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

Cellulose nanofibers/graphene flexible supercapacitors

Preparation of cellulose nanofibers dispersion

Cellulose fibers (2 g) was suspended in water (400 ml) containing TEMPO (0.033 g) and sodium bromide (0.33 g). The oxidation reaction was started by adding the desired amount of the NaClO solution (15 mmol/g celluose). The pH of the reaction solution was maintained to be 10.00 at 25 ^{0}C by adding 0.5 M NaOH for 6 h. The oxidized cellulose was thoroughly washed with water by filtration. 2 mg/ml oxidized cellulose/water slurries were sonicated for 15 min at power of 300 W in an ice bath. Cellulose nanofibers dispersion was centrifuged at 10000 g for 10 min to remove the unfibrilated cellulose. The transparent cellulose nanofibers dispersion was stored at 4 ^{0}C before used.

Preparation of graphene oxide dispersion

Graphite powder (6 g) was added into 100 ml beaker containing concentrated H2SO4 (25 ml), $K_2S_2O_8$ (5 g), P_2O_5 (5 g) with continuous stirring at 80 ^{0}C. The resulting mixture was kept at 80 0C for 4.5 h in oil bath, then DI water (~1 L) was added to the resulting mixture and left overnight. Pretreated graphite was thoroughly washed with water by filtration to remove all soluble substances and then dried in the oven at 60 ^{0}C. Pretreated graphite was added into 1000 ml beaker containing concentrated H_2SO_4 (230 ml) in ice bath. $KMnO_4$ (30 g) was added slowly to dissolve completely. The resulting mixture was allowed to react at 35 0C for hours, and then 460 ml DI water was slowly added. In the process of adding water, the temperature of the mixture was remained constant. Another 1.4 L DI water was added to the mixed solution with continuous stirring at room temperature for 2 h. afterward, 25 ml of 30% H_2O_2 was added to the mixture with continuous stirring at room temperature. The color of the mixed solution becomes golden yellow. The resulting mixture was stand for about 12 h and then the supernatant was decanted. The graphite oxide was thoroughly washed with 5% HCl solution and then DI water to remove all soluble substances. 8 mg·ml^{-1} graphite oxide was sonicated for 30 min using an ultrasonic generator at an output

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power of 600 W. The graphene oxide solution was centrifuged at 10000 g for 5 min to remove the unexfoliated graphite oxide. The inorganic ions in graphene oxide suspension were removed by dialysis.

Preparation of cellulose nanofibers/graphene nanohybrid aerogels

A variety of graphene oxide dispersions (13 mg/ml) were added to a quantitative amount of cellulose nanofibers (1.5 mg/ml) aqueous solution under continuous magnetic stirring at room temperature to yield a homogeneous dispersion (pH8.5). Then homogeneous dispersion (pH 8.5) was mixed with 0.19 g VC-Na. The mixture was stired for about 3 minutes to mix them well. The resulting mixture was poured into mould, and then exposure to the hydrochloric acid vapor for 2 h to get well formed CNFs/RGO nanohybrid hydrogel.

CNFs/RGO nanohybrid hydrogel was thoroughly rinsed in distilled water to remove inorganic ions, the hydrolysis product of VC-Na. the resulting hydrogel was further turned into the alcogel by using alcohol to replace the water within the network of the hydrogel, and then dried with supercritical CO_2 to obtain CNFs/RGO aerogel.

Preparation of the flexible supercapacitors

6 g of H_2SO_4 was added into 60 ml of deionized water, and then 6 g of PVA was added with continuous stirring at 80 ^{0}C until the solution became clear. Two pieces of CNFs/RGO (20%) aerogel were compressed into aerogel sheets under a pressure of 0.1 MPa, then two pieces of aerogel sheet (the edge of one side glued to the aluminum foil with silver paste, about 10 mm×20 mm) were soaked in the H_2SO_4-polyvinyl (PVA) gel electrolyte for 15 min and picked out. after that, two electrode sheets were left in the fume hood at room temperature for about 4 h to vaporize the excess water, then the two electrode sheets were assembled into all-solid-state flexible supercapacitors under a pressure of 0.2 MPa.

Electrochemical characterization

The electrochemical performances of all-solid-state flexible supercapacitors were tested by cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS, on a CHI 660D, CH Instruments, Inc).

All the electrochemical characters of supercapacitors are calculated as follows,

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The gravimetric capacitance:

$$C_g=4(\int i\mathrm{d}V)/(v\times \mathrm{m}\times V) \qquad \text{or} \qquad C_g=4I\times\Delta t/(\Delta V\times m)$$

The area capacitance:

$$C_s=(\int i\mathrm{d}V)/(v\times S\times V)$$

The specific capacitance of supercapacitor devices:

$$C_{spe}= I\times\Delta t/(\Delta V\times m)$$

$$\mathrm{E}=(1/2)\ C_{spe}\times \mathrm{V}_{IR}^{2}$$

$$\mathrm{P}= \mathrm{V}_{IR}^{2}/(4m\times \mathrm{R}_{\mathrm{ESR}})$$

Where I is the applied current, Δt is the discharged time, ΔV is the discharged potential, m is the total mass of two symmetrical electrodes, VIR is voltage after IR drop, v is the voltage scan rate, V is the cell voltage, and S is the area of the supercapacitor.

Characterization of cellulose nanofiers

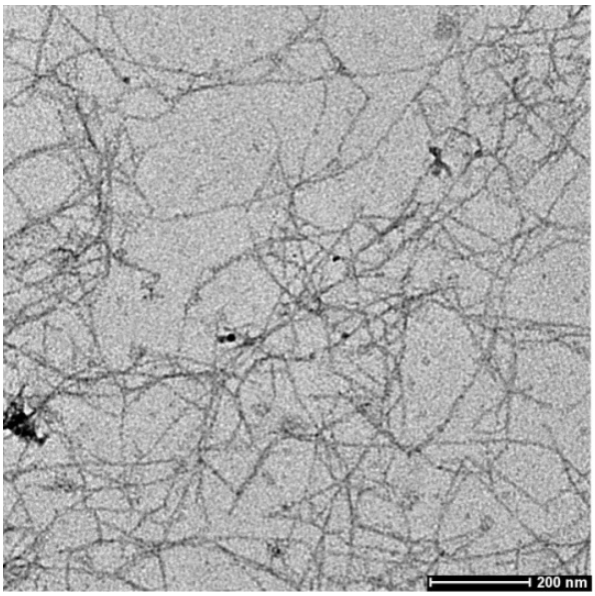

Fig.S1 TEM image of cellulose nanofiber samples

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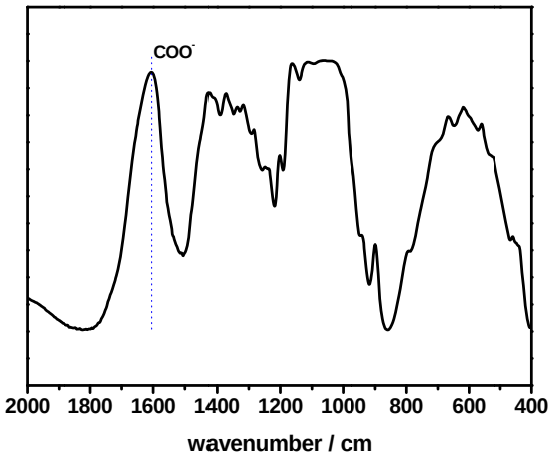

Fig.S2 FT-IR spectra of cellulose nanofiber samples

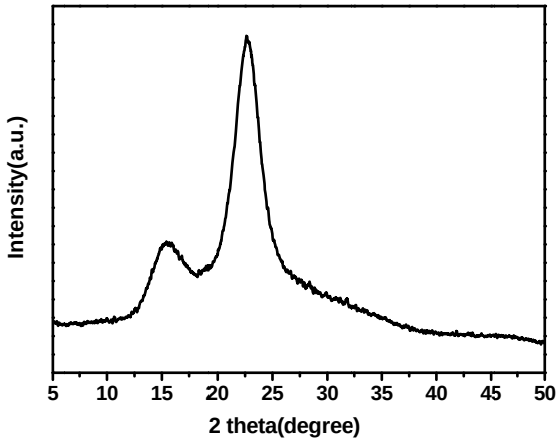

Fig.S3 XRD spectra of cellulose nanofiber samples

Characterization of GO

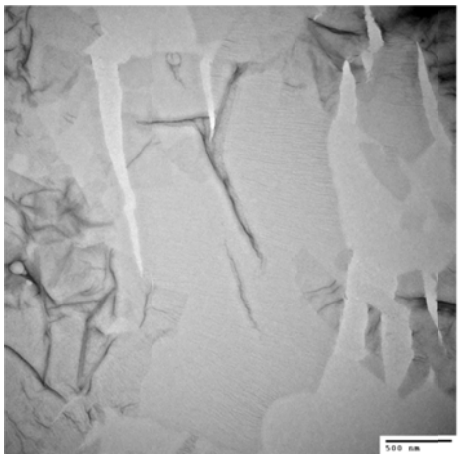

Fig.S4 TEM image of GO

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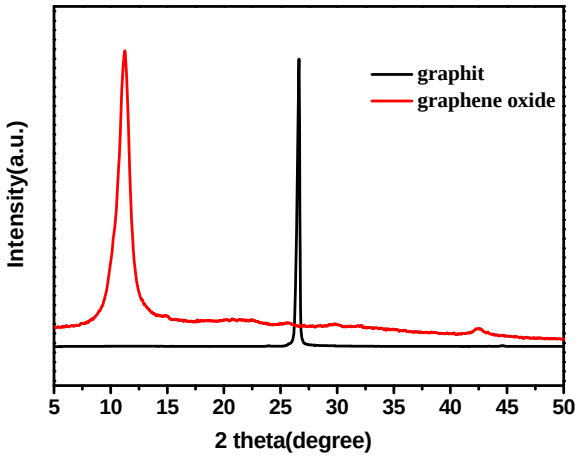

Fig.S5 XRD spectra of GO

Fig.S6 Demonstration of the flexibility of CNFs/RGO (20%) aerogel film

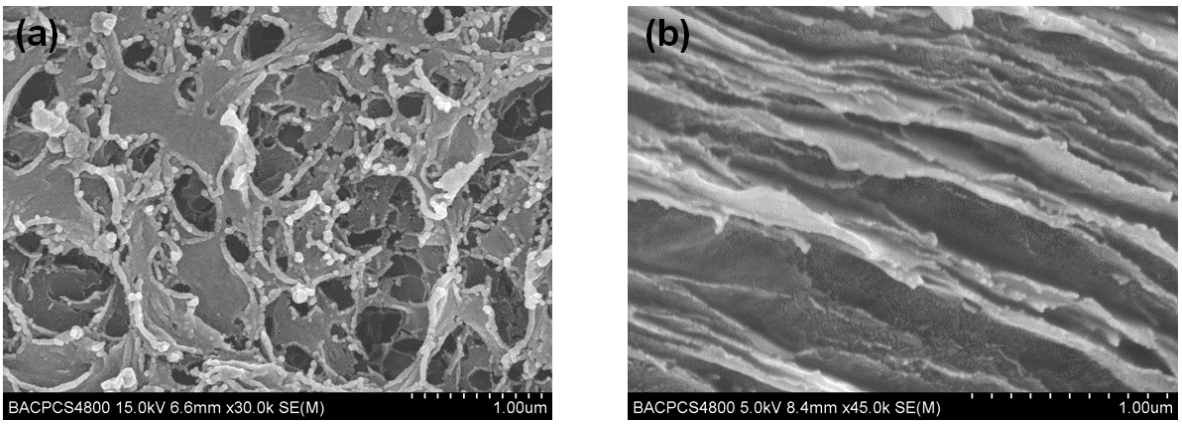

Fig.S7 (a) SEM image of RGO/CNFs (20%) hybrid aerogel film, (b) cross-section SEM image RGO/CNFs (20%) hybrid film

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Fig.S8 Photograph of A-SCs

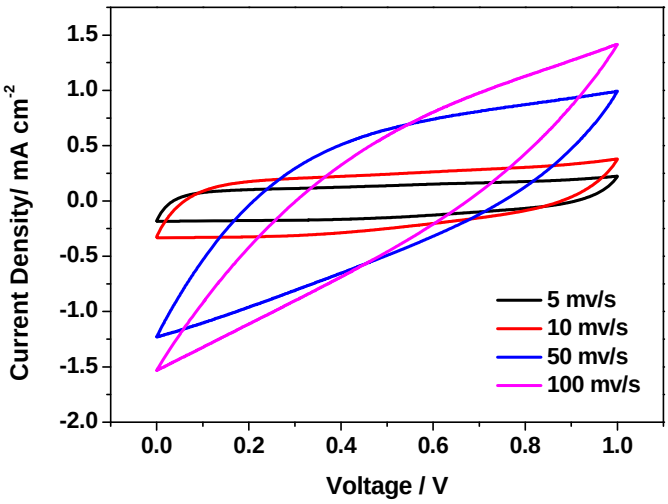

Fig.S9 CV curves for F-SCs

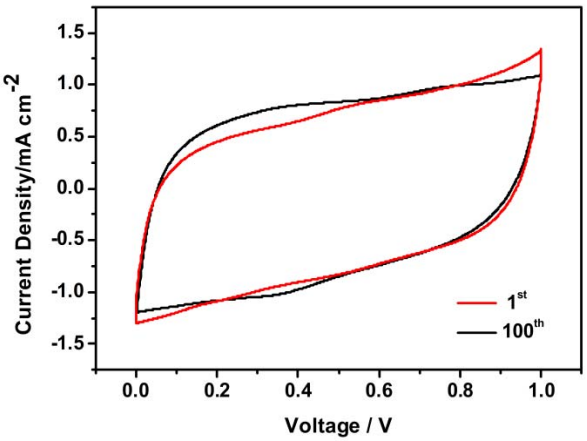

Fig.S10 CV curves measured before and after 100 bending cycles at 10 mV s^{-1}

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Table S1. The specific electrode capacitance of some flexible or thin-film supercapacitors

Materials	specific capacitance (F g^{-1})	Source
CNFS/RGO aerogel	207	Our work
RGO aerogel film	172	Adv. Mater, 2012 [S1]
RGO	215	Adv. Mater, 2011 [S2]
GO	189	Energy Environ. Sci, 2011 [S3]
CNPs/RGO	198	Energy Environ. Sci, 2011 [S4]
RGO/cellulose	120	Adv. Energy Mater, 2011 [S5]
RGO aerogel	128	J. Mater. Chem, 2011 [S6]

Table S2. The Capacitance per geometric area of some flexible or thin-film supercapacitors

Materials	Area capacitance (mF cm^{-2})	Source
CNFS/RGO aerogel	158	Our work
GCP	81	Adv. Energy Mater, 2011 [S5]
RMGO	0.39	Nano Lett, 2011 [S7]
Graphite	2.3	Energy Environ. Sci, 2011 [S3]
CNPs/MnO_2	109	ACS NANO, 2012 [S4]
BNC/CNT	18.8	ACS NANO, 2012 [S5]
SWCNT/cotton	34	Nano Res, 2010 [S6]
SWCNT/PET	26	Nano Res, 2010 [S7]
RGO	45.6	Adv.Mater, 2012 [S8]

S1 F. Liu, S. Song, D. Xue and H. Zhang, *Adv. Mater.* 2012, **24**, 1089-1094.

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S4 C. X. Guo and C. M. Li, Energy & Environmental Science, 2011, **4**, 4504-4507.

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