

Supporting Information

Atomic H-induced cutting and unzipping of single-walled carbon nanotube carpets and their enhanced supercapacitor performance

Xiujun Fan^{†‡⊥}, Zhiwei Peng[‡], Yang Yang[‡], Haiqing Zhou[‡], Xia Guo[†]*

*[†]College of Electronic Information and Control Engineering, Beijing University of Technology,
Beijing 100124, China*

*[‡]Department of Chemistry, [⊥]Richard E. Smalley Institute for Nanoscale Science and Technology,
Rice University, Houston, Texas 77005, United States*

Corresponding Author

fxiujun@gmail.com (X. J. Fan)

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1. Experimental Procedure

Synthesis of VA-SWCNTs carpets and atomic H treatment

The substrate for growing VA-SWCNTs carpets was prepared by electron-beam evaporating a 10 nm Al_2O_3 buffer layer and 0.8 nm Fe catalyst layer sequentially onto a SiO_2 wafer in an electron-beam evaporator. VA-SWCNTs carpets were grown on this substrate with hot-filament chemical vapor deposition (HF-CVD) method. Typically, a mixture of H_2 (210 sccm), C_2H_2 (2 sccm) and H_2O (200 sccm) gas was flowed into the reactor at 750 °C at an elevated pressure (~25 Torr). A tungsten wire (~ 8 mm long and 0.25 mm in diameter) hot filament was activated with a power of 30 W for 30 s to reduce catalyst with atomic H. The pressure was then decreased immediately to 6.4 Torr to start the VA-SWCNTs carpet growth. A 15-min-growth process produced a VA-SWCNT carpet with a height of 80-100 μm . And then 4 tungsten wires (~ 8 mm long and 0.25 mm in diameter) were used to make a filament array assembly. The VA-SWCNTs carpet samples were loaded into the CVD furnace chamber below the hot filament and treated with atomic H. Typically, the reaction used a mixture of H_2 (140 sccm), H_2O (15 sccm) and CH_4 (0-1.5 sccm) at a pressure of ~ 25 Torr for 0-4 h. The temperature of furnace was keep at 850 °C, and the hot filament power was 65 W. The VA-GNRs treated with 0.5 sccm CH_4 for 2 h was chosen as the VA-GNRs electrode. After atomic H treatment, the obtained VA-GNRs were immersed into a buffered oxide etch solution (buffered HF, to remove the SiO_2) to detach the VA-GNRs from the substrate. After ~30 min etching, the VA-GNRs film floated to the surface of solution. The free standing VA-GNRs film was then rinsed with DI water for several min to remove residual acid until the rinse water was pH neutral. The VA-GNRs films were air dried before assembling them into supercapacitor device.

Fabrication of VA-GNRs based supercapacitors and electrochemical measurements

The VA-GNRs based capacitor was fabricated by sandwiching polypropylene foil as a separator between two VA-GNRs carpet sheet electrodes. In one experiment, about 200-500 μg (Citizen scale, model: CM 21x, weighing accuracy 1 μg) of the VA-GNRs carpet was used as the active material. Symmetric two-electrode

cells were assembled into coin-cells (CR2032, MTI Corporation, USA) in an argon-filled glove box (VAC NEXUS, USA) with both moisture and oxygen content < 1.5 ppm. 1 M tetraethylammonium tetrafluoroborate (TEABF₄, 99.0%, Sigma-Aldrich) in acetonitrile (AN, 99.8%, Sigma-Aldrich) was used as the electrolyte and polypropylene foil (Celgard, USA) as the separator. The two electrodes were then compacted and sealed with two stainless steel plates without using other current collectors. After assembly, the cells were aged for 12 h before electrochemical measurements. The CVs, constant current discharge/charge testing and EIS measurements were carried out with an electrochemical analyzer (CHI 608D, CH Instruments, USA).

Characterization

XPS was conducted on a PHI Quantera SXM scanning X-ray microscope. An Al anode at 25 W was used as the X-ray source with a pass-energy of 26.00 eV, 45° take off angle, and a 100 μm beam size. SEM images were taken at 10 kV on a FEI Quanta 400 ESEM FEG scanning electron microscope (SEM). For TEM sample preparation, the material was dispersed in chloroform by bath-sonication using an ultrasonic cleaner (Cole-Parmer model 08849-00) for 1 h, followed by deposition on a 300 mesh Lacey Formvar/carbon copper grid (Ted Pella, 01883-F). TEM imaging was conducted on a JEOL 2100 field emission gun transmission electron microscope. AFM images were obtained on a Digital Instrument Nanoscope IIIA atomic force microscope. BET surface area was measured on a Quantachrome autosorb-3b BET surface analyzer.

Supplementary Figures.

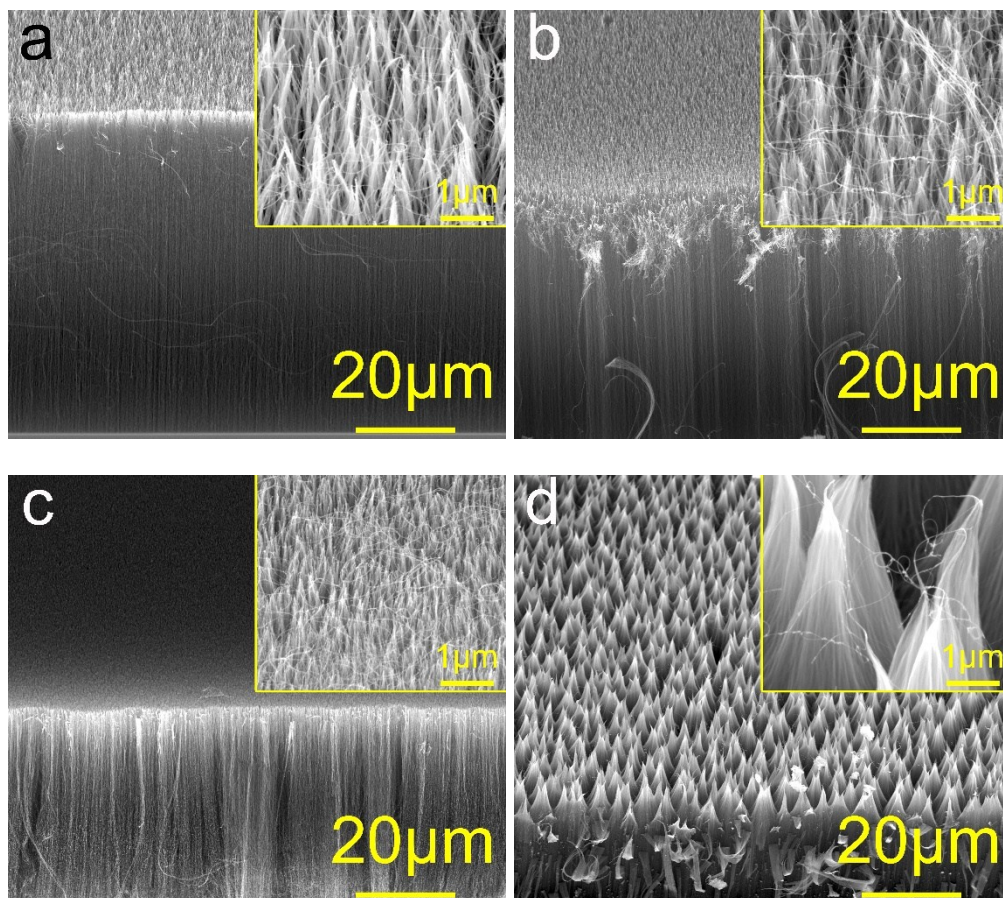


Figure S1. SEM images of VA-SWCNTs carpets treated with atomic H at various time and CH₄ flow rates: (a) 30 min, CH₄: 0.5 sccm; (b) 1 h, CH₄: 0.5 sccm; (c) 2 h, CH₄: 1.0 sccm; (d) 30 min, CH₄: 0.1 sccm.

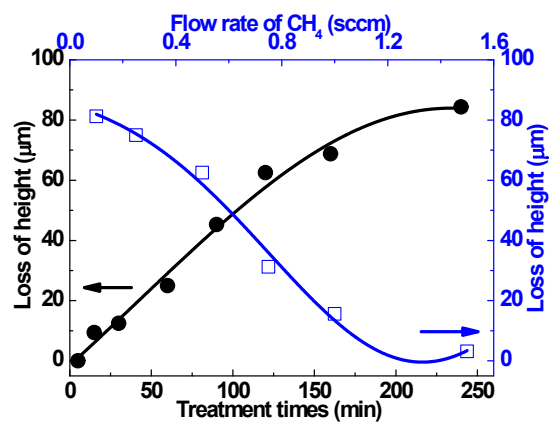


Figure S2. Height losses of VA-SWCNTs carpet treated with atomic H at different CH₄ flow rates (top axis in both panels) and treatment times (bottom axis in both panels).

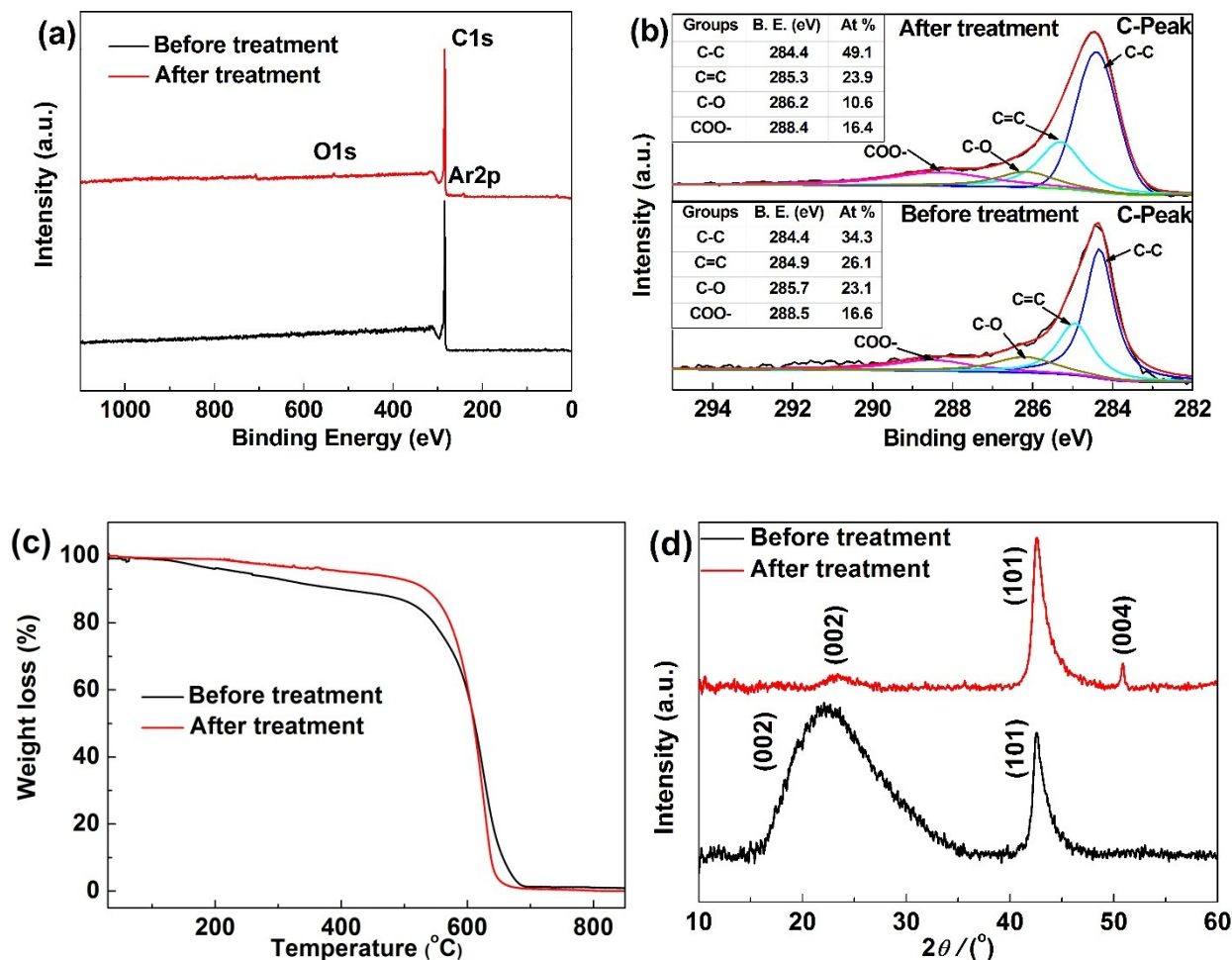


Figure S3. (a-b) XPS spectra, (c) TGA curves and (d) XRD pattern of as-produced VA-SWCNTs carpets before and after treatment with atomic H for 2 h, CH₄ flow rate of 0.5 sccm.

By changing atomic H treatment operational parameters, it was possible to tune the distribution of carbon groups on the surfaces of the nanotubes². **Figure S3a-b** depicts the characteristic XPS spectra of VA-SWCNTs and VA-GNR carpet treated with atomic H for 2 h, whereas the Tables inset summarizes the main information related to the peaks obtained from the deconvolution and the atom% composition. The slight increase in oxygen signal after the atomic H treatment can be attributed to physisorbed oxygen³ (**Figure S3a**). The evaluation of bonding content consists of spectral background subtraction, followed by the fitting of Guassian-Lorentzian asymmetric functions to the measured spectra, selecting the relevant binding energy value from the literature. The deconvolution of C1s spectra is split into several peaks: C-C, C=C, C-O and C=O. As exhibited

in **Figure S3b**, the atomic percentage in the C1s spectra of graphitic carbon (C-C) on the VA-SWCNT surface is 34.3%. With atomic H treatment for 2 h, the percentage of C-C increases to 49.1%. With a given hot filament power and carbon source flow rate, the longer the treatment time, the stronger of atomic H etching effect, and more graphitic carbon (C-C bond) form. Thermo gravimetric analysis (TGA) was carried out for the VA-SWCNT and VA-GNR at a heating rate of 5 °C/min in air. The weight loss for VA-SWCNTs start at about 450 °C and continue to increase rapidly with temperature, until a stable plateau at 690 to 850 °C (final point of measurement) is reached, leaving a very litter residual weight. The weight loss for VA-GNRs started at 530 °C, until a stable plateau is reached at 730 to 850 °C, leaving the same residual weight as VA-SWCNTs (0.5 wt%). Thus a purity of ~ 99.5% of the total mass can be estimated. The remainder in both two samples is presumably from the remaining iron catalyst. The graphitic carbon impurities in the VA-SWCNTs samples is already decomposed with atomic H treatment. So the VA-SWCNTs show a high weight loss at the starting temperature. XRD patterns of the VA-SWCNTs and VA-GNR samples are shown in **Figure S3d**, where, except for the carbon peak, there is no any other impurity in the samples. The (002) peak becomes narrow and shifts slightly to higher 2θ , (101) peak is sharpened and becomes the main peak after atomic H treatment, due to atomic H removal of graphitic carbon impurities^{1, 4, 5}, which is consistent with the TGA result.

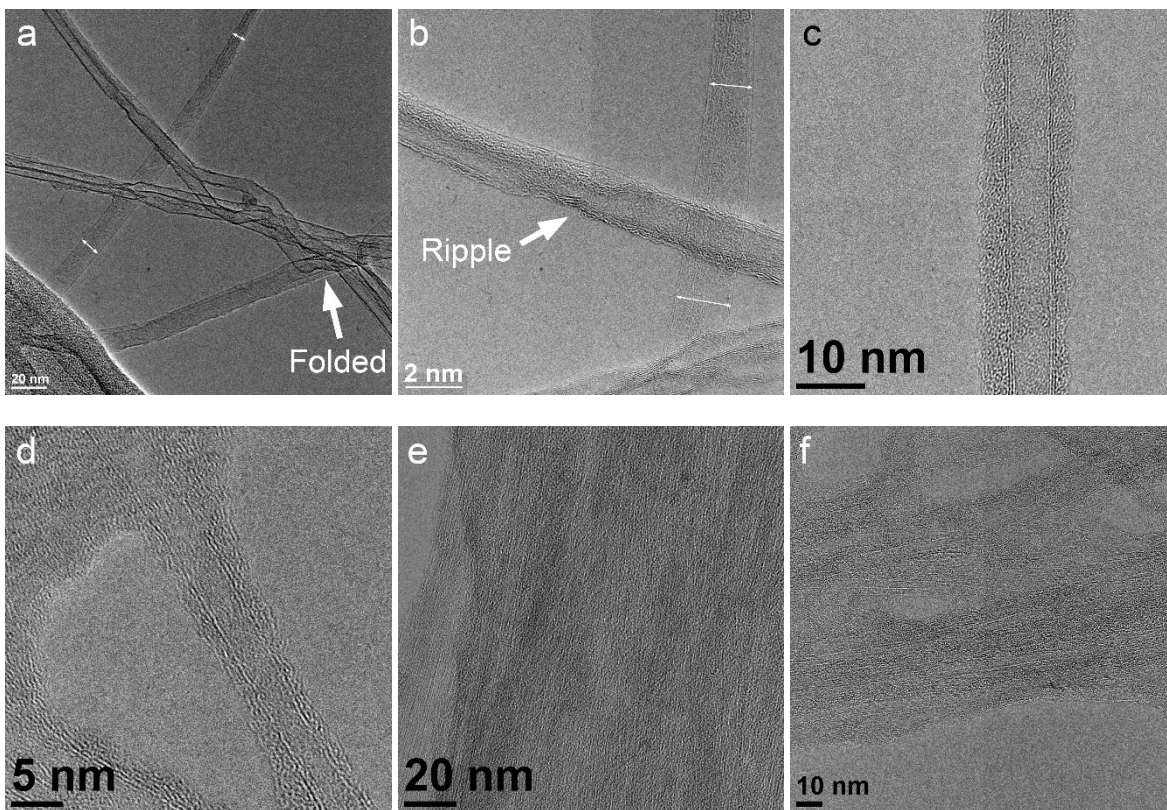


Figure S4. TEM characterizations of nanotubes from the VA-SWCNTs that had been atomic H treated, (a-b) at a CH₄ flow rate of 0.5 sccm for 1 h, (c-d) at a CH₄ flow rate of 0.5 sccm for 2 h, (e-f) at a CH₄ flow rate of 0.1 sccm for 2 h.

Figure S4a and b show GNRs at an intermediate stage of unzipping. The image clearly shows the unzipping along the folded edge of the SWCNTs and the unzipped GNRs are partially exfoliated from the bundle, with the splitting front halted at the bundle surface. It appears that the unzipping of VA-SWCNTs proceeded from the top of the VA-SWCNT carpet to the bottom. This is confirmed by the SEM image (**Figure 1, Figure S1**), suggesting a complete transformation of 2 to 15 nm diameter SWCNTs to few-layer GNRs, having more or less (5 to 50 nm) similar widths and a few micrometers in length, strikingly similar to the dimensions of high-quality graphene prepared by chemical methods. TEM images indicate that the obtained GNRs are exfoliated into graphene sheets, but partial tube structure can still be identified (**Figure S4b**).

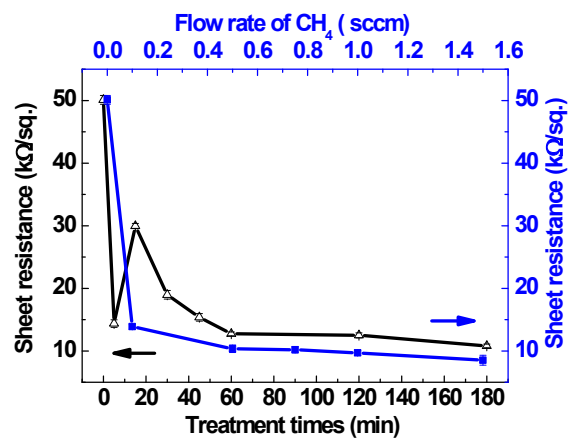


Figure S5. Sheet resistances of VA-SWCNTs carpet treated with atomic H at different CH₄ flow rates (top axis in both panels) and treatment times (bottom axis in both panels).

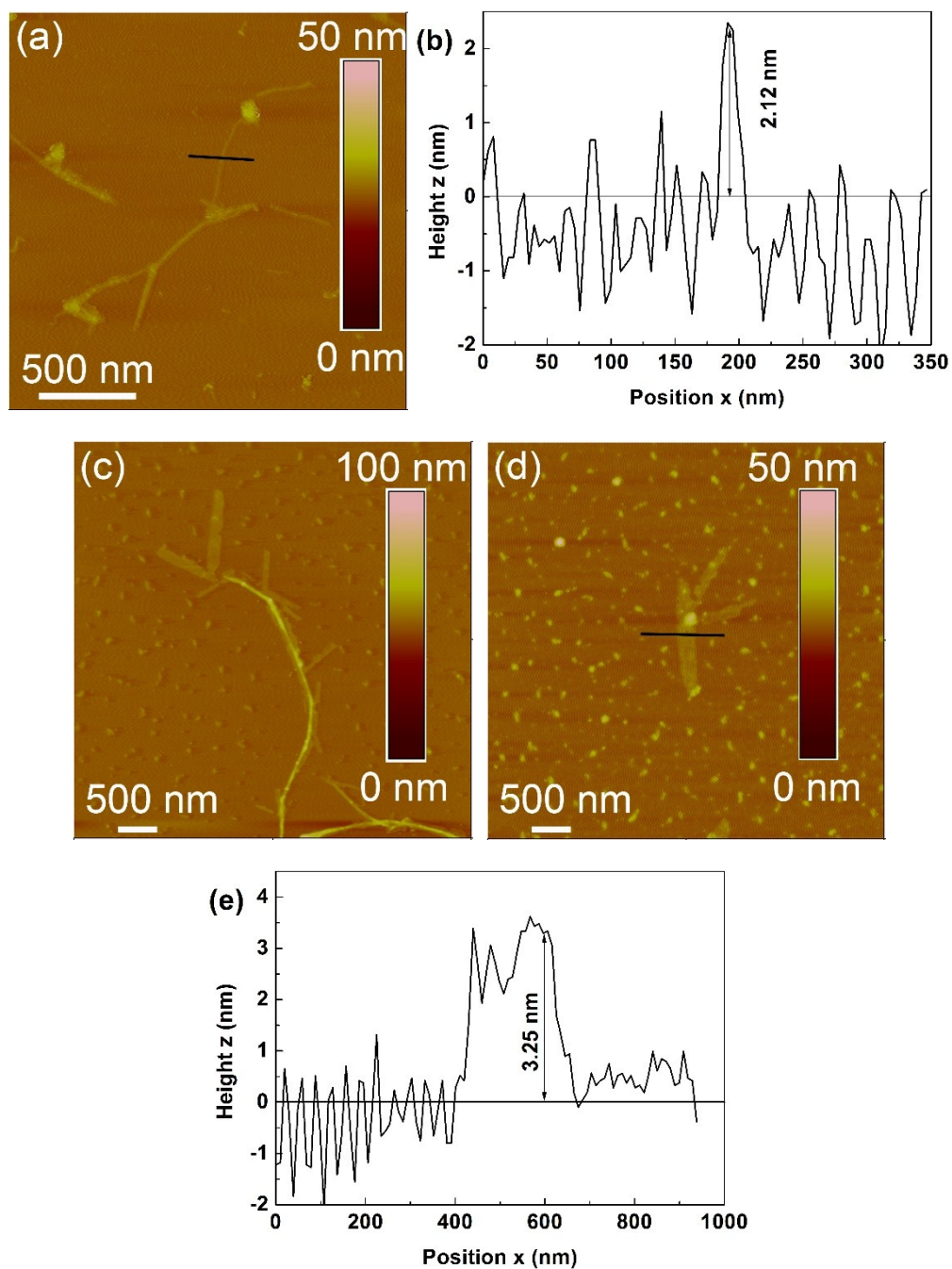


Figure S6. AFM characterization of an individual nanostructure from the VA-SWCNTs, (a, b) before and (c-e) after atomic H treatment with CH₄ flow rate of 0.5 sccm for 2h.

AFM characterization was also carried out to demonstrate the structural changes in the VA-GNRs. AFM images (**Figure S6a-b**) indicates that the nanotube has a height measurement of ~2.1 nm, which is the typical

height for SWCNTs. **Figure S6c** shows typical AFM images of GNRs prepared from VA-SWCNTs carpet with atomic H treatment; a long carbon nanotube bundle is connected to a graphene nanoribbon. **Figure S6d** reveals long ribbons (0.5 to 1 μm) with straight edges and widths ranging from 10 to 50 nm, revealing bilayer GNRs of thickness ranging from 3 to 5 nm. This is also confirmed by the HR-TEM images (**Figure 3c-d**), suggesting a complete transformation of 1.5 to 3 nm diameter SWCNTs to two-layer GNRs having similar width (10 to 50 nm), strikingly similar to the dimensions of high-quality graphene prepared by chemical methods. The mechanism of cutting SWCNTs along the longitudinal direction could arise because of the atomic H reaction of C-C bonds at sidewall defect sites¹. Consequently, highly aligned, narrow GNRs are synthesized from VA-SWCNTs using this chemical approach.

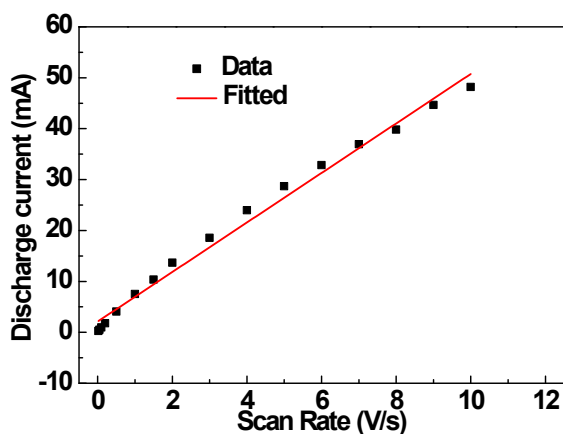


Figure S7. Discharge current densities as a function of scan rate.

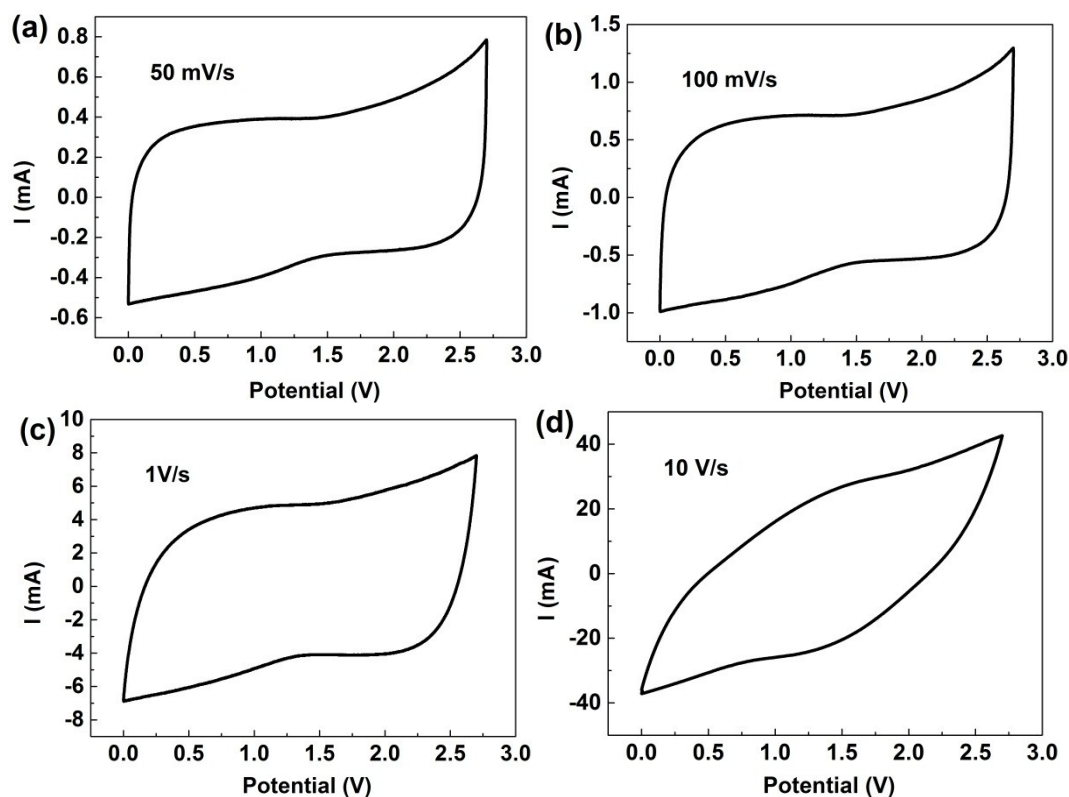


Figure S8. Measurements of supercapacitor performance, CVs obtained at scan rates of (a) 50 mV, (b) 100 mV, (c) 1 V and (d) 10 V s⁻¹.

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