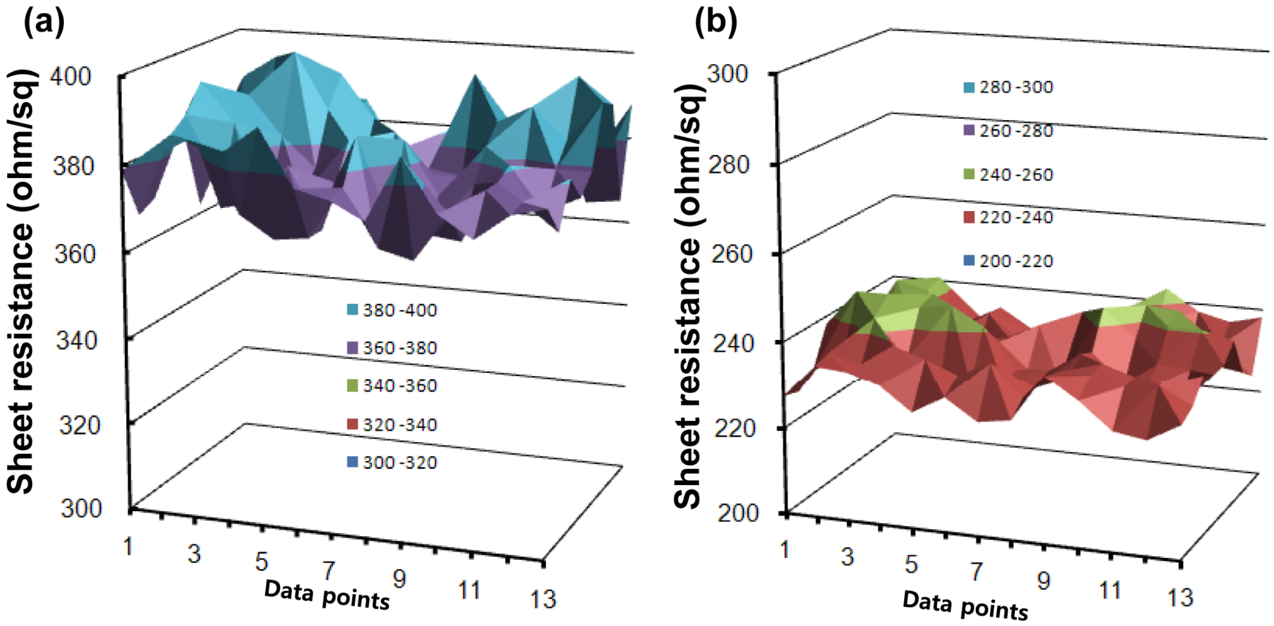

Figure S4. Sheet resistance measurements (pitch size of data point = 30mm) of (a) the pristine SWCNT film (uniformity 5.9%) and (b) the GO-modified SWCNT film (uniformity 5%), showing uniformity across the surfaces.

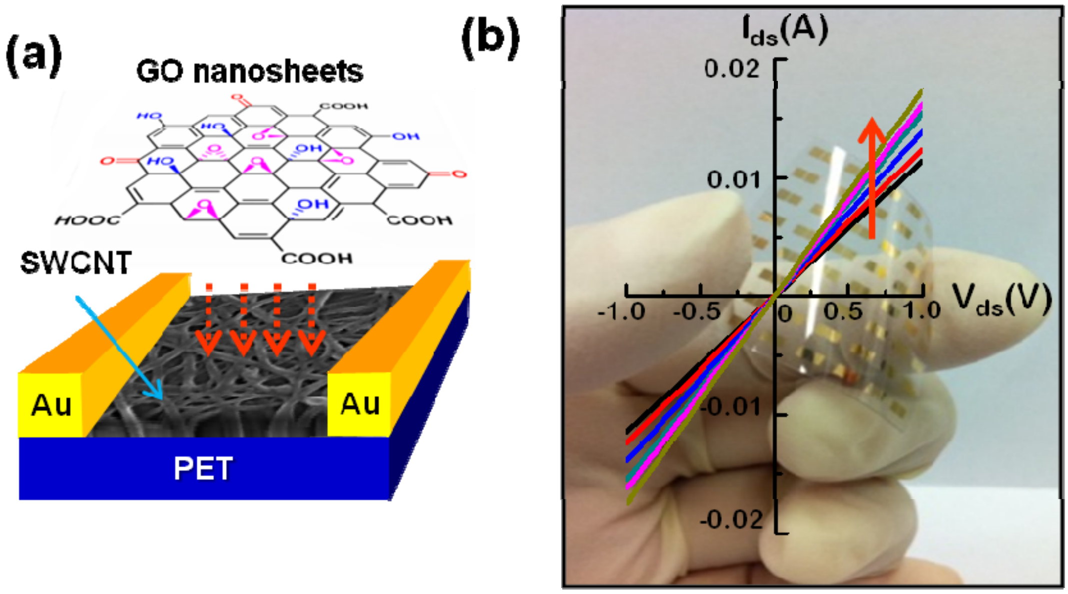

Figure S5. (a) Schematic diagram of the I-V measurements performed on SWCNT films after the deposition of the GO solution. (b) Photograph of a gold-patterned SWCNT film, and I-V plots for the SWCNT films as a function of the amount of spray-coated S1-GO solution, as the amount of deposited GO solution was increased (arrow direction).

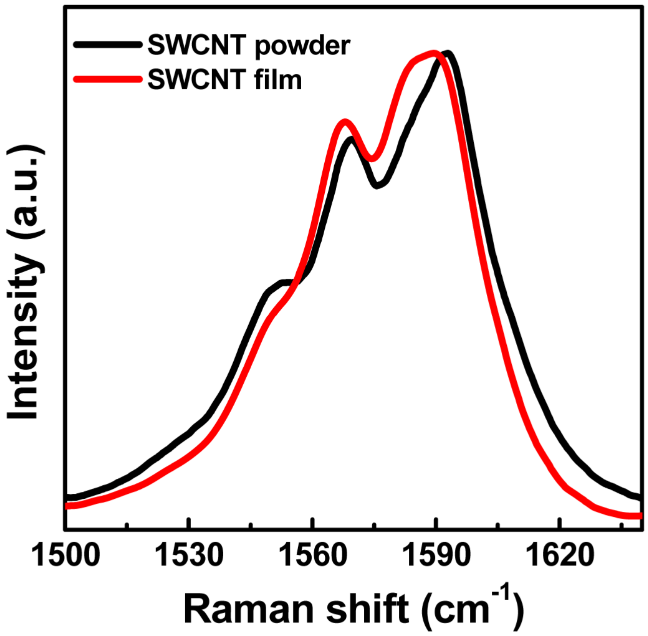

Figure S6. Raman spectra of the SWCNT powder and film.

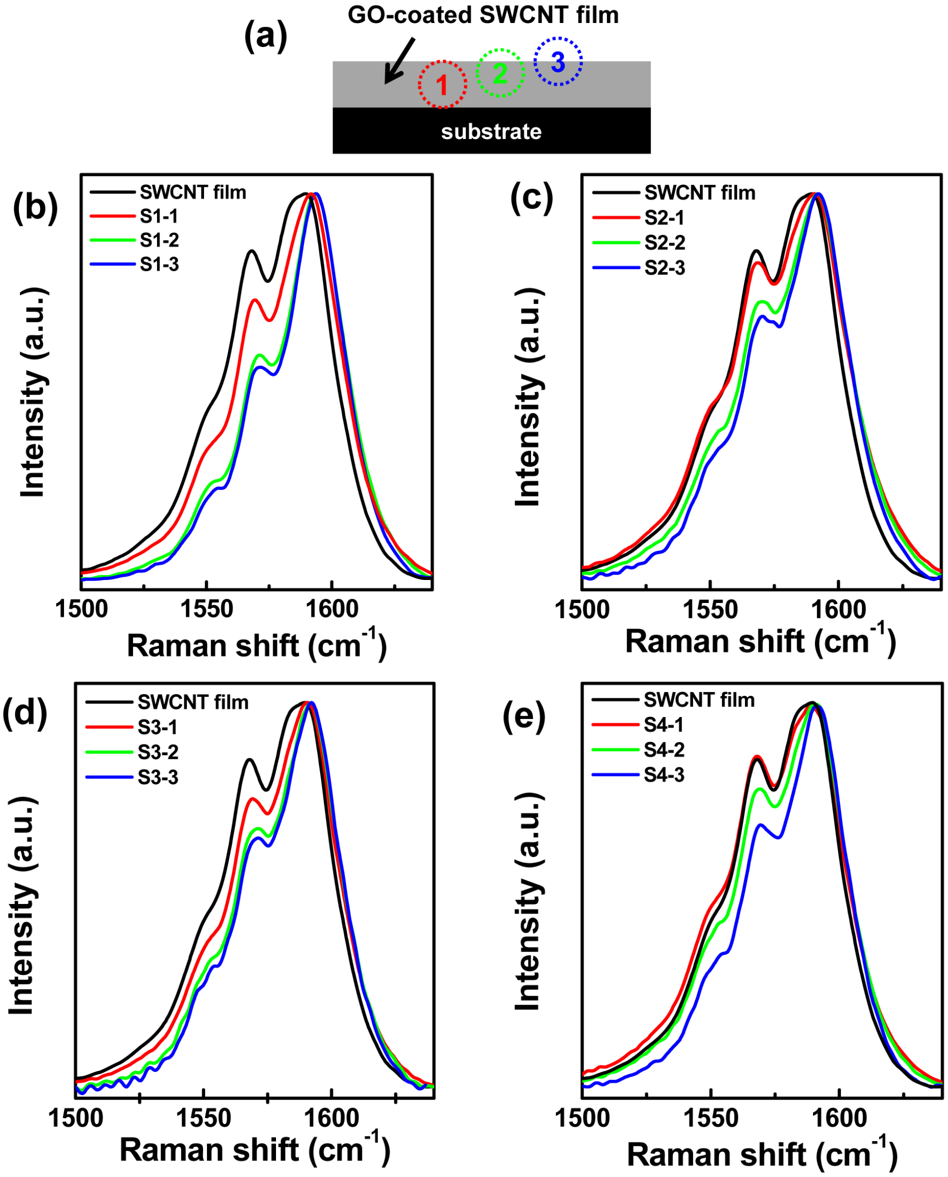

Figure S7. (a) Schematic diagram of a Raman study in which the laser focusing position was shifted to measure the film composition at several depths. Raman spectra of the SWCNT films coated with (a) S1-GO, (b) S2-GO, (c) S3-GO, and (d) S4-GO. The laser focus position was shifted from the film (1) to the air interface (3).

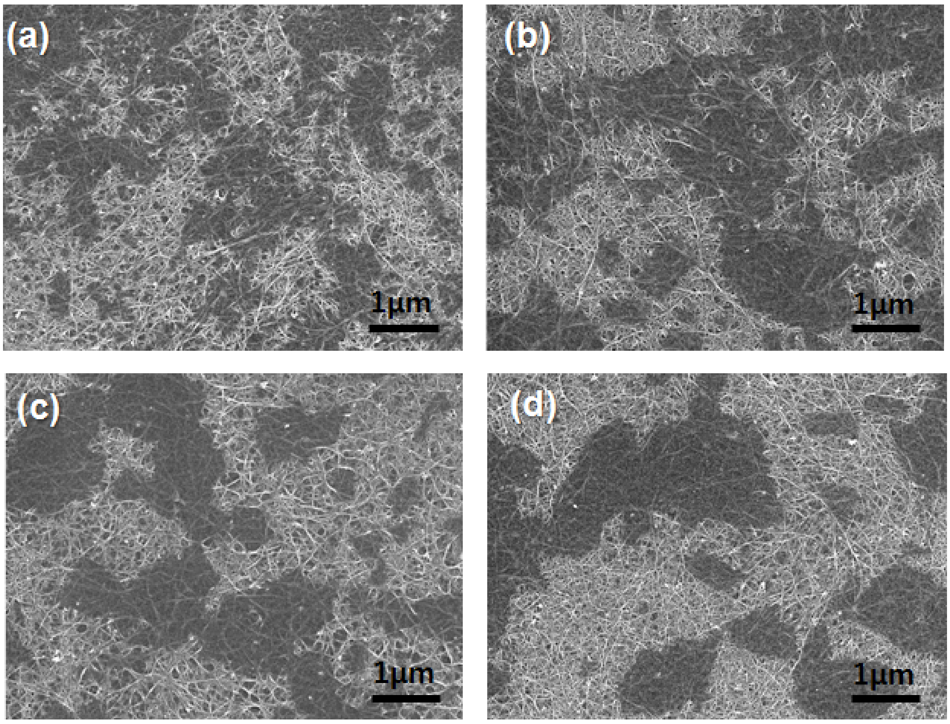

Figure S8. SEM images of the SWCNT films partially covered with (a) S1-GO, (b) S2-GO, (c) S3-GO, and (d) S4-GO after deposition of the same amount of GO solutions.