Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Electronic Supplementary Information

Graphene Oxide-assisted Deposition of Carbon Nanotubes on Carbon Cloth as Advanced Binder-free Electrodes for Flexible Supercapacitors

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1. *Experimental details*

Synthesis of graphene oxide. Graphene oxide was synthesized by following the classical modified Hummer's method using nature graphite powder as the precursor. Briefly, 0.9 g of graphite powder was added into a mixture of 7.2 mL of 98% H_2SO_4, 1.5 g $K_2S_2O_8$, and 1.5 g of P_2O_5. The solution was kept at 80 ℃ for 4.5 hours, followed by thorough washing with water. Thereafter, the as-treated graphite was put into a 250 mL beaker, to which 0.5 g of $NaNO_3$ and 23 mL of H_2SO_4 (98%) were then added while keeping the beaker in the ice bath. Subsequently, 3g of $KMnO_4$ was added slowly. After 5 min, the ice bath was removed and the solution was heated up to and kept at 35 ℃ under vigorous stirring for 2 h, followed by the slow addition of 46 mL of water. Finally, 40 mL of water and 5 mL H_2O_2 was added, followed by water washing and filtration. The exfoliation of graphene oxide was then performed by ultrasonication.

Preparation of G/CC. The graphene oxide was first dispersed in water with a concentration of 1 mg/mL. Two pieces of carbon cloth were used as the positive electrode and the negative electrode, respectively. The electrodes were vertically oriented and separated by 1 cm in a beaker containing the GO solution. A voltage of 6 V was applied for 10 hours. After drying at room temperature, the sample was subject to H_2 thermal reduction at 300 ^oC for 2 hours.

Preparation of G-CNT/CC. For the electrophoretic deposition of GO-CNT, a mixture suspension of graphene oxide and CNT (1:1, mass ratio) was first dispersed in water by ultrasonication with a concentration of 1 mg mL^{-1}. Two pieces of carbon cloth were used as the positive electrode and the negative electrode, respectively. The electrodes were vertically oriented and separated by 1 cm in a beaker containing the GO-CNT solution. A voltage of 6 V was applied for 10 hours. After drying at room temperature, the sample was subject to H_2 thermal reduction at 300 ^oC for 2 hours. The weight

percentage of G-CNT in G-CNT/CC was estimated to be around 17.2 wt% by measuring the weight difference before and after the EPD process

Assembling supercapacitor devices with the flexible electrode prepared by the EPD method. A supercapacitor device is composed of two pieces of G-CNT/CC or G/CC electrodes, a separator membrane and 1.0 M H_2SO_4 aqueous solution as electrolyte. The weight of active materials was obtained by measuring the weight different of carbon cloth before and after the EPD process.

Assembling supercapacitor devices by the traditional paste/press technique.

To construct p-G-CNT/CC based supercapacitor devices, G-CNT composites used for the electrode was prepared by mixing reduced graphene oxide-CNTs (90 wt%) with 10 wt% PVDF binder, then loaded on the carbon cloth and pressed and further dried. The two electrodes were separated by a filter paper soaked with electrolyte to get an assembled supercapacitor device.

Electrochemical measurements. Cyclic voltammetry, galvanostatic charge/discharge, and electrochemical impedance spectroscopy tests of assembled two-electrode supercapacitors were carried out using an Autolab potentiostat/galvanostat. CV measurements were conducted in the applied voltage window of 0-0.8 V. Galvanostatic charge/discharge tests were operated under a constant charge/discharge current density within an applied voltage window range from 0 to 0.8 V. The capacitance retention tests were carried out at a constant current density of 2 A g^{-1} from 0 to 0.8 V for 2000 charge/discharge cycles. In EIS tests, the frequency range was within 0.01 Hz and 100,000 Hz with 5 mV amplitude, and the applied dc bias potential was 0V.

The specific capacitance was calculated from the galvanostatic charge/discharge curves using the following equations:

$$C_{\mathrm{sp}} = \frac{4I}{M\mathrm{d}V/\mathrm{d}t}$$

Where I is the applied current, M is the mass of active materials on both electrodes, dV/dt is the discharging slope after the IR drop. The specific energy density and power density in the Ragone plot were calculated by using the equations E=0.5$C_{sp}\Delta V^{2}$ and P=E/Δt, respectively, where ΔV is the discharge voltage after the IR drop, Δt is the discharge time. The maximum power density could be calculated using the equation P_{max}=V^2/4RM, where V is the voltage after IR drop, R is the ESR, and M is the total mass of the electrode materials.

2. *Supplementary Results*

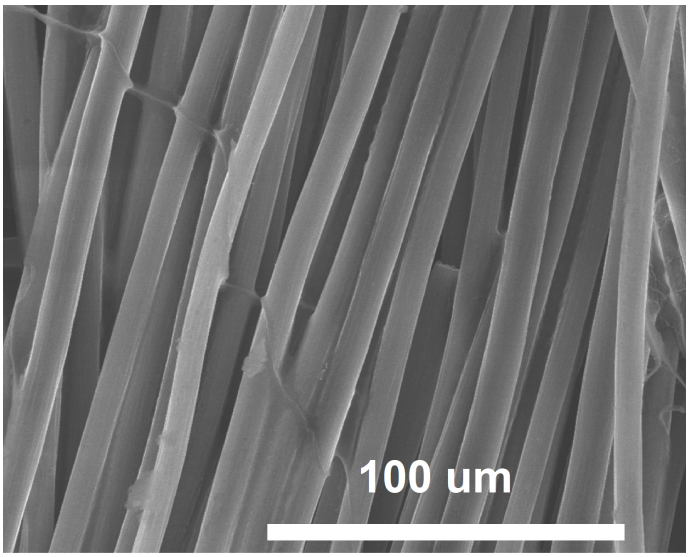

Figure S1. SEM image of pristine carbon cloth showing relatively smooth surface of carbon fibers.

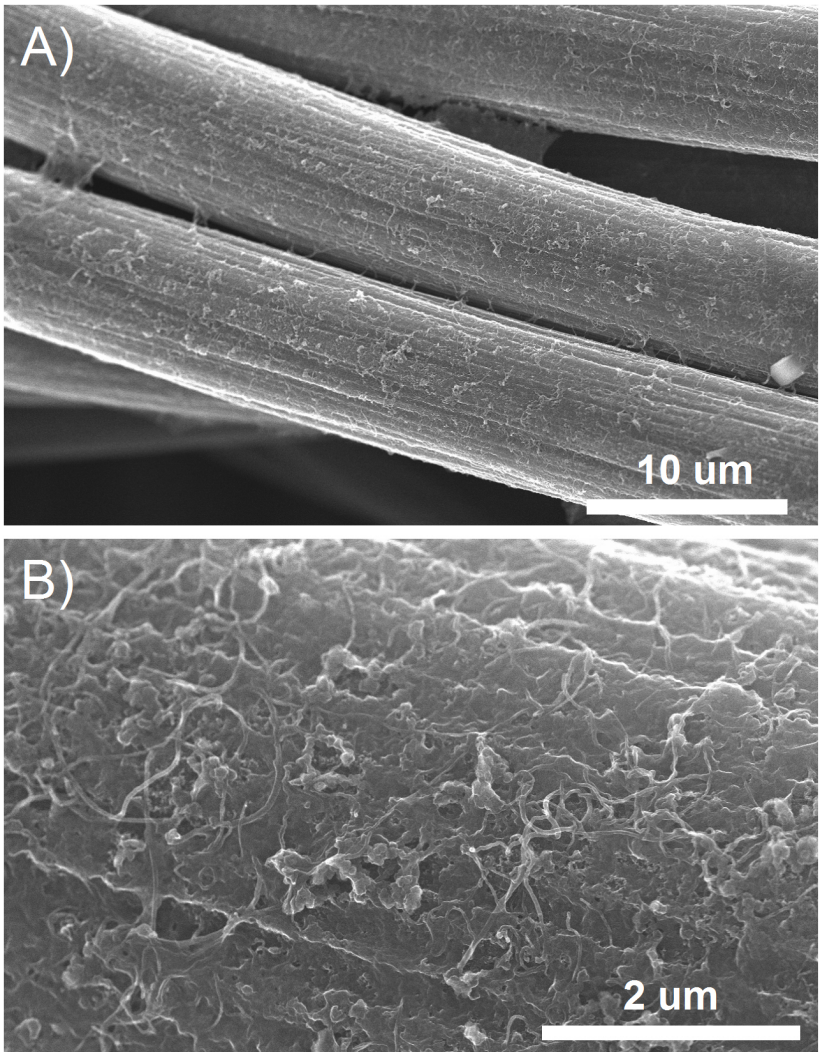

Figure S2. SEM images of G-CNT/CC prepared from GO-CNT suspension with 1:2 mass ratio.

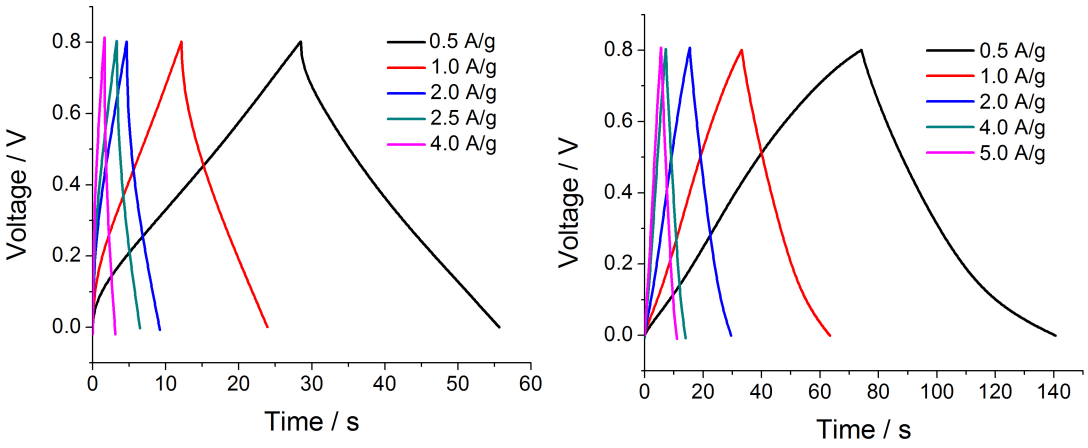

Figure S3. Charge/discharge curves of G/CC (left) and G-CNT/CC (right) at different discharge current densities.

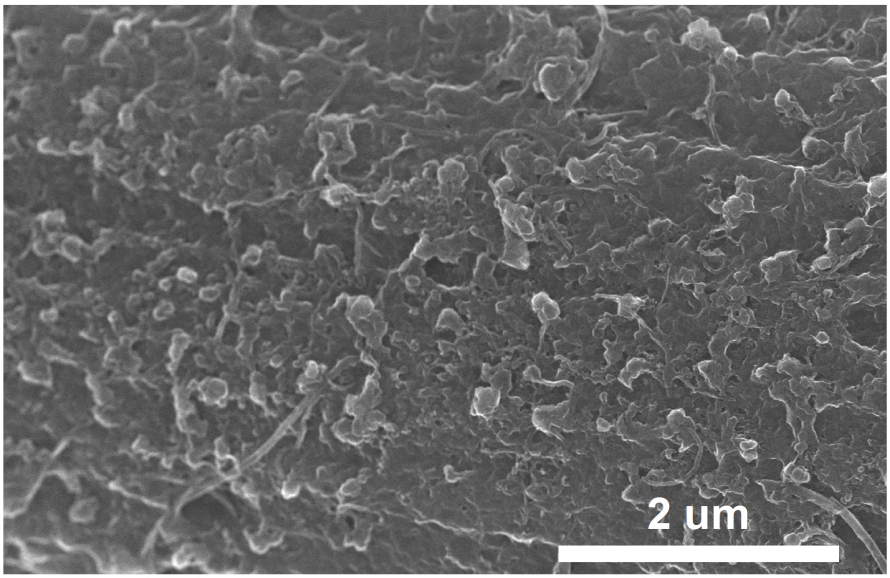

Figure S4. SEM image of G-CNT/CC after durability testing.

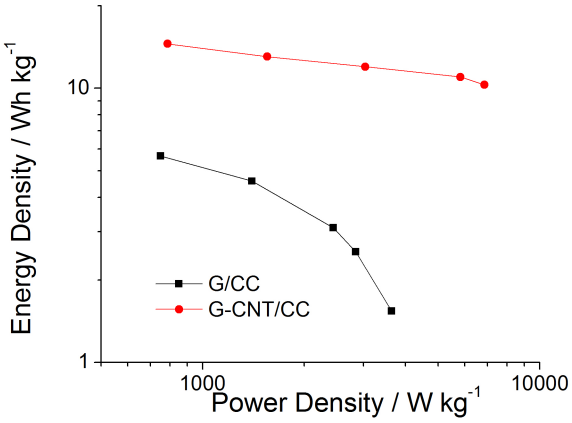

Figure S5. Ragone plot of G/CC and G-CNT/CC based flexible supercapacitor devices.

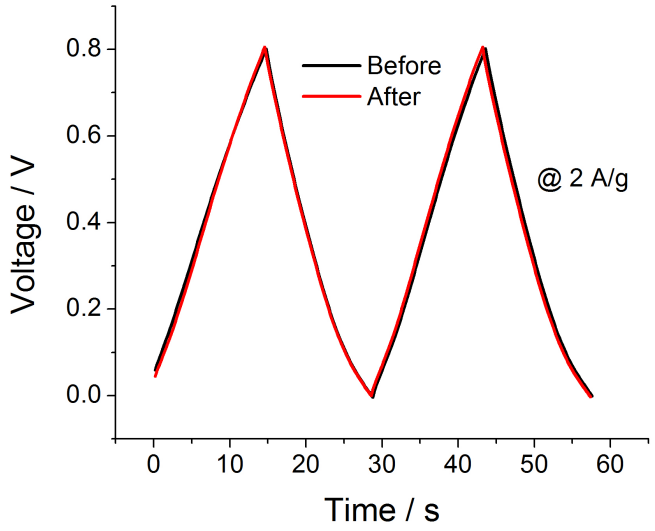

Figure S6. Charge/discharge curves of G-CNT/CC supercapacitors before and after bending.

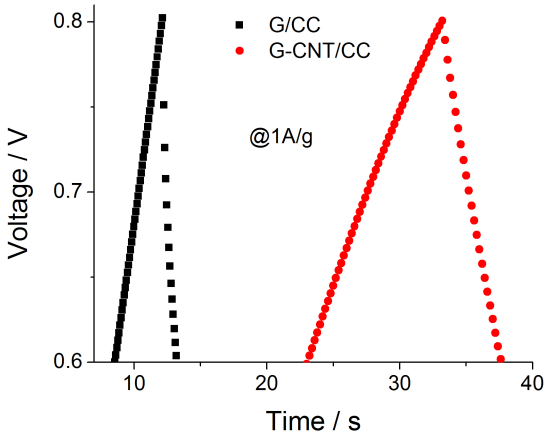

Figure S7. Zoomed IR drop from Figure 3D

Table S1. Specific capacitance comparison with literature papers.

Sample	Specific Capacitance (F/g)	Electrolyte	Device Configuration	Reference
G-CNT/CC	151 (1 A/g)	H_2SO_4	Full Cell	This work
Graphene-Activated Carbon	122 (0.1 A/g)	KOH	Full Cell	S1
Graphene-SWCNT	145.2 (0.5 A/g)	KCl	Half-cell	S2
MWCNT@mesoC	60.2 (5 mV/s)	KOH	Half-cell	S3
Sponge Graphene	125 (0.1 A/g)	H_2SO_4	Half-cell	S4
3D Mesoporous Graphene	168 (2 A/g)	H_2SO_4	Half-cell	S5
Microwave Expanded Graphene	160 (0.2 A/g)	KOH	Half-cell	S6
Crumped Graphene	85 (200 mV/s)	KOH	Half-cell	S7
Carbon Nanocage	170 (200 mV/s)	H_2SO_4	Half-cell	S8
Nitrogen doped thermal carbon	155 (1 A/g)	KOH	Half-cell	S9
Graphene-CNTself-assembled film	120 (200 mV/s)	H_2SO_4	Half-cell	S10

Supporting Reference

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