

Graphene fiber-based asymmetric
micro-supercapacitors†Cite this: *J. Mater. Chem. A*, 2014, 2,
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Fiber-based micro-supercapacitors (F-mSCs) are new members of the energy storage family, which facilitate SCs with flexibility and expand their application to fields such as tiny, flexible and wearable devices. One of the biggest challenges for F-SCs is to enhance the energy density (E) and keep the flexibility at the same time. Here, for the first time we assembled a type of fiber-based asymmetric micro-supercapacitors (F-*asym*-mSCs) with two different graphene fiber-based electrodes. The excellent electrochemical performances (59.2 mF cm^{-2} and 32.6 mF cm^{-2}) of both electrodes offered a chance to achieve high performance two-ply F-*asym*-mSCs. The potential window of F-*asym*-mSCs was expanded to 1.6 V, and both the area energy density (E_A : $11.9 \mu\text{W h cm}^{-2}$) and the volume energy density (E_V : $11.9 \text{ mW h cm}^{-3}$) are the highest E ever reported in F-SCs. The F-*asym*-mSCs exhibit good cycling stability with a 92.7% initial capacitance retention after 8000 cycles and can be integrated into a fiber-like device to realize the flexibility of fibers.

Introduction

Supercapacitors (SCs), also known as electro-chemical capacitors, are widely used in many fields such as hybrid electric vehicles and as memory back-up devices because of their high power density, fast charge-discharge rate and long cycling life.^{1,2} To meet the fast growing energy demands of human life, light-weight, flexible and portable devices with high power (P) and energy density (E) are the new targets nowadays in the energy storage research field.

One approach to fulfill these targets is to assemble hybrid SCs which integrate the excellent cycling stability of the carbon materials^{3–7} with the high specific capacitance of metal oxides^{8–11} and conducting polymers.^{12–14} Apart from optimizing the electrode materials of symmetric supercapacitors (*sym*-SCs), asymmetric supercapacitors (*asym*-SCs) are an upgraded version of the hybrid SCs because they can improve the energy density by expanding the operating voltage window in an aqueous electrolyte.⁵¹ Even though conventional button *asym*-SCs^{15,16} and flexible paper *asym*-SCs^{17–21} have been widely recognized, fiber-based *asym*-SCs (F-*asym*-SCs) have never been reported to our knowledge possibly because of the difficulty of accessing different, compatible fiber electrodes.

Fiber-based micro-supercapacitors (F-mSCs) are new members of the SC family and have increasingly attracted the attention of researchers because of their flexibility and weavability. The main challenge of F-mSCs is to significantly improve their E while keeping a relatively high P . Intensive efforts have been devoted to improve the area energy density (E_A) of F-SCs from 0.027 to $9.8 \mu\text{W h cm}^{-2}$ by increasing the specific capacity (C).^{12,22–31,52} Since every material has its theoretical maximum C , such a methodology is limited to highly improve the E of F-mSCs for a specific system. Alternatively, we consider improving the E of F-SCs by enlarging their operating voltage window ($E = 1/2CV^2$) via construction of F-*asym*-mSCs. Considering the high conductivity, high mechanical strength, outstanding flexibility and light weight of graphene fibers,^{32–38,52,57} here for the first time we have developed a novel kind of flexible two-ply F-*asym*-mSC device assembled by using a MnO₂-coated core-sheath graphene fiber (GMF) and graphene-carbon nanotubes hybrid fibers (GCF) in a PVA/LiCl gel electrolyte. Our F-*asym*-mSCs had an E_A up to $11.9 \mu\text{W h cm}^{-2}$ (or a volume energy density of E_V $11.9 \text{ mW h cm}^{-3}$), the highest value for F-mSCs. The use of F-*asym*-mSCs increases the performance improvement of F-SCs and offers a greater chance of creating lightweight, flexible and high energy density storage devices.

Results and discussion

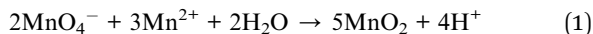
To assemble the F-*asym*-mSCs, we firstly made the different fiber electrodes of GMF and GCF. GMF was obtained by depositing a flower-like MnO₂ nanocrystal sheath on the graphene fiber (GF). The GFs were fabricated by wet-spinning of a

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graphene oxide liquid crystal dispersion into a coagulation bath containing Mn^{2+} , followed by chemical reduction.^{32–34,39} After immersing the GFs in a potassium permanganate (KMnO_4) solution for a given time (1–24 h), GMFs with a controlled thickness of their MnO_2 sheath were achieved. With different reaction times (1, 5, 9, 12 and 24 h), GMFs are named GMF1, GMF5, GMF9, GMF12 and GMF24, respectively. The GMFs showed good mechanical strength and flexibility (Fig. S1†).

Reactions between Mn^{2+} , carbon and KMnO_4 led to the formation of MnO_2 (eqn (1) and (2)).⁴⁰



Flower-like MnO_2 nanocrystals were evenly distributed on the surface of the GMFs, resulting in a core–sheath morphology as seen in the scanning electron microscopy (SEM) images (Fig. 1(a)–(f)). The surfaces of both graphene fibers (Fig. S2(a)†) and GMFs (Fig. 1(a)) showed many continuous wrinkles along the fiber's axis, which were caused by the shrinking of the graphene sheets during the drying procedure in the wet-spinning process. The wrinkles enhance the surface area of the fibers and create more room for the stable growth of MnO_2 nanocrystals. In the magnified image (Fig. 1(b)–(d), S2(d), (f) and (h)†), compared with the clean surface of GFs (Fig. S2(b)†), vivid flower-like nanoribbons are uniformly distributed on the GMF surface, giving rise to a core–sheath structure (Fig. 1(e) and (f)).

Fig. 2(a)–(d) show the energy-dispersive spectroscopy (EDS) mapping of the cross section for GMF24, demonstrating the existence of C, O and Mn elements. The distributions of C and Mn are perfectly complementary with each other, confirming

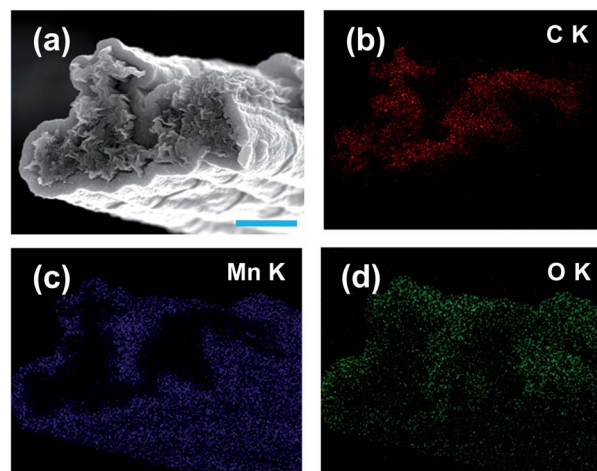


Fig. 2 (a)–(d) Elemental mapping images of GMF24 by EDAX, scale bar: 10 μm .

the core–sheath morphology. The thickness of the MnO_2 sheath increased with the reaction time, and the maximum thickness is about 1 μm (GMF24, Fig. S2(i)–(k)†).⁴¹ Some cleavage exists on the fiber with the increase of MnO_2 sheath thickness (Fig. S2(c), (e) and (g)†). The cleavage has a dual influence on the fibers. Firstly, more ions could be inserted into the electrode system which may contribute to the fast charge–discharge process. Secondly, cleavage may also bring about the separation and exfoliation of the MnO_2 sheath from the GF surface which may reduce the amount of electrochemical active materials and cause a decrease in capacitance. The fracture tip of GMF was also observed by transmission electron microscopy (TEM), as

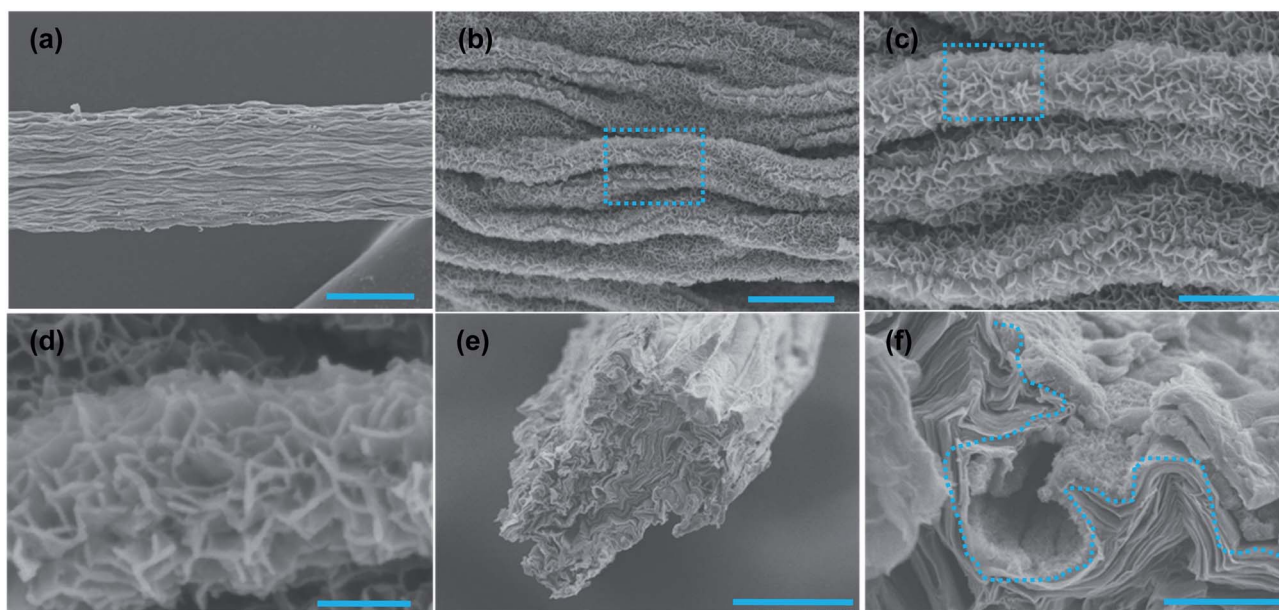


Fig. 1 (a) Overview of GMF1 observed by SEM. (b) Surface morphology of GMF1. (c) Magnified picture of the region in the blue dotted square of (b). (d) Magnified picture of the region in the blue dotted square of (c). (e) Cross sectional image of GMF1 observed by SEM. (f) Magnified picture of (e), and the boundary between MnO_2 and graphene is marked as a blue dotted line. Scale bars from (a)–(f) are 10 μm , 1 μm , 500 nm, 150 nm, 10 μm and 1 μm , respectively.

shown in Fig. S2(l).† The dragged out graphene sheets were clearly observed. Inside the dashed box, typical MnO_2 nanostructures were found around the fiber.

Fig. 3(a) shows the X-ray diffraction (XRD) patterns of GMFs with different reaction times. The peak at around 24° corresponds to the (002) plane of carbon (stacked graphene sheets, d space = 0.37 nm). According to the PDF card (30-820) of $\epsilon\text{-MnO}_2$, peaks at around 37° and 67° correspond to the (100) and (110) planes of MnO_2 , respectively.⁴² With the increase of sheath thickness, the characteristic peaks of MnO_2 become more intense. The $\epsilon\text{-MnO}_2$ structure was also verified by the typical peaks at wavenumbers of 575 cm^{-1} and 649 cm^{-1} in corresponding Raman spectra (Fig. 3(b)).²⁰

X-ray photoelectron spectroscopy (XPS) was used to further determine the compositions of GMF (Fig. 3(c)–(e)). In Fig. 3(c), the peaks at 284.8 eV (C–C/C=C bonds), 286.5 eV (C–O bonds), 287.6 eV (C=O bonds), and 288.8 eV (C(=O)–O bonds) indicate the chemically reduced graphene structures with strong C–C/C=C bonds.⁴³ Fig. 3(d) showed the O_{1s} peaks at 529.9 eV (C=O, C(=O)–O or Mn–O) and 533 eV (C–OH).¹⁵ In Fig. 3(e), two strong peaks are clearly observed at 642.6 eV and 653.9 eV, which can be assigned to the binding energy values of Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively.¹⁸ The multiplet splitting which will result in the separation of peak energies (ΔE) of Mn_{3s} peaks according to the literature,⁵⁹ and the ΔE of MnO, Mn_3O_4 , Mn_2O_3 and MnO_2 are 5.79, 5.50, 5.41 and 4.78 eV, respectively. The ΔE of GMF9 is 4.8 eV as shown in Fig. 3(f), indicating that the sheath of GMF9 is MnO .

The flexible GMFs were assembled into F-mSCs as illustrated in Fig. 4(a): two GMFs were fixed by a current collector of silver

paint and immersed in aqueous electrolyte (1 M Na_2SO_4). The electrochemical performance of the GMFs was initially measured by cyclic voltammetry (CV). As shown in Fig. 4(a), CV curves of GMF9 are all shaped like a parallelogram which means a continuous, fast and reversible redox reaction took place around the surface of the GMFs.¹⁸ The integral area of the GMFs with different reaction time first increased and then decreased after 9 h (Fig. 4(b)). Similar tendencies were also observed in the corresponding galvanostatic charge–discharge (GCD) curves (Fig. 4(c)). The area specific capacitances for single electrodes (C_A) calculated from CV curves for different samples are shown in Fig. S5.† The C_A at a 10 mV s^{-1} scanning rate increased from 11.7 mF cm^{-2} for neat GFs to 55.0 mF cm^{-2} for GMF9 because of the coating of MnO_2 nanocrystals, and then decreased to 31.4 mF cm^{-2} for GMF12 possibly because of the inefficient charge transportation caused by the thick sheath.⁴¹ The highest C_A associated with GMF9 is 55 mF cm^{-2} which is ~ 5 times that of neat GF (11.7 mF cm^{-2}), and also much higher than those obtained for previous graphene-based F-mSCs.^{28,29,48,52} The C_A of GMF9 calculated by GCD is 59.2 mF cm^{-2} at a current density of 0.1 mA cm^{-2} , which is about 5 times the value obtained for neat GF (12.6 mF cm^{-2}). Using the length and diameter of GMF9, the volume specific capacitance (C_V) of 169 F cm^{-3} and linear specific capacitance (C_L) of 0.026 F m^{-1} were calculated (see calculation in the ESI†). The E_A have also improved dramatically from $0.27\text{ }\mu\text{W h cm}^{-2}$ for GFs to $1.2\text{ }\mu\text{W h cm}^{-2}$ for GMF9. The E_A ($1.2\text{ }\mu\text{W h cm}^{-2}$) and E_V (3.4 mW h cm^{-3}) for GMF9 have also exceeded the majority of values previously reported for F-SCs^{26,28,30,46,47,49,50} and at the same orders of magnitude of F-SCs constructed by CNT/ MnO_2 ,²² CNT-ordered

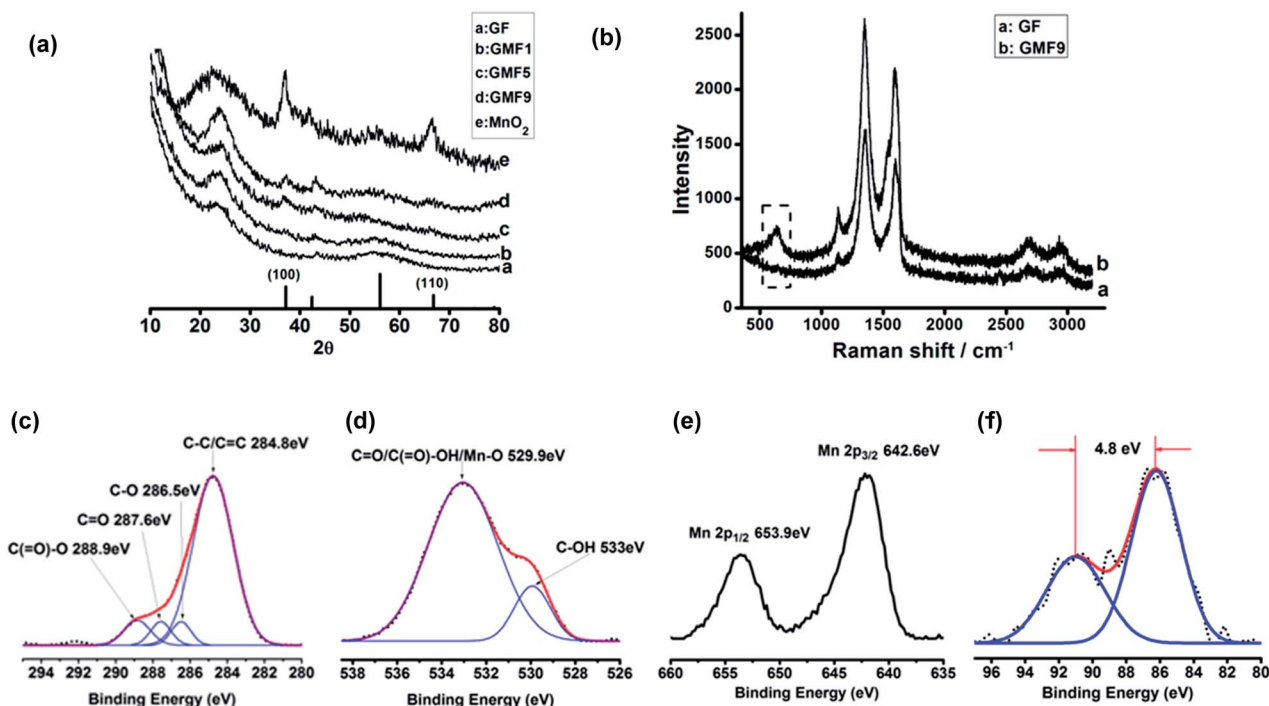


Fig. 3 (a) XRD spectra of neat GF, GMF1, GMF5, GMF9, and MnO_2 compared with standard XRD peak of $\epsilon\text{-MnO}_2$. (b) Raman spectra of neat GF and GMF9. (c), (d), (e) and (f) C_{1s} , O_{1s} , Mn_{2p} and Mn_{3s} peaks in XPS of GMF, respectively.

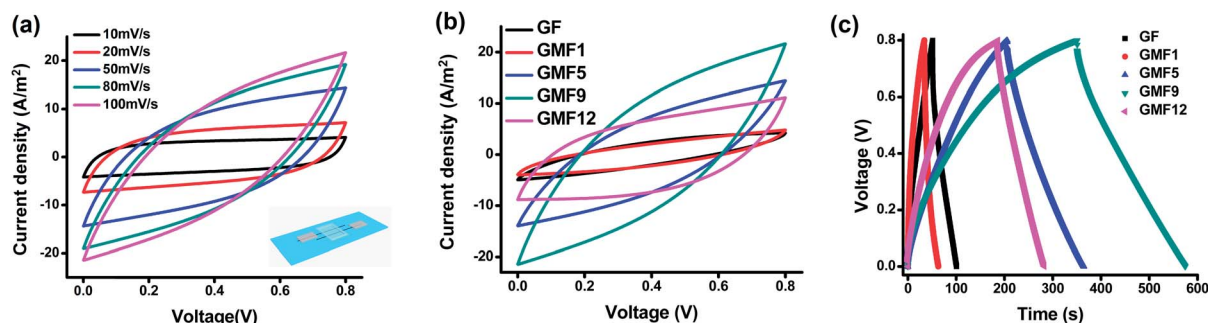


Fig. 4 (a) CV curves of GMF9 at different scan rates, inset: cartoon illustration of F-mSC. (b) CV curves of neat GF, GMF1, GMF5, GMF9, and GMF12 at 100 mV s⁻¹ (c) GCD curves of neat GF, GMF1, GMF5, GMF9, and GMF12 at a current density of 0.1 mA cm⁻².

mesoporous carbon (OMC)²⁵ and pen ink.³¹ Cyclic stability of GMF9 was conducted by GCD tests between 0 and 0.8 V at a current density of 0.1 mA cm⁻² (Fig. 4(d)). After 1000 charge–discharge cycles, GMF9 showed good stability and still retained 95.7% of the initial specific capacitance (Fig. S3†).

Another electrode which was also used to construct *F-asym*-mSCs was GCF. The synergistic effect between graphene and carbon nanotubes (CNTs) has been recognized in aerogels and flat SCs,^{3,44,45,60} but rarely reported in F-SCs.^{54–56} Here, multi-walled CNTs (MWNT) were evenly dispersed in the grapheme oxide (GO) liquid crystal aqueous solution (GO–MWNT = 1 : 1 by weight) and assembled into continuous macroscopic fibers by wet-spinning. The typical accordion-like wrinkles still exist on the cross section of the GCFs and the hairy MWNTs were dragged out from graphene sheets (Fig. S4(a) and (b)†). After chemical reduction by hydriodic acid (HI), GCFs are ideal

candidates for electrical double-layer supercapacitors because the sandwich-like structure not only guarantees good electric conductivity but also provides channels for efficient ion transportation. In CV tests, the charge–discharge loop of GCF (Fig. S4(c)†) at different scanning rates showed rectangle-like shapes, which prove the electrical double-layer behavior of GCFs. C_A calculated from CV curves of GCF reached 29 mF cm⁻² at a scanning rate of 10 mV s⁻¹. The GCD curves of GCFs at different current densities are shown in Fig. S4(d).† The C_A calculated from the GCD curves reached 32.6 mF cm⁻² at 0.1 mA cm⁻², which is about 3 times the value of those obtained for GFs. E_A (1.1 μW h cm⁻²) and E_V (1.0 mW h cm⁻³) for GCF were also improved when compared with other neat graphene F-SCs.

The performances of GMFs and GCFs are summarized in Table 1 and Fig. S4.† Both GMFs and GCFs are superior to the

Table 1 Capacitance and energy density comparison of F-mSCs

Ref.	Electrode materials	C			E	
		C_A (mF cm ⁻²)	C_V (F cm ⁻³)	C_L (mF cm ⁻¹)	E_A (μW h cm ⁻²)	E_V (mW h cm ⁻³)
This work	GMF9	59.2	169.0	0.33	1.2	3.4
	GCF	32.6	29.1	0.46	1.1	1.0
	Two-ply <i>F-asym</i> -mSC ^b	33.6 ^a	33.6 ^a	0.42 ^a	11.9	11.9
	Two-ply <i>F-asym</i> -mSC ^c	16.8 ^a	16.8 ^a	0.21 ^a	5.5	5.5
12	PANI/CNT ^c	38				
22	CNT/MnO ₂ ^b		25.4			3.52
23	CNT/CNF ^b	86.8		6.3	9.8	
25	CNT/OMC ^c	39.7		1.91	1.77	
26	CNT/MnO ₂ ^c	3.01		0.015		1.73
27	CNT ^c	8.66	32.09	0.029		
28	Graphene ^c	1.7			0.17	
29	Graphene ^c	0.726		0.01		
30	ZnO nanowires ^b	2.4			0.027	
31	Pen ink ^c	26.4		1.008	2.7	
46	PEDOT/CNT ^b	73	179	0.47		1.4
47	CNT and Ti fibers ^c	0.6		0.024	0.15	
48	ZnO nanowires/graphene ^b	2		0.025		
49	PANI/stainless steel ^c	41			0.95	
50	Carbon/MnO ₂ ^c		2.5			0.22
52	PANI/graphene ^c	66.6				
55	CNT/graphene ^c	0.98				

^a Specific capacitance of total cell (C_{tA}). ^b Data obtained from CV tests. ^c Data obtained from GCD tests.

neat GFs, offering the opportunity of assembling high performance F-*asym*-mSCs. Due to the light weight of the fibers, it is hard to give the exact weight of active materials of both electrodes. So we chose GMF9 and GCF with the same diameter (40 μm) and by controlling the wet-spinning parameters to construct F-*asym*-mSCs, the surface areas of both electrodes were nearly the same. According to CV curves obtained by using a three-electrode system (Fig. 5(a)), GMF and GCF have stable potential windows of 0 V–0.8 V and –0.8 V–0 V (vs. Ag/AgCl), respectively. Thus, the operating voltage was extended to 1.6 V when GMF and GCF were assembled into parallel-type F-*asym*-mSCs. GMF was assembled as positive electrode and GCF was the negative electrode (Fig. 5(d)). Fig. 5(b) shows CV curves of different operating voltages at 100 mV s^{-1} for the parallel-type F-*asym*-mSCs. When tested by GCD at 0.5 mA cm^{-2} with different voltage windows ranging from 0.8 V to 1.6 V (Fig. S6(a)†), the area capacitances of the total cell (C_{TA}) were 14.9, 14.1, 18.1, 18.9, and 23.6 mF cm^{-2} . The highest C_{TA} can also be converted to specific volume capacitance (C_{TV}) and specific linear capacitance (C_{TL}), which were 23.6 F cm^{-3} and 0.3 mF cm^{-1} , respectively. Correspondingly, the E_A also increased significantly from

1.2, 1.8, 3.4, 4.9, to 8.0 $\mu\text{W h cm}^{-2}$ when P_A s were 0.9, 1.2, 1.5, 1.7 to 1.9 W m^{-2} . However, because of the imperfect device design of parallel-type F-*asym*-mSCs, current leakage happened when electrochemical reactions took place (Fig. S6†). Development of a new type of F-*asym*-mSC that can avoid current leakage while giving good flexibility is essential. According to the literature,^{12,58} two-ply FSCs integrated closely by two fiber electrodes are helpful. Accordingly, we also made two-ply F-*asym*-mSCs with the different electrodes of GMF and GCF, using PVA/LiCl gel as electrolyte (Fig. 5(e)).²¹ The two fiber electrodes were glued by PVA/LiCl gel after they were covered by pure PVA gel as shown in Fig. 5(f)–(h).

Fig. 5(c) and (i) show the performances of two-ply F-*asym*-mSCs at different scanning rates and current densities when the operating voltage is 1.6 V in CV and GCD tests. The C_{TA} of F-*asym*-mSCs were 33.6 mF cm^{-2} and 19.1 mF cm^{-2} when tested by CV at 10 mV s^{-1} and by GCD at 0.1 mA cm^{-2} , respectively. Values of C_{TA} and E_A in CV and GCD are also shown in Table S1, S2 and Fig. S7.† Furthermore, the two-ply F-*asym*-mSCs showed almost overlapping CV curves at flat and bending states (Fig. 5(j)), confirming their good flexibility, which indicates a

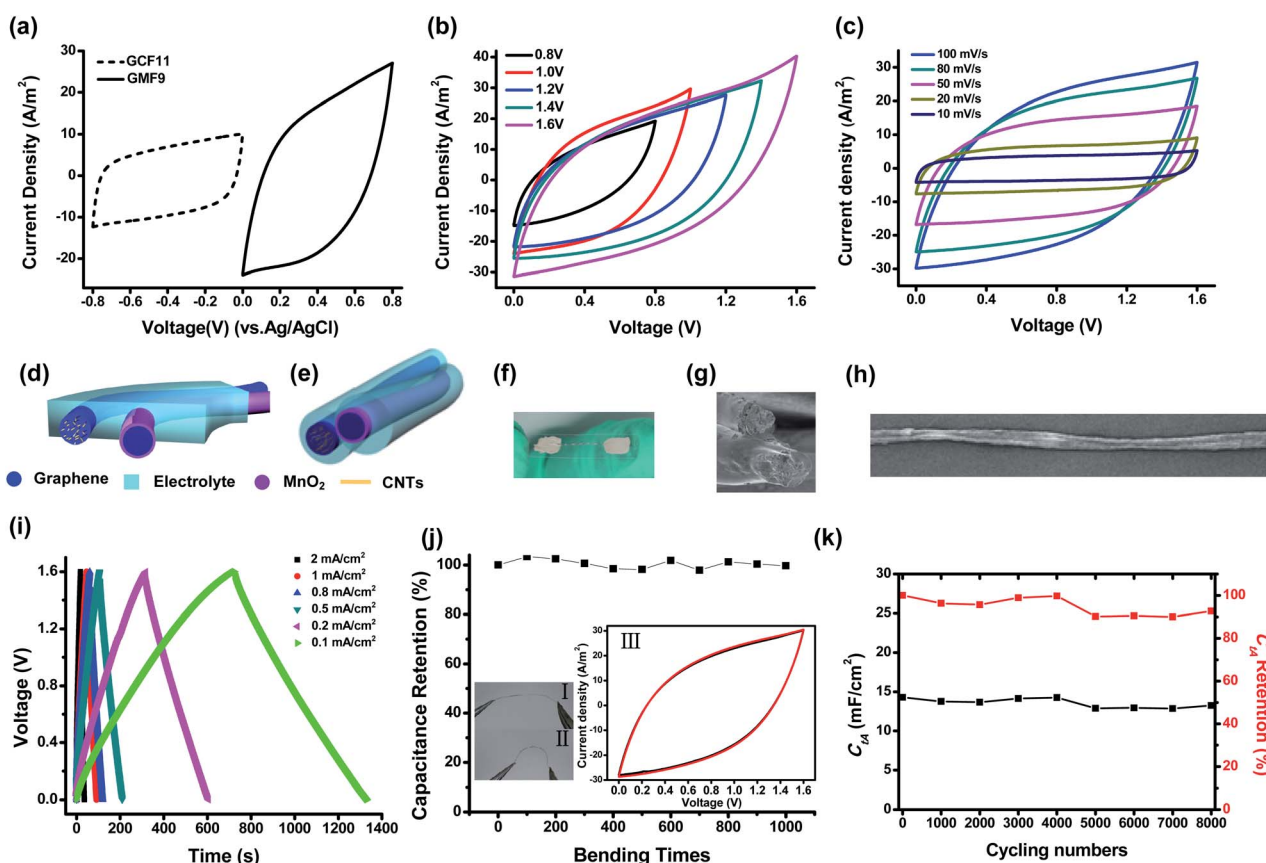


Fig. 5 (a) CV curves of GMF and GCF in a three-electrode system (vs. Ag/AgCl). (b) CV curves of parallel F-*asym*-mSCs at different potential windows (scanning rate 100 mV s^{-1}). (c) CV curves of two-ply F-*asym*-mSC at different scanning rates when the operating voltage is 1.6 V. (d) Schematic of parallel F-*asym*-mSCs. (e) Schematic of two-ply F-*asym*-mSC. (f) Photograph of two-ply F-*asym*-mSC. (g) Cross sectional image of two-ply F-*asym*-mSC obtained by SEM, scale bar: 100 μm . (h) Surface image of two-ply F-*asym*-mSC observed by SEM, scale bar: 500 μm . (i) GCD curves of two-ply F-*asym*-mSC at different current densities when the operating voltage is 1.6 V. (j) Capacitance retention at different bending times, inset: photograph of two-ply F-*asym*-mSC at flat (i) and bending (ii) states, (iii) CV curves of two-ply F-*asym*-mSC at flat and bending states (scanning rate 100 mV s^{-1}). (k) Cycling performance of two-ply F-*asym*-mSC tested by GCD at 1.0 mA cm^{-2} .

potential application in practical flexible devices. Cycling stability tests of two-ply F-*asym*-mSCs was conducted at a high current density of 1.0 mA cm^{-2} (Fig. 5(k)) and 92.7% initial capacitance were retained after 8000 cycles.

In CV tests, energy densities increased from $6.1 \mu\text{W h cm}^{-2}$ (6.1 mW h cm^{-3}) at 100 mV s^{-1} to $11.9 \mu\text{W h cm}^{-2}$ ($11.9 \text{ mW h cm}^{-3}$) at 10 mV s^{-1} . In GCD measurements, energy densities increased from $3.2 \mu\text{W h cm}^{-2}$ (3.2 mW h cm^{-3}) at 2.0 mA cm^{-2} to $6.7 \mu\text{W h cm}^{-2}$ (6.7 mW h cm^{-3}) at 0.1 mA cm^{-2} . Fig. 6(a) shows clear P - E comparison plots of this research and results from the literature. Notably, the energy density obtained from both CV and GCD tests for two-ply F-*asym*-mSCs are the highest values ever reported for F-SCs to our knowledge (Table 1), which obviously exceeded the highest published E_A ($9.8 \mu\text{W h cm}^{-2}$)²³ and E_V (3.5 mW h cm^{-3}).²² Moreover, our F-*asym*-mSCs dramatically increased the E of graphene-based F-mSCs by about 70 times from $0.17 \mu\text{W h cm}^{-2}$ to $11.7 \mu\text{W h cm}^{-2}$.²⁸

Electrochemical impedance spectroscopy (EIS) was carried out over the frequency range from 10^{-2} – 10^6 Hz as shown in Fig. 6(b). The intercepts at the x -axis and slopes for F-*asym*-mSCs shown in the Nyquist plots mean the equivalent series resistance (ESR) and charge transport resistance in parallel F-*asym*-mSCs were smaller than those in two-ply F-*asym*-mSCs. The above phenomena explain the slight differences of

electrochemical performances in the parallel and two-ply F-*asym*-mSCs. After 1000 cycles, the ESR showed no significant changes in the equivalent resistances ($\sim 10 \text{ k}\Omega$) which indicates the stable electrochemical performance of two-ply F-*asym*-mSCs in the cycling test. It is likely that the large equivalent resistances were caused by the large distance between the two fibers and the contact resistance of the current collectors. How to reduce the ESR of the device is the next target of our F-*asym*-mSC research and research reported by other groups may offer some inspiration.^{23,25}

Experimental

Preparation of GMFs

Graphene fibers were prepared by injecting liquid-crystal graphene oxide (GO) into a rotating coagulation bath of 5 wt% manganese acetate ($\text{Mn}(\text{Ac})_2$) in ethanol–water (1 : 3 by volume). After being immersed in the coagulation bath for 15 min, the gel-like fibers were taken out and immersed in an ethanol–water solution for 0.5 h. Then the GO fibers were dried at 90°C in a vacuum oven overnight and then reduced using diluted HI at 90°C for 1 h. The GFs were then immersed in 0.05 wt% KMnO_4 solution for a specific reaction time and the fibers were then washed in water. After drying at 90°C overnight, GMFs were obtained.

Preparation of GCFs

Dispersible MWNTs were prepared according to a previously reported protocol.⁵³ MWNTs were mixed with GO (1 : 1 by weight) liquid crystal aqueous solution and vigorously stirred for 1 h at room temperature. The mixtures were injected into a rotating coagulation bath of CaCl_2 in ethanol–water (1 : 3 by volume). After immersion for 15 min, fibers were taken out and washed with ethanol–water solution for 0.5 h. Then the GO/CNT fibers were dried at 90°C in a vacuum oven overnight and reduced by diluted HI at 90°C for 1 h. After washing with ethanol and drying at room temperature, GCFs were obtained.

Fabrication of F-mSCs

Two fiber electrodes with the same diameter were fixed at two ends by silver paint. A 1 M Na_2SO_4 solution was sealed into the cell constructed by poly(ethylene terephthalate) film and glass cement, giving parallel F-*sym*-mSCs or F-*asym*-mSCs. For two-ply F-*asym*-mSCs, fiber electrodes were first covered by pure PVA solution and dried under an infrared lamp and then glued by a PVA/LiCl gel electrolyte as previously reported.²¹ The two ends of the electrodes were fixed to PET film by silver paint.

Characterizations

SEM images were produced using a Hitachi S-3000N field-emission SEM; TEM images were produced using a JEM-1200 EX (JEOL); XRD data were collected with a X'Pert PRO diffractometer (PANalytical) using monochromatic Cu $\text{K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV; Raman measurements were conducted on an inVia-Reflex microscope (Renishaw); XPS measurements were carried out on a PHI 5000C ESCA system (Physical

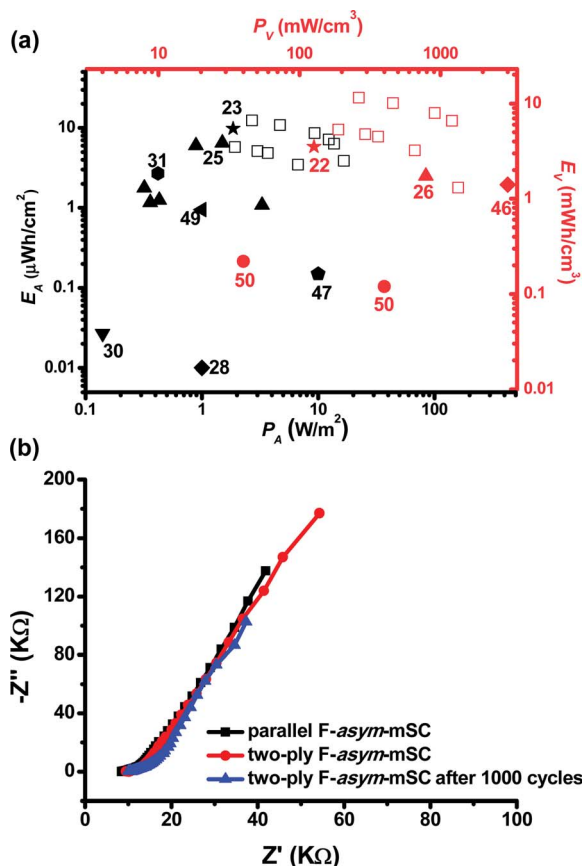


Fig. 6 (a) E_A - P_A and E_V - P_V plots of F-*asym*-mSCs and references, where the black symbols are calculated by area and red symbols are calculated by volume, square symbols are data obtained in this research. (b) Nyquist plots of F-*asym*-mSCs.

Electronics) operated at 14.0 kV and all the binding energies were referenced to the C_{1s} neutral carbon peak at 284.8 eV. CV, GCD and EIS measurements were conducted on a CHI660E workstation (CH Instruments, Inc.).

Conclusion

In summary, two different graphene-based fiber electrodes based on the facile wet-spinning assembly method were prepared. The core-sheath GMFs integrated the advantages of the pseudo-capacitance of MnO₂ and the conductivity of graphene. The C_A of GMFs reached 59.2 mF cm⁻², five times that of the neat GFs. The synergistic effect of graphene and CNTs improved the value of C_A of the GCFs to 32.6 mF cm⁻². For the first time, we fabricated asymmetric fiber-based supercapacitors, F-*asym*-mSCs, from the excellent GMF and GCF electrodes. The capacitances of the total cell (C_{tot}) achieved were up to 23.6 mF cm⁻² when the operating voltage window was increased to 1.6 V. Because of the large voltage window, the energy densities of flexible F-*asym*-SCs were significantly improved to 11.9 μW h cm⁻², the highest values ever reported for all F-SCs. The F-*asym*-SCs exhibited good cycling stability with a 92.7% initial capacitance retention after 8000 cycles. This approach opens a new avenue to design and fabricate high performance yarn supercapacitors, and paves the way for production of high energy density, wearable electronic devices.^{61,62}

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