Supporting Information

Stacked Multilayer of Alternating Reduced Graphene Oxide and Carbon Nanotube for Planar Supercapacitor

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Materials and methods

1. **Materials.** The chemicals used in this study were sulfuric acid (H₂SO₄, 96.2%, Fisher Scientific), phosphoric acid (H₃PO₄, >85wt% in H₂O, Sigma-Aldrich), hydrochloric acid (HCl, 37.1%, Fisher Scientific), poly(vinyl alcohol) (PVA, M_w =88,000, hydrolyzed, ACROS Organics), potassium permanganate (KMnO₄, 99+%, Sigma-Aldrich), hydrogen peroxide (H₂O₂, 30%, Fisher Scientific), hydrazine hydrate (N₂H₄, 64% in water, Acros Organics), ammonium hydroxide (NH₄OH, 28% in water, Fluka), graphite flake powder (Aldrich, Lot#:MKBK4082V). Multi-walled CNTs used in this study were from Hanwha Nanotech (Grade : CM-150).

2. Synthesis of reduced graphene oxide (rGO). Graphene oxide (GO) was synthesized from high purity graphite flake powder using a modified Hummer's method^[11] with improved purification method as reported previously.^[6] In short, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (135:15 mL) was added to a mixture of graphite flakes (1.0 g) and KMnO₄ (6.0 g). The reaction was heated to 50 °C under stirring for 12 h. The reaction was cooled to room temperature and poured into ice (400 mL) containing H_2O_2 (2 mL). The oxidized graphite flake

was washed with 200 mL of 5% HCl by a centrifuge at 11,000 rpm for 20 min several times. The graphene oxide was reduced by chemical reduction as reported previously.^[7] The exfoliated graphene oxide was redispersed in 20 mL of water (0.5 mg/mL) after sonication for 1h. Then, it was mixed with water (20 mL), N₂H₄ (60 μ L, 35% Aldrich), and NH₄OH (420 μ L, 28% Aldrich). The reaction was heated to 70 °C for 1h and centrifuged with H₂O three times.

3. Fabrication of the solid-state stacked supercapacitor. The monolayers of rGO and CNT were produced as previously reported.^[9] Multi-walled CNTs (400 mg) were treated with a mixture of H₂SO₄ and HNO₃ (vol:vol=3:1) at 65 °C for 14h to disperse in polar solvents. After the reaction, the CNTs were washed with H₂O several times and redispersed in alcohol for later use. Reduced graphene oxide nanosheets and CNTs were redispersed in ethanol and 1-butanol, respectively. These suspensions were dropped on a water surface in separate Petri dishes with a pipette until a robust film was formed. The electrode was prepared by making an assembled rGO and CNT film on the water surface, followed by transferring onto the substrate. The film was then scooped up by a substrate and repeated to make a multi-layer film. The randomly stacked rGO/CNT electrode was made by dropping a mixed solution of rGO and CNTs in ethanol (0.5 mg/mL for both) on a water surface and transferring to a current collector. All solid-state devices were assembled by pouring polymer gel electrolyte (100 μ L/cm²) onto the stacked rGO/CNT electrodes. The device was left overnight in a desiccator for complete drying of the gel electrolyte. The polymer gel electrolyte used in this study is a mixture of poly (vinyl alcohol) (PVA, $M_w = 88,000$, hydrolyzed, ACROS Organics) and phosphoric acid (H₃PO₄). The electrolyte was prepared as described elsewhere.^[12] Two electrodes were assembled face-to-face and left overnight until the electrolyte solidified.

4. Characterization. The morphologies of the graphene oxide, reduced graphene oxide and

CNTs were investigated with transmission electron microscopy (TEM, Philips Tecnai 12, 200 kV). The cross-section images of the stacked rGO/CNT film were taken by a scanning electron microscope (SEM, JSM-6700F, JEOL). The height profile was obtained with an AFM (Model dimension 3100, Digital Instrument Co.).

5. Electrochemical measurements of the stacked supercapacitor. The electrochemical properties of the samples were measured with cyclic voltammetry (CV) and galvanostatic charge-discharge measurements in a conventional three-electrode system by using a potentiostat (VersaSTAT 4, Princeton Applied Research). The area of electrodes was confined to 1×1 cm². Electrochemical impedance spectra (EIS) experiments were carried out at an open circuit potential with a sinusoidal signal with an amplitude of 10 mV in a frequency range of 1 MHz to 10 mHz. Tandem stacked rGO/CNT supercapacitors were made simply by connecting two and four devices together in series and parallel combinations.

6. Calculations. The capacitance of each device was calculated from the galvanostatic charge/discharge curves at different current densities using the following equation:

$$C = I / (-dV/dt) \quad (1)$$

Where *I* and dV/dt are the constant discharging current (A) and the slope of the discharge curve (V/s) (excluding voltage drop due to internal resistance). Specific capacitances of each device were calculated based on area and volume by using the following equations:

Areal capacitance = C/area of the electrode, $[F/cm^2]$ (2) Volumetric capacitance = C/volume of the device, $[F/cm^3]$ (3) It should be noted that the volumetric capacitances were calculated by taking into account the volume of the stacked device including electrolyte and current collector as in Fig. S4.

The electrochemical performance of each device in this study was based on the volume of the stacked electrode and measured under the same conditions from galvanostatic charge/discharge curves. The power of each device was also calculated from the galvanostatic charge/discharge curves at different current densities by using the following equation:

$$P = (\Delta E)^2 / 4R_{ESR} V \quad (4)$$

Where P is the power (W/cm3), ΔE is the operating voltage window (obtained from the discharge curve excluding the IR drop), V is the volume of the stacked electrode (cm³), and R_{ESR} is the internal resistance of the device calculated from the voltage drop (V_{drop}) at the beginning of the discharge curve at a constant current density (i) by using the equation $R_{ESR} = V_{drop}/2i$. The energy density of the device was calculated from the following equation:

$$E = C_{\nu} \times \left(\Delta E \right)^2 / (2 \times 3600) \quad (5)$$

Where E is the energy density (Wh/cm³), C_v is the volumetric capacitance calculated from eq. (3) and ΔE is the operating voltage window in volts.



Figure S1. TEM images of as-prepared reduced graphene oxide (a) and CNTs (b). Scale bars are 1 μ m and 200 nm, respectively. Insets show the 10 layers of rGO by repeated transfer (a) and single layer of CNT (b) onto glass.



Figure S2. TEM images of randomly-mixed rGO/CNT (R-rGO/CNT) showing partial coverage by rGO nanosheets (A) and phase separation of the two components (B).



Figure S3. Cross-section SEM images of alternately stacked rGO/CNT films consisting of (A) 4, (B) 8, and (C) 32 rGO layers. The scale bars are 100 nm.



Figure S4. Schematic diagram showing cross-section of the electrochemical capacitors with their device dimensions. Two rGO/CNT electrodes are supported on a metal foil current collector and separated with polymer gel electrolyte. The effective thickness of the device is 60.4 μ m with an active area of 1 cm² in the case of 16 alternating layers of rGO/CNT film. However, the effective thickness of the device made only with 16 layers of rGO (60.1 μ m) is thinner than the rGO/CNT electrode



Figure S5. Galvanostatic charge-discharge curves of the layer-by-layer stacked rGO/CNT (L-rGO/CNT) at various current values.



Figure S6. CV curves of each device consisting of 16 layers of various carbon materials at a scan rate of 10 mV/s.



Figure S7. Bode plots of each device consisting of 16 layers over a frequency range from 1 MHz to 10 mHz.



Figure S8. Cycling performance of four different devices consisting of 16 layers.



Figure S9. Galvanostatic charge-discharge curves of the large-sized device $(5 \times 7 \text{ cm}^2)$ consisting of layered rGO/CNT (L-rGO/CNT) at various current values.



Figure S10. Cycle performance of the large-sized (5×7 cm²) layered rGO/CNT (L-rGO/CNT) by changing current density.