

Supplementary information for *Carbon Nanotube Conducting Arrays* by *Consecutive Amidation Reactions*

Dae-Hwan Jung,^a Myung Sup Jung,^{ab} Young Koan Ko,^a Seung Joo Seo^b and Hee-Tae Jung^{*a}

^a Department of Chemical & Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea.

Fax: 82 42 869 3910; Tel: 82 42 869 3931; E-mail: heetae@kaist.ac.kr

^b Samsung Advanced Institute of Technology, San 14-1, Nongseo-ri, Giheung-eup, Yongin-si, Gyeonggi-do 440-600, Korea.

Supplementary Information 1: Experimental details

Materials.

The as-prepared SWNTs (AP-SWNTs) purchased from CarboLex Inc., which were purified, shortened and polished as previously reported by the method of Smalley and colleagues.¹ Aminopropylsilane-modified slide glasses (Corning[®] GAPS □ Coated slides, 25 X 75mm) were obtained from Corning Incorporated. *N,N*-Dimethylformamide (DMF) (Aldrich, 99.9%) was dried by refluxing at 130 □ for 20h with triphenylchlorosilane (5g/L), then distilling at *ca* 5mm pressure. Dichloromethane (Aldrich, 99.8%) was pre-dried with CaCl₂, and distilled from CaH₂. 4,4'-Oxydianiline (ODA) (99%), O-(7-Azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU) (97%), *N,N*-Diisopropylethylamine (DIEA) (99%) and other organic solvents used here were purchased from Aldrich and used as received.

Preparation of the SWNTs multilayer films & the patterned conducting arrays.

The fabrication scheme is illustrated in Figure 1. First, the SWNTs were shortened by ultrasonication

in strong acids, which is known to generate carboxyl groups at SWNT open-ends and sidewall defect sites.² The shortened SWNTs were dispersed in DMF (15ml, 0.1 mg/ml) by ultrasonication for 1hr, forming a dark-brown-colored suspension. DIEA (5ml, 1.2 mM) was added into the suspension and the mixture was stirred for 30min before use. HATU (5ml, 1.0 mM) was added into the mixture. The SWNT layer was prepared by immersing an aminopropylsilane-modified glass substrate into the SWNT mixture containing condensation agents (HATU/DIEA) for 10 hour. The carboxyl groups on the SWNTs react with the amino groups on the aminopropylsilane-modified glass (Figure 1a). The resulting sample was then rinsed with sufficient anhydrous DMF and anhydrous CH₂Cl₂ to remove unreacted SWNTs and possible surface contaminants. After drying in a high-purity argon stream, the sample was immersed in a fresh DIEA (5 ml, 1.2 mM) solution. Following stirring for 30 min, fresh HATU (5 ml, 1.0 mM) and ODA (20 ml, 10 mM) solutions were added and stirred for 2 hours. All reaction steps were performed at 60°C. The resulting ODA-SWNT immobilized sample was washed and dried using the procedure described above (Figure 1b). In these systems, ODA is used as a linker between the SWNT layers. Thus, we refer to treatment of an SWNT layer with ODA followed by addition of further shortened SWNTs as one “reaction cycle”. In this reaction cycle, the amino group of the immobilized ODA reacts with the carboxyl group of the SWNTs, forming a new SWNT layer. Repeated applications of the reaction cycle leads to formation of SWNT multilayer films (Figure 1c).

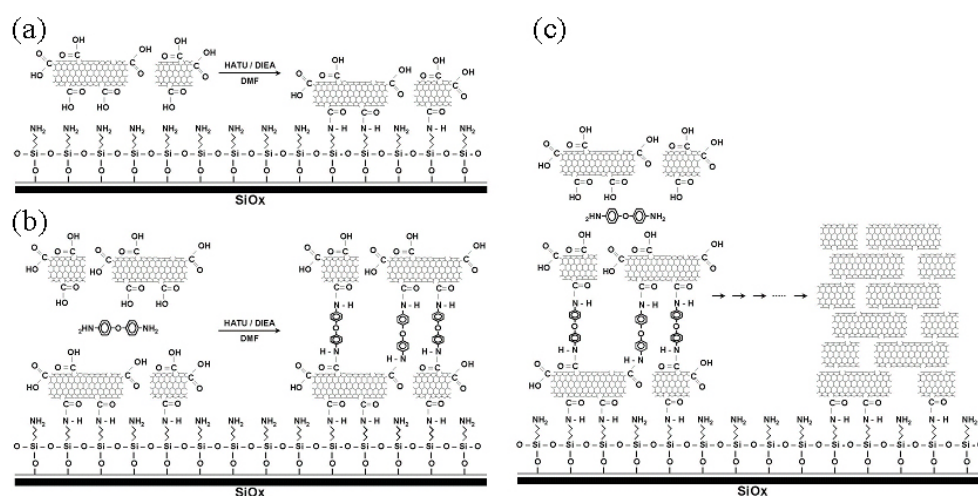


Figure 1. Schematic representation of the SWNTs multilayer with growth. (a) Chemical attachment of SWNTs on aminopropylsilane modified slide glass, (b) Chemical bonding of SWNTs layers *via* ODA linker at between each layer, and (c) SWNTs multilayer formation through the repeated procedures.

To create SWNT multilayer patterns with micro-scale resolution, we used a photolithographic mask to selectively attach the SWNTs (Figure 2). To prepare the patterned substrate, aminopropylsilane-modified slide glass was treated with 6-(BOC-amino) caproic acid containing the BOC protection group³ and the photogenerated acid (PGA)⁴ used as the acid to remove the protection group from amino acids respectively. The substrate was covered with a photolithographic mask of the desired pattern, and finally treated with UV light causing the acid generation of PGA that removed the protection group from the amino acids. A photolithographic mask with three groupings of parallel lines of different widths (1.25 μm , 2.5 μm , or 3.75 μm) was used to constrain the locations for the selective layers of SWNTs. The photogenerated acid was obtained by irradiating the precursor with UV light at its absorption wavelength. Thus, deprotection occurred only in the locations not covered by the photolithographic mask. The patterned SWNT multilayers were fabricated at the desired locations using the fabrication procedure outlined above.

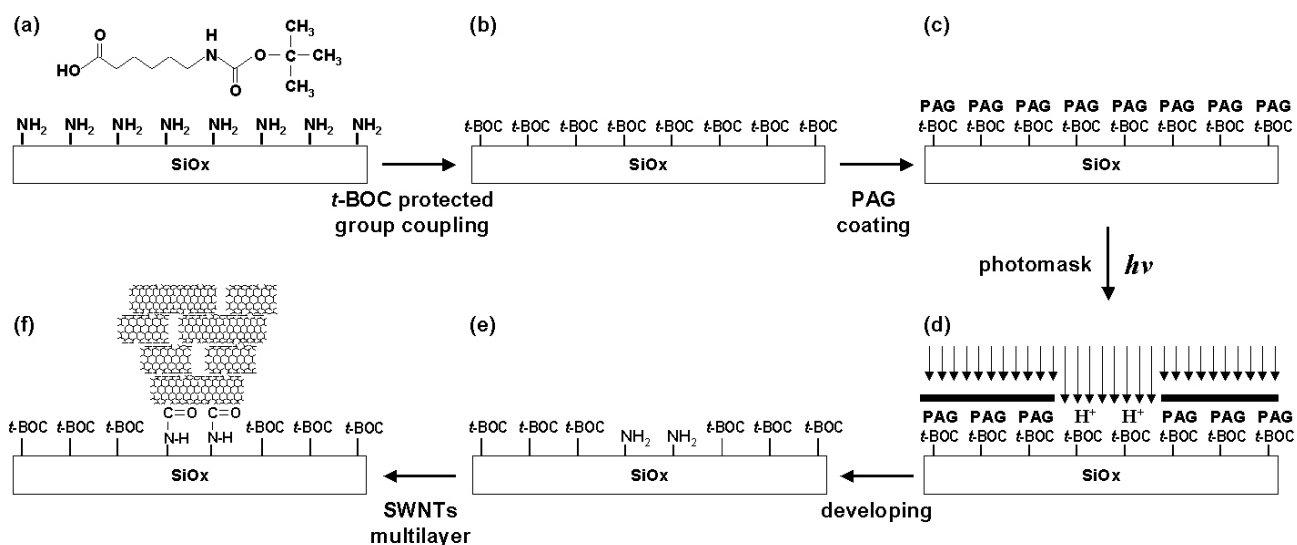


Figure 5. Overview illustrating the SWNTs multilayer film patterned: (a) 6-(BOC-amino) caproic acid containing the BOC protection group and amine-modified slide glass, (b) substrate coupled with *t*-BOC protected group, (c) substrate treated with PGA, (d) covering with a photolithographic mask and irradiation of UV light, (e) developing of substrate, and (f) SWNT multilayer film formation through repeated condensation reactions.

Characterization.

X-ray photoelectron spectroscopy (XPS) spectrum was obtained by a V.G. Scientific ESCALAB MK II spectrometer equipped with a Mg K α X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. The X-ray source was run at 12kV, a filament current of 10 mA, and a take-off angle of 75° to the sample surface. The pressure in the analysis chamber was maintained at 10⁻⁸ mbar or lower during measurements. All binding energies were referenced to the C1s peak for benzene as calibration, which was assigned a value of 284.6 eV. The XPS nitrogen (1s) spectrum was curve-fitted using Gaussian function.

The images of SWNTs multilayers were taken at various magnifications using a field emission scanning electron microscope (FE-SEM, XL30SFEG, Philips) equipped with a Schottky Based Field Emission Gun.

To investigate the resistivity of the SWNT multilayers, the voltage drop (V) between 2 points and the thickness (t) of the SWNT multilayers were measured repeatedly. The voltage drop and thickness

measurements were carried out at ten different locations using a four-point probe (CMT-SR 2000 SPEC) and surface profiler (KLA-Tencor, alpha-step 500), respectively. Surface profiler provides comprehensive films metrology control using optical, electrical and surface topography measurements. Four-point probe was used to measure a voltage drop. The current is passed from contact 1 to 4, and the voltage drop is measured with a voltmeter of very high impedance between points 2 and 4. The resistivity was calculated using the equation $\rho = (\pi t / \ln 2)(V/I)$, where ρ is the sheet resistivity, t is the thickness of SWNTs layer, V is the voltage, and I is the current. The current remained constant at 1.0 nA, and all measurements carried out at room temperature.

Supplementary Information 2: Photographs of SWNT multilayer film

The high-density multilayer structure could be constructed *via* consecutive condensation reactions that created stacks of SWNT layers linked together with the aid of a linker molecule and a condensation agent. Repeated treatments of the reaction cycle led to formation of SWNT multilayer film. This approach makes possible the formation of the SWNT multilayer film with high-surface density. To observe if the amount of SWNTs linked per reaction cycle was uniform, the stacked SWNT films were monitored by UV-vis-NIR. Fig.1(a) of the main manuscript shows the increase in absorbance for various cycles after each SWNT treatment on amine-modified slide glass. The images shown in Figure 3 are photographs of the SWNT multilayer films for various reaction cycles on glass with amino group (top), and on glass without amino group (bottom). The SWNT multilayer films, prepared on glass with amino group, had a very dark brown appearance after more reaction cycles, whereas the surfaces were hardly dark on glass without amino group.

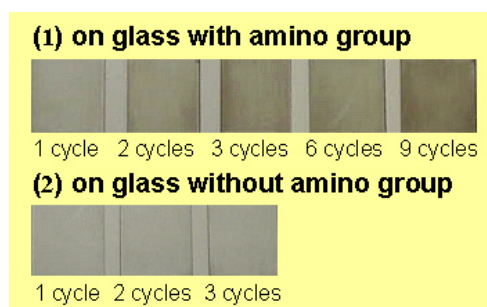


Figure 3. Photographs of SWNT multilayer film versus the number of reaction cycles on glass with amino group (top), and on glass without amino group (bottom).

Supplementary Information 3: Absorbance analyzed at 1020 nm of UV-vis-NIR spectra

To investigate the degree of darkness, that is, the surface-density of SWNT, the absorbance was analyzed at 1020 nm of UV-vis-NIR spectra. As shown in Figure 4, the surface-density of SWNTs on glass with amino group was confirmed by the linear increase as a function of the number of reaction cycles (-●-). On glass without amino group, however, surface-density remained constant at absorbance near zero (-▲-).

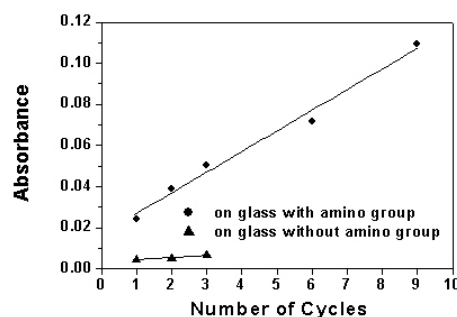


Figure 4. The measured absorbance at 1020 nm versus the number of reaction cycles (on glass with amino group, ●; on glass without amino group, ▲). The lines are a linear least-squares fit to the data.

These observations indicate that the SWNT films were formed through the covalent bonding between functional groups, which were increased linearly for the surface-density (not thickness) during subsequent reaction cycles.

Supplementary Information 4: XPS analysis for the linker molecule ODA

To determine whether ODA acts as a chemical linker, SWNT multilayer systems were analyzed by XPS. Figure 5 shows the XP spectrum of N1s. The N1s peak could be deconvoluted into two component peaks: a peak at 400.2 eV attributed to the amine nitrogen, and a peak at 401.5 eV attributed to the amide nitrogen.⁵ The amine N1s peak at 400.2 eV may arise from amino side groups of ODA that remain unreacted after reaction with the SWNTs. However, the presence of the amide N1s peak at 401.5 eV indicates that amide bonds were formed by reaction of the amino group of ODA with the carboxyl group of the SWNTs.

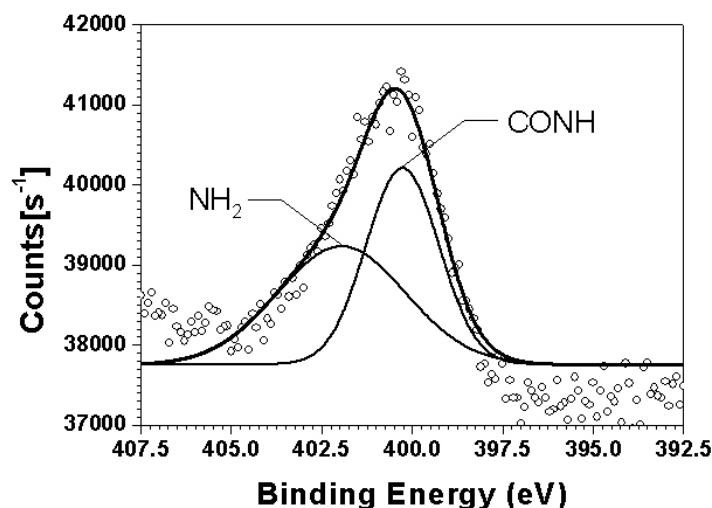


Figure 5. XP spectrum of N1s region for SWNTs multilayer constructed *via* ODA linker.

Supplementary Information 5: Various patterning of SWNT multilayer films

To show the unrestricted patterning of SWNT multilayer film, we used various photolithographic masks with the parallel lines and the chessboard-like pattern. We used both relief and intaglio photolithographic masks to show the raised and recessed regions. As shown in figure 6, the various SWNT multilayer patterns were fabricated at the desired locations. The SEM images clearly show the obvious boundaries between the SWNT regions (light gray) and the areas of clean substrate (dark gray). Importantly, the widths of the SWNT lines are the same as those of the photolithographic mask used to

define the pattern. Consequently, the SWNT multilayer film could be patterned freely to predefined locations on the substrate.

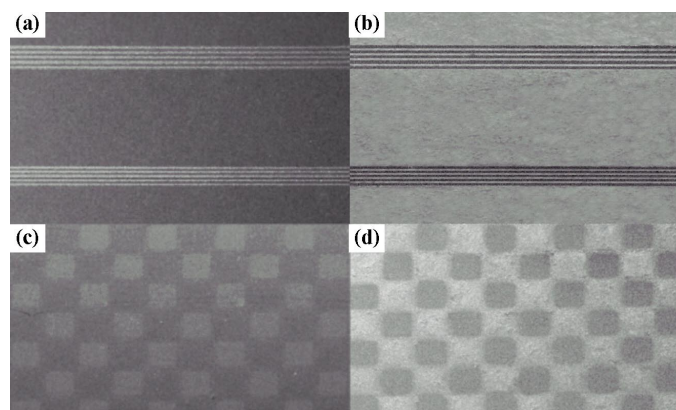


Figure 6. SEM images of the variously patterned SWNT multilayer films. (a) Parallel lines with 1.25 μm and 2.5 μm widths; the lines are the raised regions of relief. (b) Parallel lines with 1.25 μm and 2.5 μm widths; the lines are the recessed regions of intaglio. (c) Chessboard-like relief patterns with 80 μm width. (d) Chessboard-like intaglio patterns with 80 μm width.

REFERENCES

- 1 A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smally, G. Dresselhaus, M. S. Dresselhaus *Science*, 1997, **275**, 187
- 2 J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. R. Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert, R. E. Smalley *Science*, 1998, **280**, 1253
- 3 J. P. Pellois, W. Wang, X. Gao *J. Comb. Chem.* 2000, **2**, 355
- 4 K. Komolpis, O. Srinannavit, E. Gulari *Biotechnol. Prog.* 2002, **18**, 641
- 5 S. R. Kelemen, M. Afeworki, M. L. Orbaty, P. J. Kwiatek *Energy & Fuels* 2002, **16**, 1507; J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben *Handbook of Photoelectron Spectroscopy* Perkin-Elmer Corporation, Physical Electronics Division: Eden Prairie, MN 55344, 1992. A 1991, **9**, 2607; G. Beamson, D. Briggs *High-Resolution XPS of Organic Polymers The Scienta ESCA300 Database*, John Wiley & Sons Ltd., Chichester, 1992