Electronic Supplementary Information

Wet-spinning of ternary synergistic coaxial fibers for high performance yarn supercapacitors

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Experimental Section

Materials: All agents were of analytical grade and used as received. Graphene oxide (GO) with average lateral size of 20 μm was bought from GaoxiTech Co. Ltd (http://www.gaoxitech.com/). Carboxyl-functionalized MWCNT was prepared by previous report.[1]

Preparation of ternary coaxial fibers by coaxial wet-spinning: Ternary coaxial fibers were prepared by coaxial wet-spinning technology. Certain amount of GO, CNTs and PEDOT:PSS (the mass ratio of GO and CNTs was set to be 1:1 and keep constant, the mass percentage of PEDOT:PSS relative to GO and CNTs is changed in different conditions) were premixed before concentrated, and transferred to an injection syringe connected with an inner core of spinneret. CMC aqueous (~14 mg mL^{-1}) was transferred to the outer layer of spinneret. The extruded velocities of inner and outer channels were set at 13 and 28 μL min^{-1}, respectively. The coagulation bath was ethanol/water (1:1 v/v) solution containing 2.5 wt% $CaCl_2$. After coagulation for 30 min, the ternary coaxial fibers were reduced in hydriodic acid ethanol/water (5:1 v/v) solution for 5 h at 95 ^oC, and washed by ethanol, drying in air. The control samples were made by a similar way.

Preparation of PVA gel polymer electrolyte: PVA (10 g, M_w 89,000-98,000) was dissolved in 90 mL water at 90 ^oC. Water (10 mL) and phosphoric acid (10 mL) were mixed and added to the above viscous PVA aqueous, after stirring for 1 h, the PVA gel polymer electrolyte was obtained.

Fabrication of free-standing all-solid fiber supercapacitors: Two coaxial fibers were twisted together to form a two-ply supercapacitor and coated with PVA gel polymer electrolyte (Fig. S6†) by dip-coating method. They were solidification at 40 ^oC for 1 h.

Characterization: SEM and EDS mapping were characterized by Hitachi S-4800. XRD was conducted on fiber debris without CMC sheath by Rigaku D/max-2500 employing CuK α radiation. Contact angle was measured on RGO, GP-35 and GCP-35 films by DCA20 (Dataphysics) and choosing water as the liquid drop. All electrochemical measurements were carried out on a 0.5 centimeter-long (unless the special stated) twisted FSCs (coated by PVA/H_3PO_4 polymer gel electrolyte), using electrochemical workstation (CHI 660E, CH Instruments, Inc.).

Calculations

(1) The area specific capacitance:

$$C_A = \frac{2 \times I \times t}{S \times \Delta U}$$

Where C_A (mF cm^{-2}) is the area specific capacitance, I (mA) and t (s) are the discharge current and discharge time, respectively. ΔU (V) stands for the potential window and S (cm^2) is the surface area of individual fiber electrode in the overlapping portion.

(2) The area specific energy density based on individual electrode:

$$E_{A-individual} = \frac{1}{2 \times 3600} \times C_A \Delta U^2$$

Where $E_{A\text{-individual}}$ (mWh cm^{-2}) is the area specific energy density based on individual electrode, C_A (mF cm^{-2}) is the area specific capacitance and ΔU (V) is the potential window.

(3) The area specific power density based on individual electrode:

$$P_{A-individual} = E_{A-individual} \times 3600 \times t^{-1}$$

Where $P_{A\text{-individual}}$ (mW cm^{-2}) and $E_{A\text{-individual}}$ (mWh cm^{-2}) are the area specific power and energy density based on individual electrode, t (s) is the discharge time.

(4) The area specific energy density based on entire FSC:

$$E_{A-entire} = \frac{1}{8 \times 3600} \times C_A \Delta U^2$$

Where $E_{A\text{-entire}}$ (mWh cm^{-2}) is the area specific energy density based on entire FSC, C_A (mF cm^{-2}) is the area specific capacitance and ΔU (V) is the potential window.

(5) The area specific power density based on entire FSC:

$$P_{A-entire} = E_{A-entire} \times 3600 \times t^{-1}$$

Where $P_{A\text{-entire}}$ (mW cm^{-2}) and $E_{A\text{-entire}}$ (mWh cm^{-2}) are the area specific power and energy density based on entire FSC, t (s) is the discharge time.

Table S1 Electrochemical performance of selected fiber supercapacitors

electrode	C_A	E_A (individual electrode)	P_A (individual electrode)	E_A (entire device)	P_A (entire device)	electrolyte
MWCNT/OMC[2]	39.7 mF cm^{-2}			1.77 μWh cm^{-2}	0.043 mW cm^{-2}	PVA-H_3PO_4
N-doped RGO/SWNT[3]	116 mF cm^{-2}	16.1 μWh cm^{-2}				PVA-H_3PO_4
MWCNT/carbon[4]	86.6 mF cm^{-2}	9.8-1.5 μWh cm^{-2}	189-8070 μW cm^{-2}			PVA-H_3PO_4
Hollow graphene/conducting polymer[5]	304.5 mF cm^{-2}	27.1 μWh cm^{-2}	66.5 μW cm^{-2}	6.8 μWh cm^{-2}	16.6 μW cm^{-2}	PVA-H_3PO_4
RGO-Ni-yarn[6]	72.1 mF cm^{-2}			0.54-1.60 μWh cm^{-2}	2.42 mW cm^{-2}	PVA-H_3PO_4
Graphene/polypyrrole[7]	107.2 mF cm^{-2}	6.6-9.7 μWh cm^{-2}				PVA-H_2SO_4
RGO+CNT@CMC[8]	177 mF cm^{-2}			3.84 μWh cm^{-2}	0.02 mW cm^{-2}	PVA-H_3PO_4
GF@3D-G[9]	1.2-1.7 mF cm^{-2}	0.04-0.17 μWh cm^{-2}	6-100 μW cm^{-2}			PVA-H_2SO_4

Fig. S1 optical photos of (a) coaxial wet spinning process and (b) ternary coaxial fibers immersed in coagulation bath.

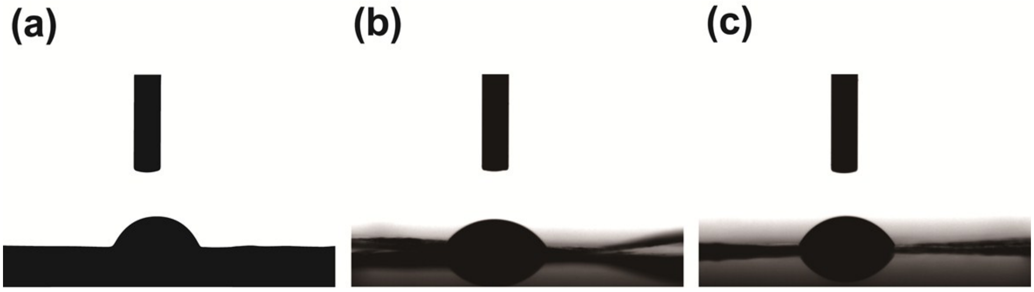


Fig. S2 Contact angel test of (a) RGO film (b) GP-35 film (c) GCP-35 PEDOT:PSS film prepared by simply blade coating.

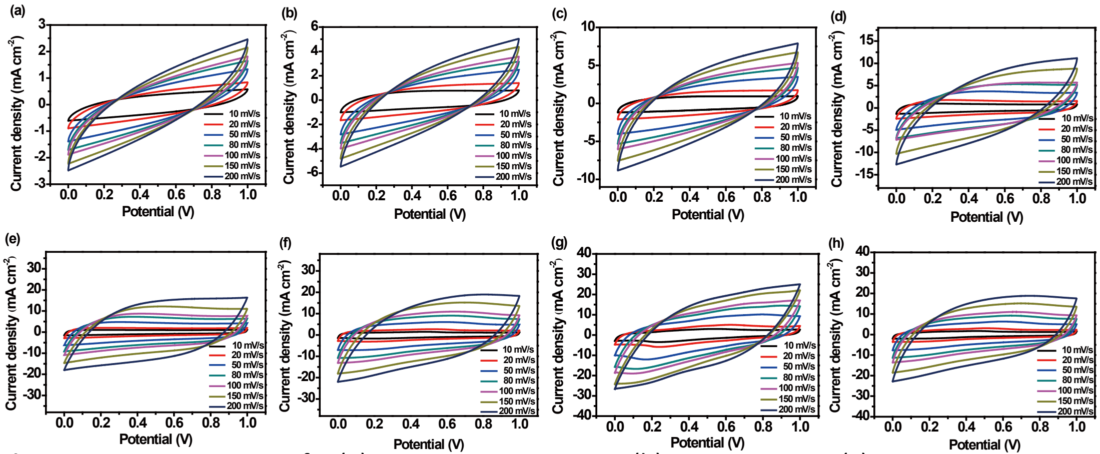
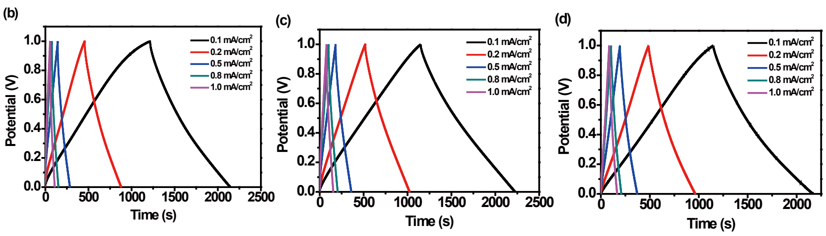


Fig. S3 CV curves of (a) RGO@CMC (b) GP-25@CMC (c) GP-35@CMC (d) GC@CMC (e) GCP-25@CMC (f) GCP-30@CMC (g) GCP-35@CMC (h) GCP-40@CMC assembled FSCs.



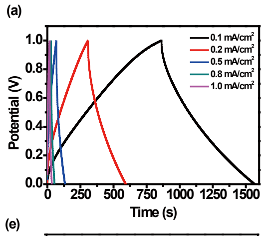
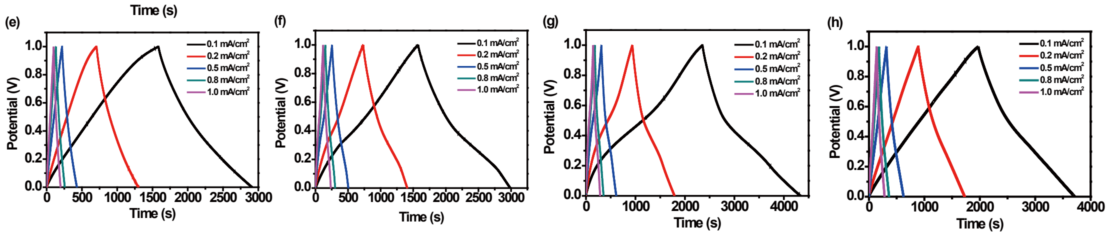


Fig. S4 GCD curves of (a) RGO@CMC (b) GP-25@CMC (c) GP-35@CMC (d) GC@CMC (e) GCP-25@CMC (f) GCP-30@CMC (g) GCP-35@CMC (h) GCP-40@CMC assembled FSCs.



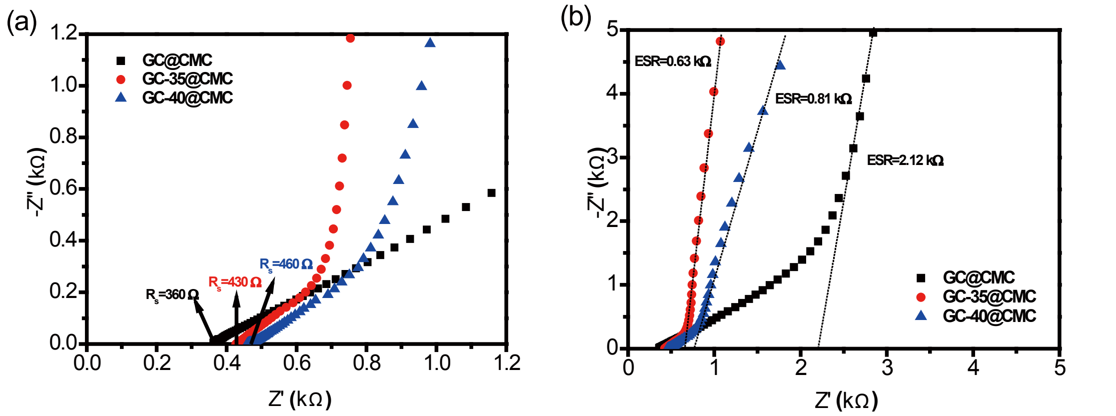


Fig. S5 (a) EIS curves of GC@CMC, GCP-35@CMC and GCP-40@CMC in high frequency region, in which R_s is intrinsic ohmic resistance. (b) Equivalent series resistance R_{ESR} of GC@CMC, GCP-35@CMC and GCP-40@CMC.

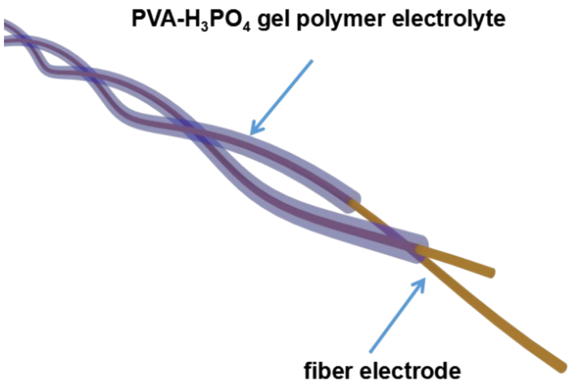


Fig. S6 Assembly method of all-solid-state FSCs by using two twisted fibers as electrodes and PVA-H_3PO_4 gel as electrolytes.

Reference

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