Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Growth of carbon hybrid materials by grafting on pre-grown vertically aligned single-walled carbon nanotube arrays and their use in high power supercapacitors

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1. Experimental Procedure

Synthesis of VA-SWCNTs Carpet and OLCs-GNRs composite VA-SWCNTs arrays were grown in a standard water-assisted chemical vapor deposition process described in detail elsewhere[1, 2]. The VA-SWCNTs were grown using 0.8 nm thick Fe films deposited on 10 nm Al_2O_3 supports, all of which was deposited on clean Si wafers with a native oxide. A 15-min-growth process enabled a vertical VA-SWCNT carpet with a height of 80-120 μm. After that, 3 nm Si was deposited on top of VA-SWCNTs with an e-beam evaporator. The vertical VA-SWCNTs carpet samples loaded into the CVD furnace chamber below the hot filament about 3-6 mm. Atomic hydrogen treatment was carried out using a mixture of H_2 (140 sccm), H_2O (15 sccm) and CH_4 (0.75 sccm) at 25 Torr and 850 °C for 2-6 h. And the hot filament power was keep at 65 W. We refer the OLCs and VA-GNRs composite materials provided with atomic hydrogen treatment as “OLCs-GNRs” and the pristine vertically aligned carbon nanotube arrays as “VA-SWCNTs”.

Structural characterization Micro-Raman spectroscopy was performed on a Raman scope 1000 Raman spectrometer (Renishaw, UK) equipped with a charged coupled device detector and an optical microscope for focusing the incident laser beam to a 1-2 μm spot size. An Ar ion laser excitation (514.5 nm) was employed. XPS was conducted on a PHI Quantera SXM scanning X-ray microscope. An Al anode at 25 W was used as an X-ray source with a pass-energy of 26.00 eV, 45 ° take-off angle, and a 100 μm beam size. The structure of the OLCs was investigated using high-resolution transmission electron microscopy (HR-TEM). The TEM samples were prepared by a 15 min sonication of the VA-SWCNTs and OLCs-GNRs in isopropanol and deposition on the lacey-carbon coated copper grid (300-mesh). A field-emission TEM (JEOL 2010F) with an imaging filter

(Gatan GIF) was used at 200 kV. Scanning electron microscopy (SEM) was performed using a Philips XL-30 environmental field-emission electron microscope. Accelerating voltage of 10 kV and a working distance of ~ 12 mm was generally employed for SEM analyses. Thermo-gravimetric analysis (TGA) used for determining the carbon content in product was performed on a Q-600 Simultaneous TGA/DSC from TA Instruments by heating the sample to 850 °C under air with a heating rate of 5 °C min^{-1}. The AFM samples were prepared by first tip sonication for 0.5 h and then bath sonication for 1 h the sample dissolved in chloroform to form a suspension, and then centrifuged at 10,000 rpm for 0.5 h, followed by picking up the top solution and spin-coating on top of a mica wafer. AFM images were obtained on a Digital Instrument Nanoscope IIIA atomic force microscope. The Brunauer-Emmett-Teller (BET) experiment was done using a Quanta chrome Autosorb-3B Surface analyzer. The sample was dried at 120 °C under vacuum for 16 h before the experiment.

Electrochemical characterization The OLCs-GNRs composite was press down in on direction and then rolled with a metal roll to make it to film. Then the OLCs-GNRs film was detached from the substrate with buffer oxide etch solution (buffered HF, known as a wet etchant to remove the Si wafer)[3]. The samples were fully dried before assembling them into supercapacitor device. The OLCs-GNRs composite film capacitor was fabricated by sandwiching polypropylene foil (Celgard, USA) as a separator between two the OLCs-GNRs composite film sheet electrodes. In one experiment, 250-500 μg of the OLCs-GNRs composite material was used as active material, as weighed by a microbalance (Citizen scale, model: CM 21x, weighing accuracy 1 μg). For the control experiment, 300 μg of pristine VA-SWCNT carpet was used. The two electrodes were then compacted and sealed with two stainless steel plates (CR2032, MTI Corporation, USA), in an argon-filled glove box (VAC NEXUS, USA) with both moisture and oxygen content < 1.5 ppm, without using other current collectors. 1 M Tetraethyl Ammonium Tetrafluoroborate ($TEABF_4$, 99.0%, Sigma-Aldrich) in acetonitrile (AN, 99.8%, Sigma-Aldrich) was used as the electrolyte. After assembling, the cells were aged for 12 h before electrochemical measurements. The cyclic voltammograms (CVs), constant current discharge/charge testing and electrochemical impedance spectroscopy (EIS) measurements were carried out with an electrochemical analyzer (CHI 608D, CH Instruments, USA). In electrochemical impedance spectrum (EIS), the intercept of the semicircle at high frequency on the real impedance axis (Z') represents a combined resistance ($\boldsymbol{R_s}$). While, the diameter of the semicircle corresponds to the charge transfer resistance ($\boldsymbol{R_{ct}}$) caused by Faradaic reactions and EDCL ($\boldsymbol{C_{dl}}$) at the electrode/electrolyte interface. The specific capacitance $\boldsymbol{C_s}$, referred to as capacitance in our paper, was calculated from galvanostatic cycling using the following equation:

$$Cs = \frac{4}{m(\frac{dV}{dt})} \tag{1}$$

Where $\boldsymbol{I}$ is the discharge current, $\boldsymbol{V}$ is the voltage, $\boldsymbol{t}$ is the discharge time, $\boldsymbol{m}$ is the mass of the carbon electrode, and $\boldsymbol{dV/dt}$ is the slope of the discharge curve. Cyclic voltammetry was carried out at various scan rates and the capacitance was derived using the following equation:

$$Cs = \frac{\int I(V)dV}{mv\Delta U} \tag{2}$$

Where, $\boldsymbol{\Delta U}$ is the width of the voltage window, and $\boldsymbol{v}$ is the scan rate. An increase of the capacitor voltage (***U***) causes a significant enhancement of the power (***P***) and energy (***E***) according to equation (3) and (4):

$$E = \frac{1}{2} \times \frac{1000}{3600} CU^2 \tag{3}$$

$$P = \frac{U^2}{4R_s} \tag{4}$$

Where, $\boldsymbol{R_S}$ stands for the equivalent series resistance. To achieve a supercapacitor with high performance, a high cell voltage and low $\boldsymbol{R_S}$ are required.

2. Supplementary Figures

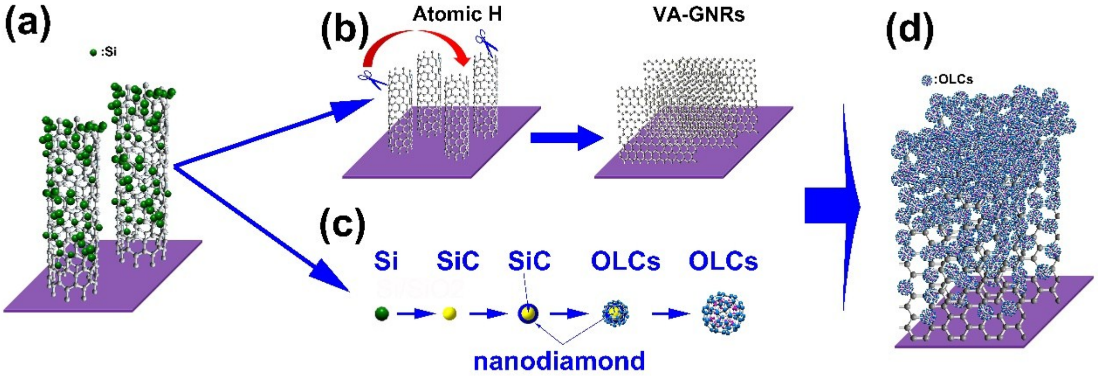

Fig. S1. Scheme illustration of the formation of composite material of OLCs-GNRs with atomic hydrogen treatment.

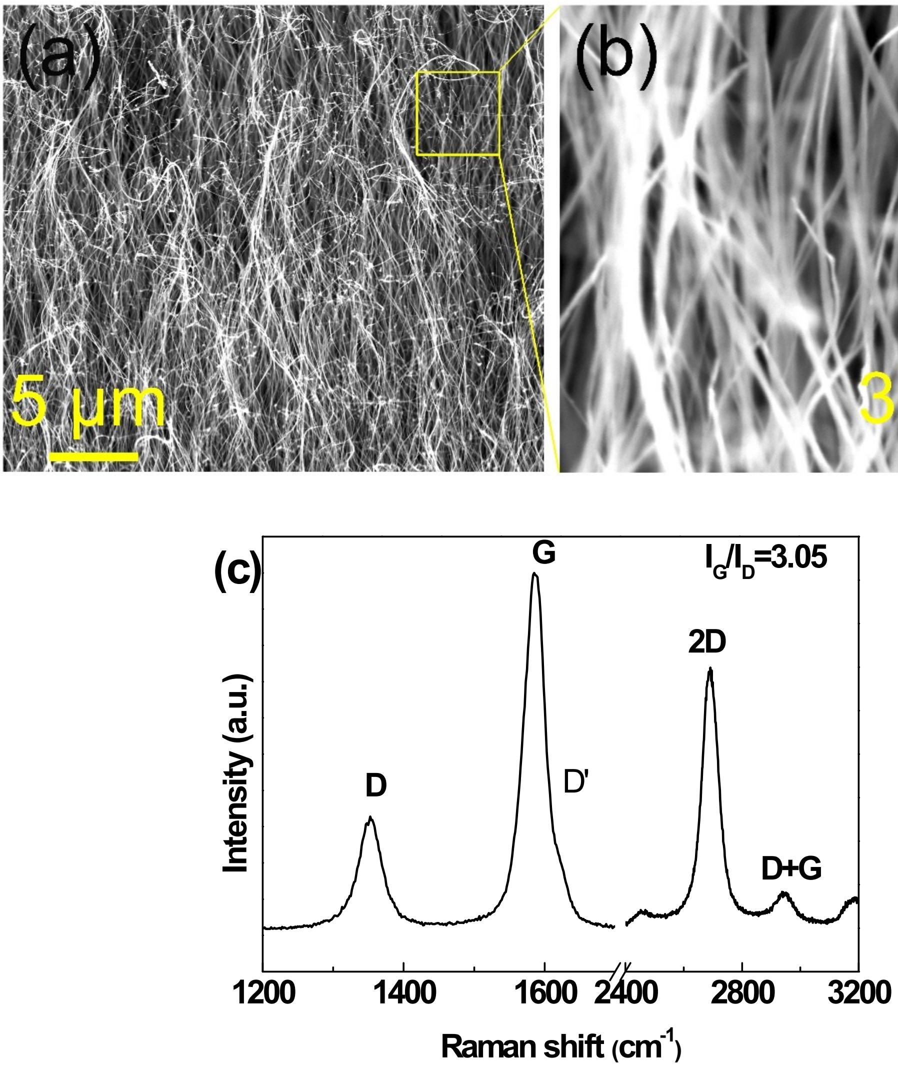

Fig. S2. (a-b) SEM and (c) Raman spectrum of the VA-SWCNTs with atomic hydrogen treated for 2 h with some carbon onion coated on the surface of the carpets.

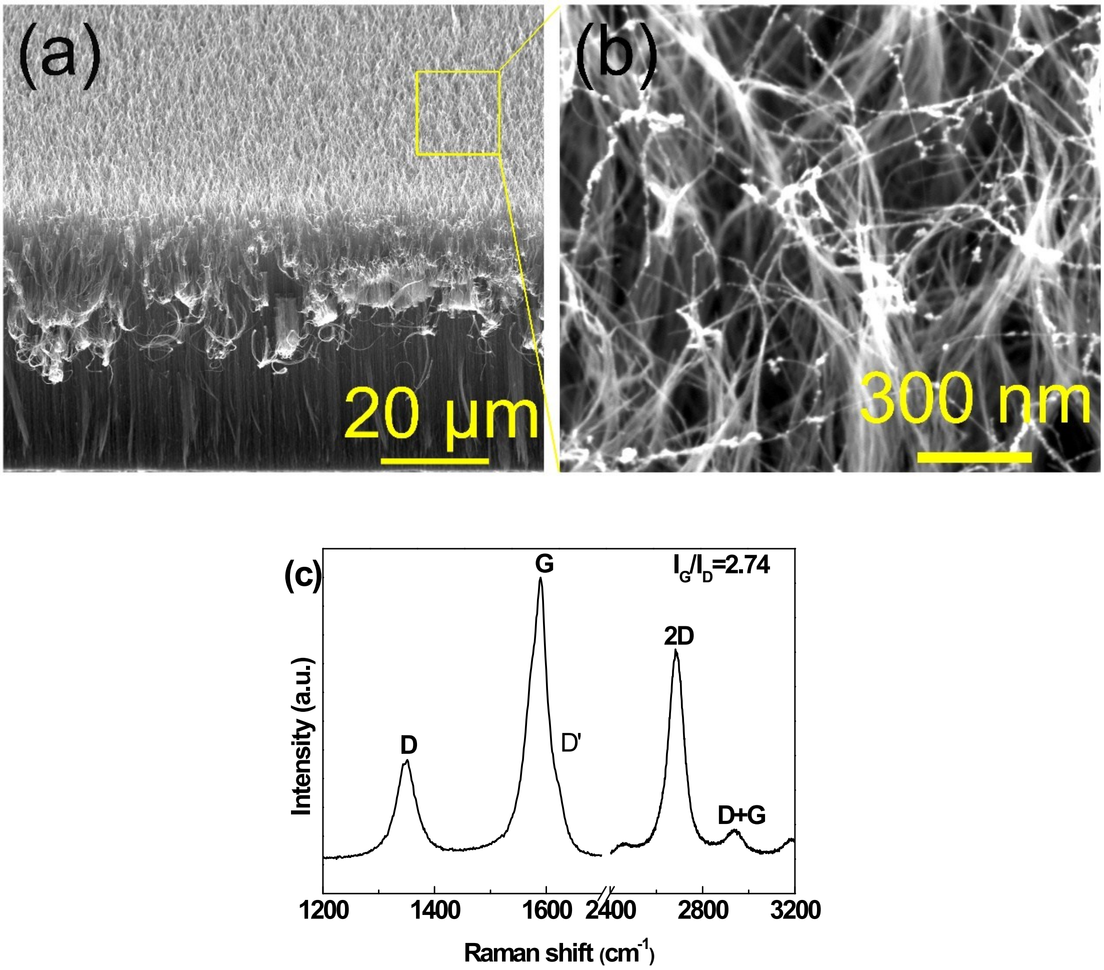

Fig. S3. (a-b) SEM and (c) Raman spectrum of the VA-SWCNTs with atomic hydrogen treated for 4 h with some carbon onion coated on the surface of the carpets.

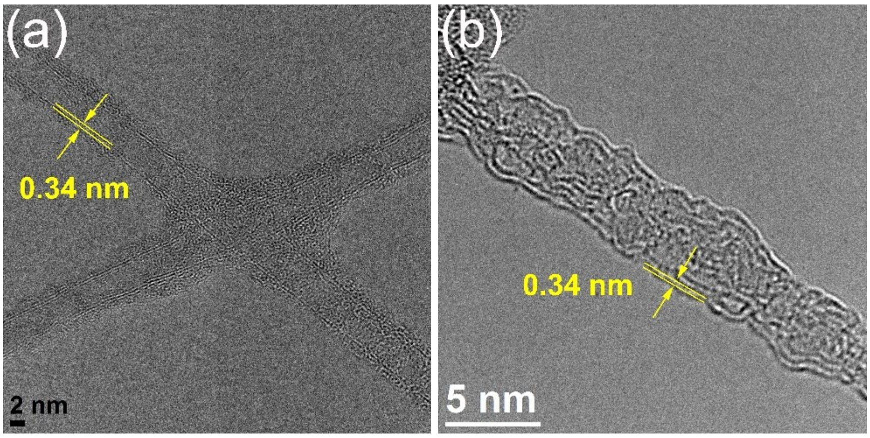

Fig. S4. TEM image of the VA-SWCNTs with atomic hydrogen treatment at temperature of 850 °C for 6 h.

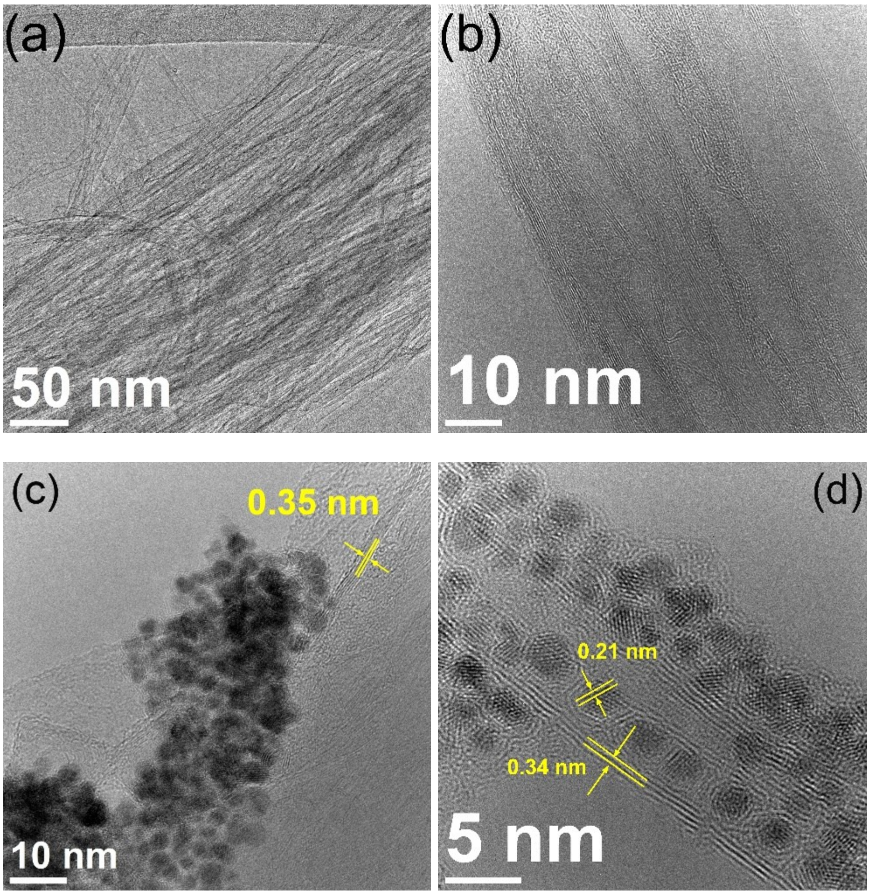

Fig. S5. TEM image of the VA-SWCNTs with atomic hydrogen treatment at temperature of 850 °C for 2 h, (a-b) VA-SWCNTs have been unzipped and form a thin bundle, (c-d) a chain of SiC and nanodiamond cluster adhere to the unzipped VA-SWCNTs bundle.

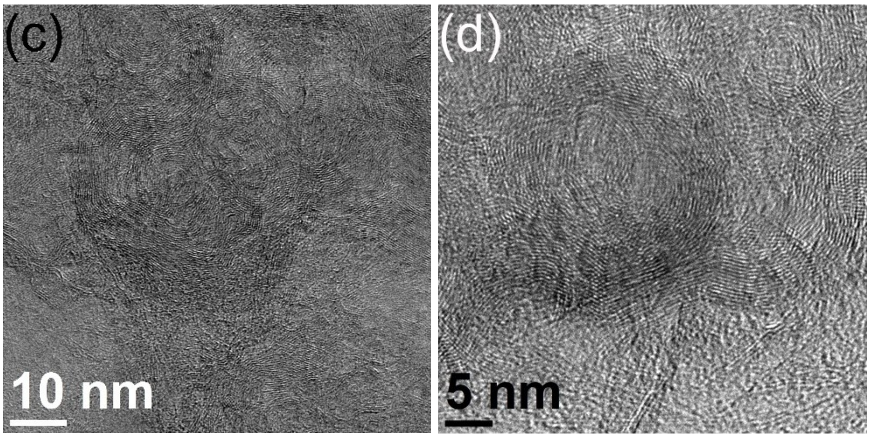

Fig. S6. (a-b) TEM images shown that nanodiamond have been converted to carbon onion with atomic hydrogen treatment at temperature of 850 °C for 4 h, the OLCs shown concentric and spherical in shape without core.

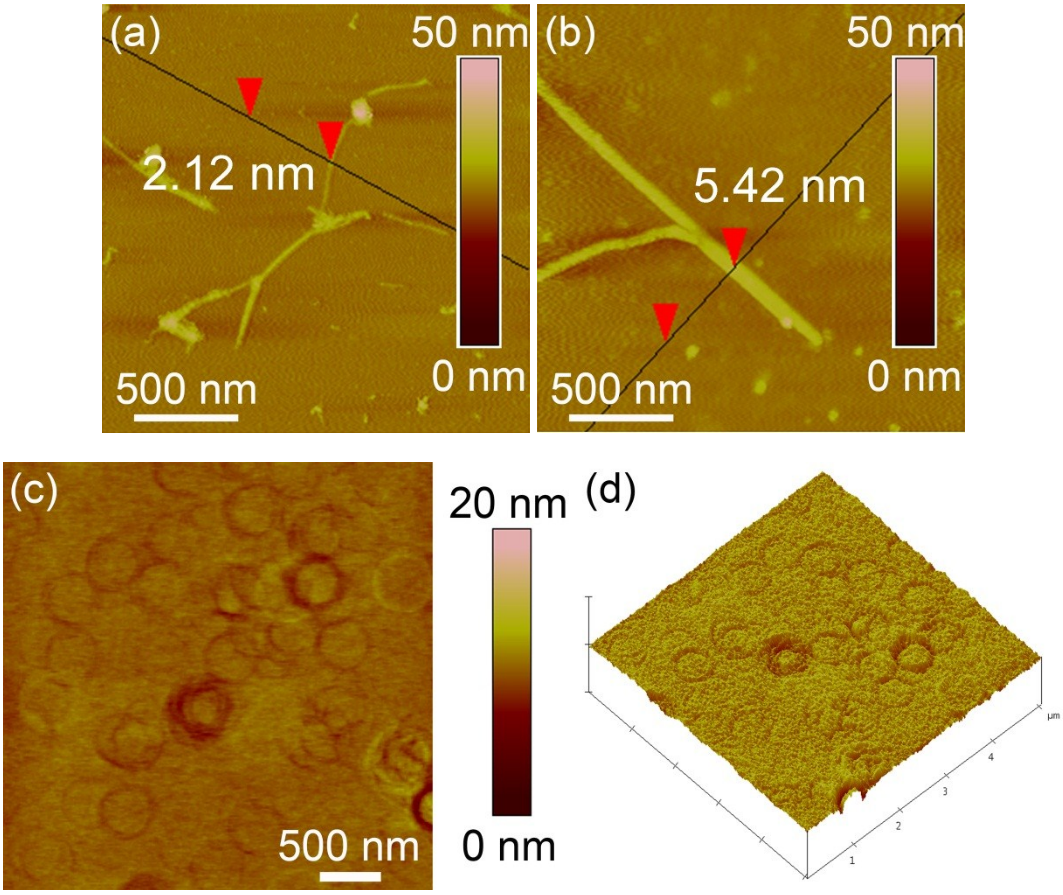

Fig. S7. AFM characterization of individual nanostructure from the (a) VA-SWCNTs and (b) OLCs-GNRs hybrid. The different heights measured from two different sections in (b) suggest the stacking of two superimposed split ribbon stacks. (c) AFM and (d) the three-dimensional images of OLCs structures.

Atomic force microscopy (AFM) was also performed to characterize the structural changes with atomic hydrogen treatment. The AFM samples were prepared by first bath sonication the sample to form a suspension, followed by spin-coating on top of a mica wafer (see the experimental section). **Fig. S7a** exhibits that the pristine CNTs have a height of ~2.1 nm. It is difficult to find SWCNTs in OLC-CNTs hybrids, and only a few large diameter nanotubes or nanotube bundles can be observed

(**Fig. S7b**). This is attributed to: 1) dense atomic hydrogen and high reaction temperatures can etch even completely remove small diameter SWCNTs likely via gasification of nanotubes to hydrocarbon molecules (hydrocarbonation)^4; 2) with atomic hydrogen treatment, most carbon nanotubes have been unzipped and transformed into a carbon bundle, which presents a rod shape with a large diameter. The carbon nanostructures depicted in **Fig. S7c** and **d** are either carbon onions, carbon capsule nano-onions without cores or holes at the center of a nanoparticle's top surface. The OLCs are collapsed and form round circles in the AFM image. The edges of the OLCs are smooth and the height of walls are 10-20 nm, which is consistent with the diameter of intact OLCs measured by TEM.

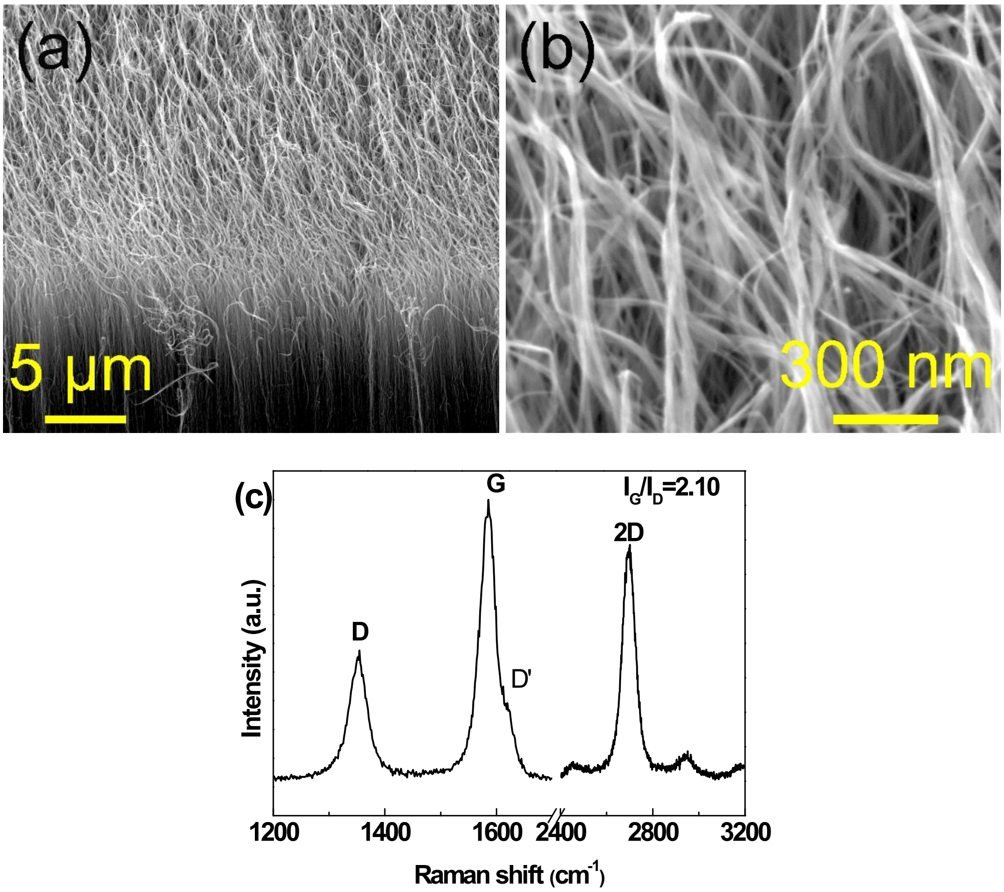

Fig. S8. (a-b) SEM and (c) Raman spectrum of the VA-GNRs with atomic hydrogen treated for 6 h.

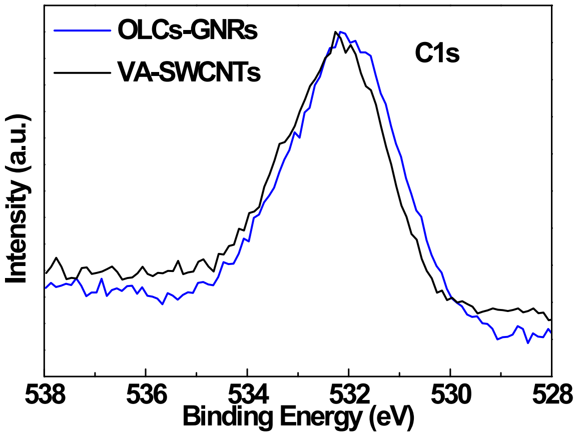

Fig. S9. High-resolution O 1s XPS spectra of pristine VA-SWCNTs and OLCs-GNRs.

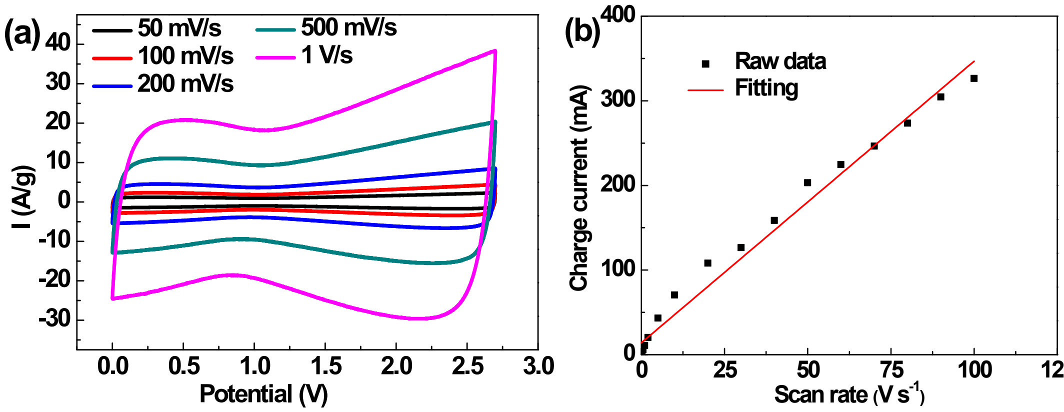

Fig. S10. (a) Electrochemical characterizations of the microdevices using 1 M Tetraethyl Ammonium Tetrafluoroborate (TEABF$_4$) as the electrolyte. CVs obtained at various scan rates of 0.05, 0.1, 0.2, 0.5 and 1 V s^{-1}. (b) Discharge current densities of OLCs-GNRs electrode as a function of scan rate.

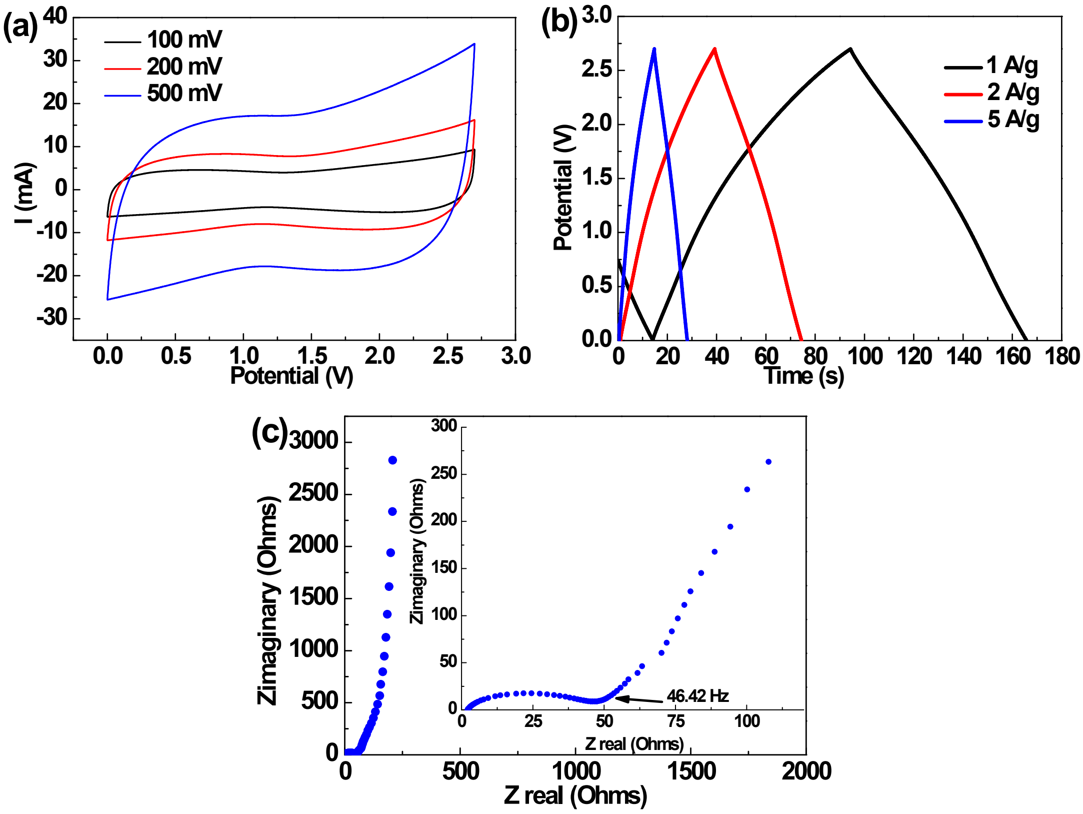

Fig. S11. Supercapacitor performance of OLC-GNRs electrode with the weight of ~ 1.0 mg: (a) CV curves under different scan rates, (b) Galvanostatic charge/discharge curves under different current density, and (C) Nyquist plot. The specific capacitance is 99.5 F/g with a scan rate of 100 mV/s and the equivalent series resistance is 2.2 Ω. The energy density and power density were estimated as 53.4 Wh/kg and 2.7 kW/kg, when normalized with the total weight of the two as OLC-GNRs electrodes.

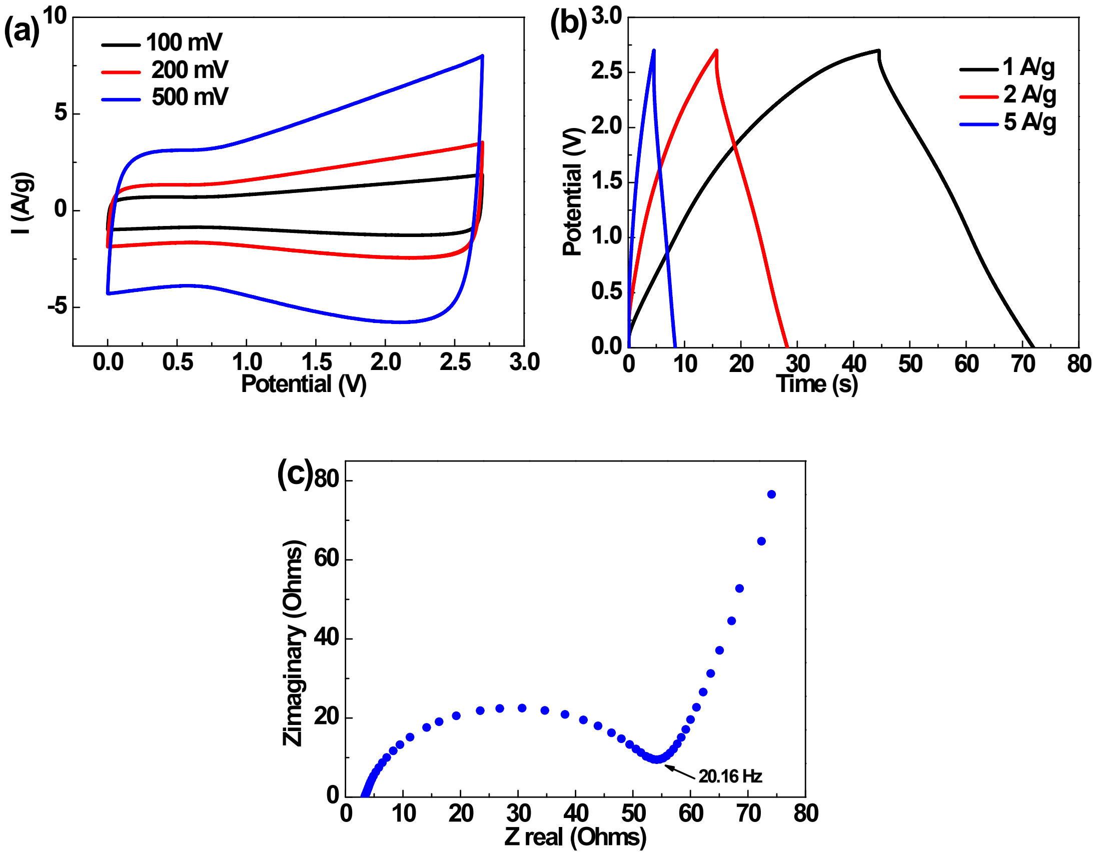

Fig. S12. Supercapacitor performance of VA-GNRs electrode: (a) CV curves under different scan rates, (b) Galvanostatic charge/discharge curves under different current density, and (c) Nyquist plot. The specific capacitance is 21.2 F/g at a current density of 100 mV/s and an equivalent series resistance is 2.2 Ω. The energy density and power density were estimated as 19.5 Wh/kg and 2.7 kW/kg, when normalized with the total weight of the two as VA-GNRs electrodes.

Table S1. Surface area and specific capacitance of VA-SWCNTs, VA-GNRs and OLCs-GNRs.

Film type	SSA m^2/g	Specific capacitance F/g	$\boldsymbol{R_{ct}}$ Ω	$\boldsymbol{R_s}$ Ω
VA-SWCNTs	105	8.3	309.6	5.6
VA-GNRs	278	21.2	50.8	3.4
OLCs-GNRs	752	104.6	15	1.0

Reference

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