Electronic Supplementary Information

Spontaneous Hybrids of Graphene and Carbon Nanotube Arrays at the Liquid-Gas Interface for Li-Ion Battery Anodes

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1. EXPERIMENTAL PROCEDURES

Funtionalization of SWNTs.

Hydrogenated cetyltrimethyl-ammonium hydroxide (CTAOH) was synthesized by replacing Br in CTAB with OH- using Dowex Monosphere 550A (OH) anion exchange resin (Sigma-Aldrich, St. Louis, MO, U.S.A.). The synthesis of CTVB was performed by neutralization of 4-vinylbenzoic acid (VBA, Sigma-Aldrich, St. Louis, MO, U.S.A.) with slight stoichiometric excess of CTAOH, followed by repeated crystallization.[1] HiPco (high-pressure CO conversion) SWNTs (Unidym, inc., Sunnyvale, CA, U.S.A.) were suspended in water (2 mg/mL) and then sonicated for 1 h after mixing with the cationic surfactant CTVB (5 mg/mL) to exfoliate bundled SWNTs. The CTVB surfactants adsorbed on the SWNT surface were permanently attached by in situ free-radical polymerization of the counter ions of CTVB using the water-soluble free radical initiator 2,2'-azobis dihydrochloride (VA-044, Wako Chemicals, Osaka, Japan) at 60 °C. In order to separate the individually isolated polymerized *p*-SWNTs from the bundles, the suspension was ultra-centrifuged at 111,000 g for 4 h and the supernatant was collected and freeze-dried at −55 °C to obtain black powders of *p*-SWNTs.[1]

p-SWNT/GNS Hybrid Thin Films.

GNSs suspension in water was purchased from Angstron Materials (Dayton, OH, U.S.A.). Similar to the method for the GNS monolayer from our previous report, we applied the LB or LS technique to fabricate the *p*-SWNT/GNS hybrid monolayer.[2] A suspension of *p*-SWNT (25 μL) in methanol at a concentration of 1 mg/mL was spread on the water subphase (total area (A) = 367 cm^2) at 20℃ and pH 7.4 in an LB trough (KSV 2000, KSV NIMA, Espoo, Finland). The pH values were measured using a pH meter (Thermo Scientific, Waltham, MA, USA). After

15 min, the *p*-SWNT film was compressed at a speed of 5 cm^2/min and the surface pressure-area (π-A) isotherm was monitored using a 25 mm-wide platinum Wilhelmy plate suspended from a microbalance by feedback motor control barriers. After reaching the surface pressure of 42 mN/m, the concentrated GNS suspension was gently injected to the water subphase until a final concentration of 100 ppm was reached. After 10 min, the compressed *p*-SWNT/GNS hybrid monolayer was horizontally deposited on the silicon substrate by LS technique. The attached *p*-SWNT/GNS sheets were gently washed several times with deionized water and annealed in vacuum at 80℃ for 2 h. The LS deposition of the *p*-SWNT/GNS monolayer was repeated up to nine times for the fabrication of the hybrid multilayer.[2]

Characterization of *p*-SWNT/GNS Hybrid Films.

The surface structure of *p*-SWNT/GNS film on the substrate was measured by AFM equipped with a piezo scanner (Nanoscope IIIa; Veeco Instruments Inc. Plainview, NY, U.S.A.). Scanning electron microscopy (SEM; Magellan 400, FEI, Hillsboro, OR, USA) was also used with a low acceleration voltage (e.g., 2 kV) and a low current (e.g., 13 pA). We applied a non-contact tapping mode using a silicon nitride tip. Unpolarized Raman spectra were recorded at room temperature for the GNS, *p*-SWNTs, and their hybrid films deposited on silicon substrates. The Raman microscope (Renishaw Ltd, Gloucestershire, U.K.) with the excitation source of the 633 nm line was used from a He-Ne laser. Neutron reflectivity experiments were carried out with the NG7 reflectometer at the Cold Neutron Facility of the National Institute of Standards and Technology (Gaithersburg, MD, USA) with a wavelength (λ) of 4.76 Å and $\Delta\lambda/\lambda$ of 0.025. The reflectivity data was collected as a function of $q_z = (4\pi/\lambda \sin\theta)$, where θ is the grazing angle of incidence. The vertical slits gradually opened as a function of the scattering wave-vector transfer

(q_z) to fix the resolution to a constant value of $\Delta q_z/q_z \approx 0.03$ while the size of the horizontal slits was set to 30 mm. XRD (D/MAX-2500, Rigaku Co., Tokyo, Japan) was performed using CuKα radiation (λ = 1.54 Å). GISAXS experiments were conducted at the 9A U-SAXS beamline at Pohang Accelerator Laboratory (PAL) in Korea. The photon energy was 11.07 keV.

Electrochemical Characterization.

The working electrode was prepared by transferring the *p*-SWNT/GNS multilayers to Cu foil, followed by drying at 50 °C. Electrochemical tests were carried out using 2032-type coin dells with Li metal as a counter electrode and 1M $LiPF_6$ in ethylene carbonate(EC)/dimethyl carbonate(DMC) (EC:DMC = 1:1, Welcos) as an electrolyte. A glass microfiber (GF/F, Whatman, U.S.A.) was used as a separator. Galvanostatic charge/discharge measurement of the *p*-SWNT/GNS electrode was performed at various current rates of 200, 300, 500, 1000, 2000 mA/g at room temperature. CV measurement of the electrode was performed over the voltage range 0.05–3.0 V (V *vs.* Li^+/Li) at a scan rate of 10–100 mV/s.

2. SUPPLEMENTARY RESULTS

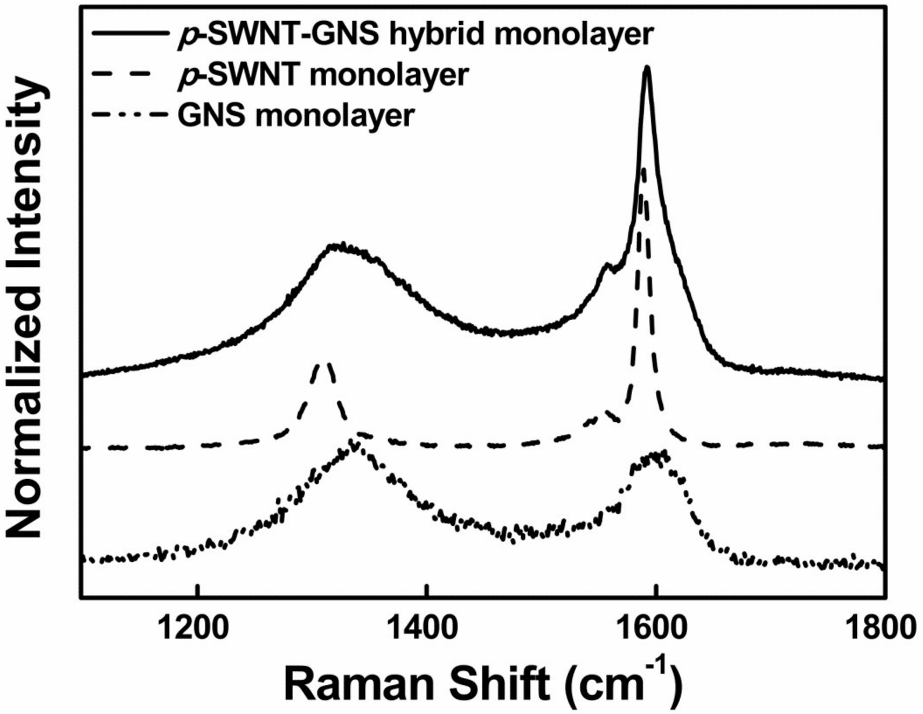

Fig. S1. Raman spectra of GNS, *p*-SWNT, and *p*-SWNT/GNS monolayer on silicon wafers. Raman spectra of single layers of GNS/CTVB, *p*-SWNT, and *p*-SWNT/GNS hybrids prepared by LB deposition on silicon substrates. Both the GNS and *p*-SWNT monolayers exhibited the G-band (1589–1602 cm^{-1}) and D-band (1310– 1337 cm^{-1}) owing to the C–C bonds in the graphite lattice and stretching of the sp^2-hybridized carbon system, respectively.[3] However, the spectral features of GNSs show that the D- and G- bands are broader than those of *p*-SWNTs because of their highly disordered structure, while the *p*-SWNT single layer exhibited multiple sharp peaks in the G-band region at 1557 and 1589 cm^{-1} because of the curvature effect of the SWNTs.[3] The Raman spectrum of the *p*-SWNT/GNS hybrid monolayers exhibited the features of both GNSs and SWNTs, such as peak extension and multiple peaks in the G-band. The peak positions of the G- and D-bands in the spectrum of the hybrid monolayers shifted to higher frequencies when compared to those of *p*-SWNTs. These features clearly demonstrate the formation of hybrid films of GNSs and *p*-SWNTs by the LB technique.

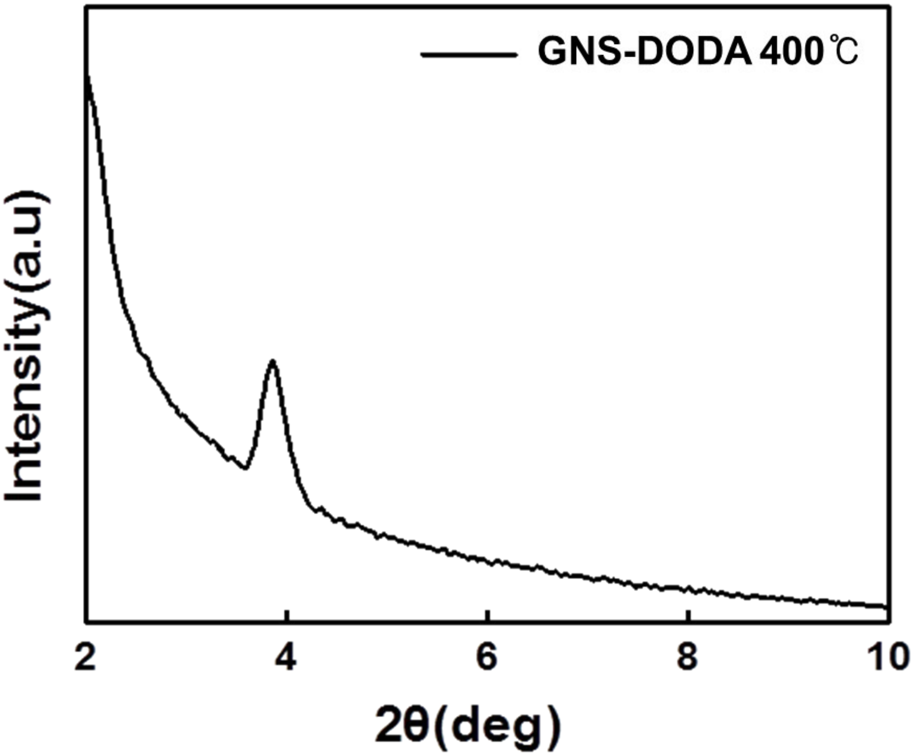

Fig. S2. XRD data of DODA/GNS multilayer at 400℃

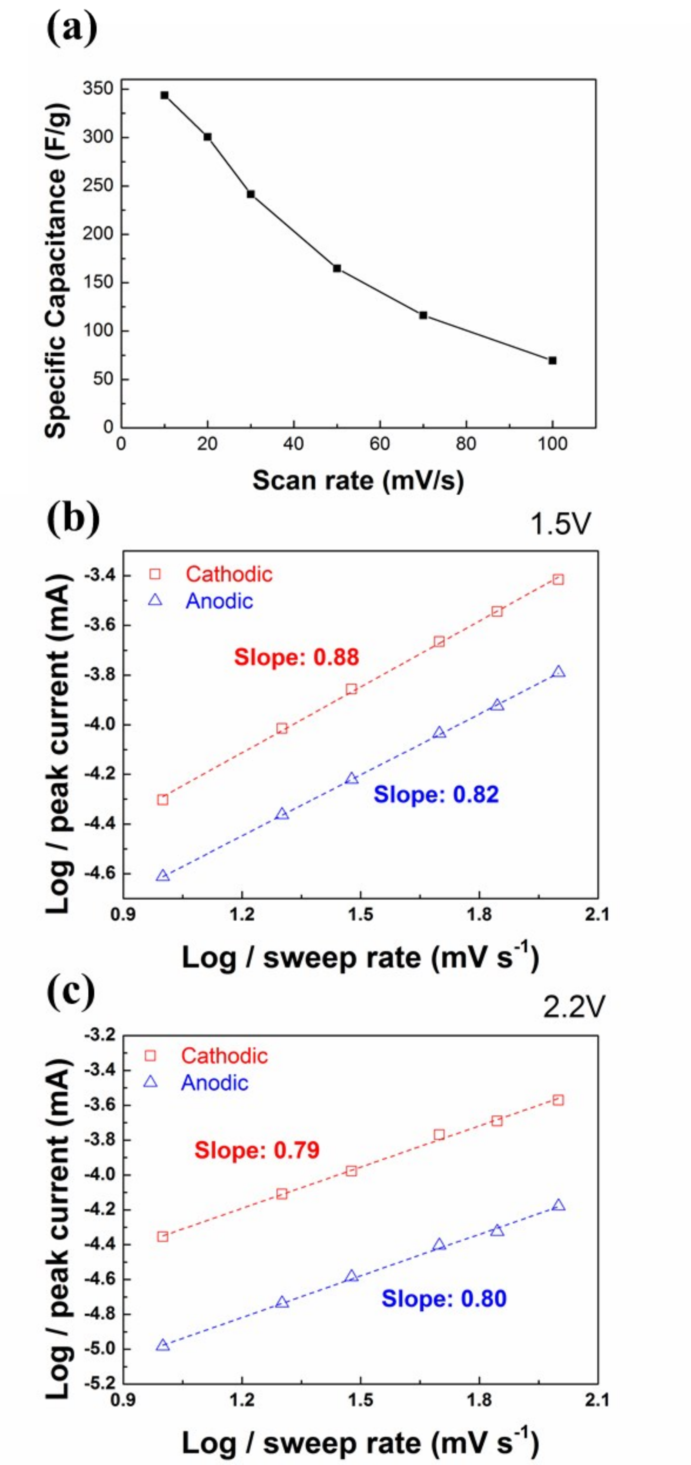

Fig. S3. (a) The calculated specific capacitance from CV data of *p*-SWNT/GNS electrode measured at various scan rates of 10, 20, 30, 50, 70, and 100 mV s^{-1}. Log-scale plot of peak current at (b) 1.5 V and (c) 2.2 V dependence on the scan rate. The dotted lines indicate the linear fit of cathodic and anodic current as scan rate.

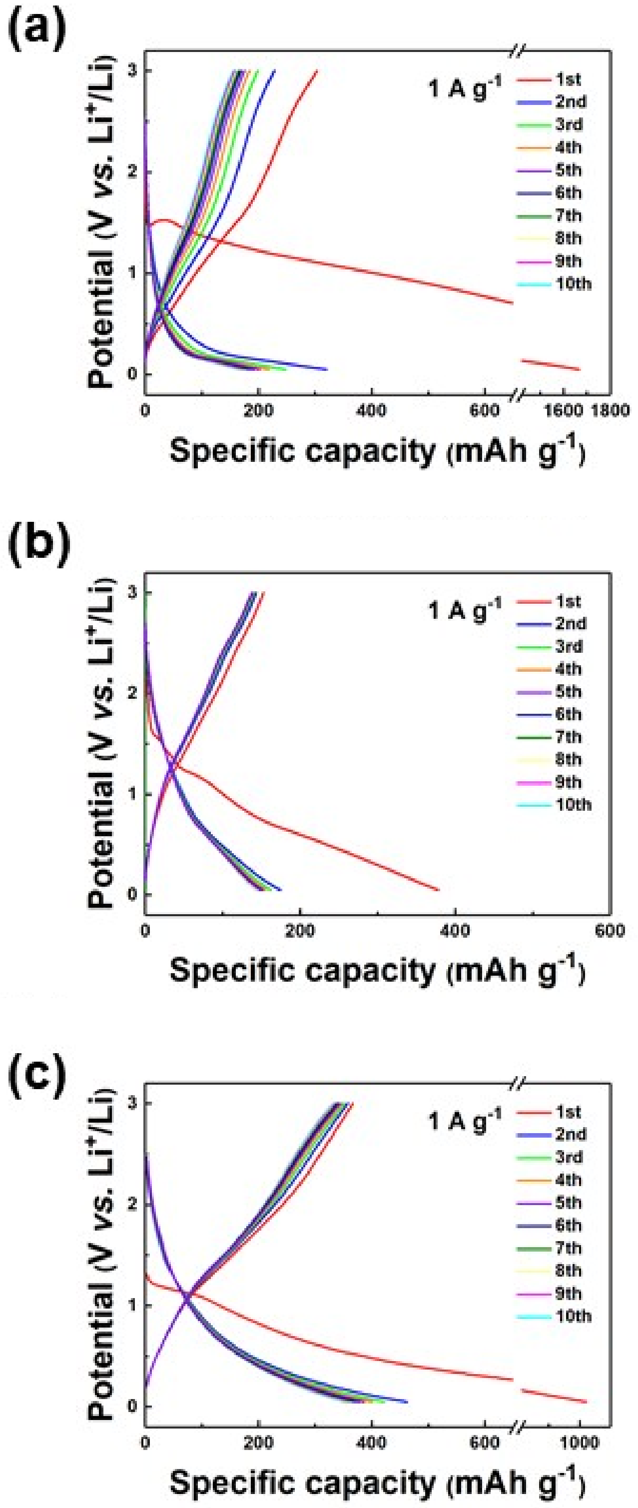

Fig. S4. Galvanostatic charge/discharge curves of (a) *p*-SWNT electrode, (b) GNS and (c) four-repeated layers of *p*-SWNT/GNS up to 10 cycles at a current density of 1 A g^{-1}. The loading masses of *p*-SWNT, GNS, four layers of *p*-SWNT/GNS were 39.7, 89.7 and 0.106 mg cm^{-2}

respectively.

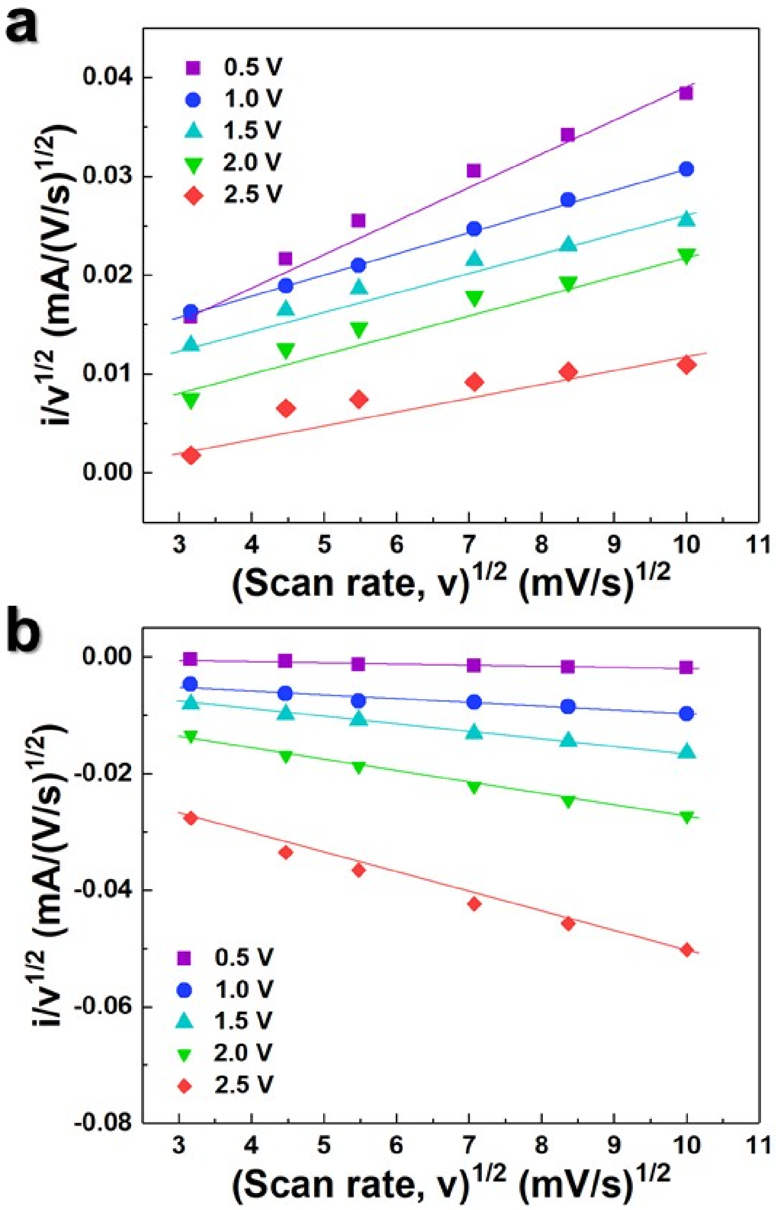

Fig. S5. Relationship between the scan rates and currents at (a) cathodic and (b) anodic scan at CV curves of the p-SWNT/GNS electrodes.

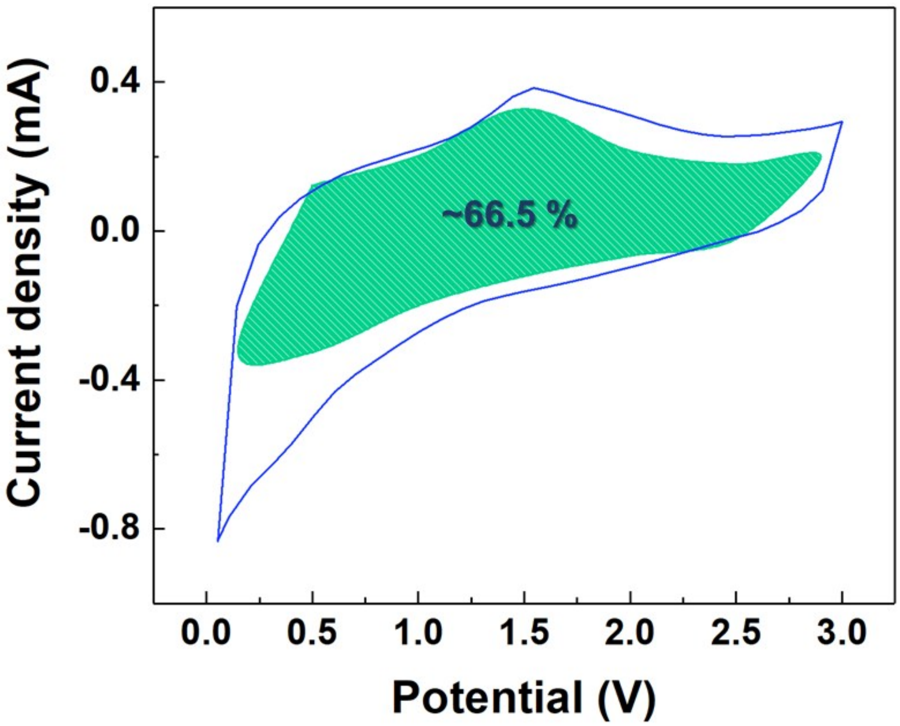

Fig. S6. CV curves of the p-SWNT/GNS electrodes with separation between total current (solid line) and surface capacitive current (shaded regions) at 100 mV s^{-1}.

REFERENCE

1 T.-H. Kim, C. Doe, S. R. Kline and S.-M. Choi, *Adv. Mater.* 2007, **19**, 929.

2 H. Kim, Y. R. Jang, J. Yoo, Y.-S. Seo, K.-Y. Kim, J.-S. Lee, S.-D. Park, C.-J. Kim and J. Koo, *Langmuir* 2014, **30**, 2170.

3 M. S. Dresselhaus, G. Dresselhaus, R. Saito and A. Jorio, *Phys. Rep.*, 2005, **409**, 47.