Electronic Supplementary Information

Strong and Highly Flexible Aramid Nanofibers/PEDOT:PSS Film for All-Solid-State Supercapacitor with Superior Cycling Stability

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Calculations

The specific capacitance (C_s) based on PEDOT:PSS and volumetric capacitance (C_V) were calculated from GCD curves according to the following equation:

$$C_s(C_V) = \frac{I \times \Delta t}{\Delta V \times m(V)} \tag{1}$$

where I (A) refers to the discharge current; ΔV (V) represents the potential change within the discharge time Δt (s), and m (g), V (cm³) corresponds to the total weight of the electrochemically active material PEDOT:PSS, the volume of the single electrode, respectively. The specific energy density E (W h Kg⁻¹, W h cm⁻³) and specific power density P (W Kg⁻¹, W cm⁻³) of SC devices were calculated according to the following equations:

$$C_s(C_V) = \frac{I \times \Delta t}{\Delta V \times M(V)}$$
(2)

$$E = \frac{1}{2}C_{\rm s}(C_{\rm V})(\Delta V)^2 \times \frac{1}{3.6}$$
(3)

$$P = \frac{3600E}{\Delta t} \tag{4}$$

where I (A) represents the discharge current; ΔV (V) represents the potential change within the discharge time Δt (s); M (g), V (cm³) corresponds to the total weight of the electrochemically active material PEDOT:PSS in both electrodes, the device volume including the two electrodes and PVA/H₂SO₄ gel electrolyte.



Fig. S1 SEM images of bulk Kevlar (a), freeze-dried aramid nanofibers (ANFs) (b), the surface (c) and cross-section (d) of pristine PEDOT:PSS film. Inset: Digital photograph of ANFs/DMSO dispersion with a concentration of 2 mg mL⁻¹.

In Fig. S1a, the bulk Kevlar has a smooth surface and a diameter of $12.4 \pm 0.4 \mu m$. The color of as-prepared ANFs/DMSO dispersion was dark red, and the diameter of freezedried ANFs was calculated to be $24.3 \pm 4.4 \text{ nm}$ (Fig. S1b). From Fig. S1c and 1d, it can be observed that the pristine PEDOT:PSS film possesses a relatively smooth surface, and compact structure.



Fig. S2 (a) TGA curves of ANFs, PEDOT:PSS and ANFs/PEDOT:PSS films. (b) XPS spectra of S_{2p} , (c) Raman spectra and (d) corresponding deconvolution of the Raman spectra for PEDOT:PSS and pristine ANFs/PEDOT:PSS and ANFs/PEDOT:PSS films.

Fig. S2a reveals the TGA curves for the three samples. The major mass loss for the pure ANFs appears at 560 °C, which is ascribed to the decomposition of the ANFs.¹ For pure PEDOT:PSS, the first weight loss up to 120 °C can be attributed to the loss of water. The degradation at 320 °C is due to the decomposition of PSS, and the degradation at 505 °C is ascribed to the polymer backbone rupturing.² For ANFs/PEDOT:PSS, the major degradation occurs at 505 °C and 580 °C, which is due to the PEDOT:PSS backbone rupturing and the decomposition of ANFs, respectively. Judging by the weight loss of the three samples at 650 °C, there is 20.4 wt% of ANFs in the ANFs/PEDOT:PSS film. In Fig. S2b, the XPS band between 166 and 172 eV is the S_{2p} band of the sulfur atoms in PSS, while the two XPS bands between 162 and 166 eV are the S_{2p} band of the sulfur atoms in PEDOT.³ From the XPS spectra, we obtain that the C/S atomic ratio changes from 11.5 (pristine PEDOT:PSS film) to 40.3 (pristine ANFs/PEDOT:PSS film), and to 53.6 (ANFs/PEDOT:PSS film). The increase of C/S atomic ratio might be related to removal of some PSS molecules.⁴ The Raman spectra of the three films are shown in Fig. S2c. The strongest band (1380-1460 cm⁻¹) in the spectra is attributed to the symmetric $C_{\alpha} = C_{\beta}$ stretching mode of the PEDOT thiophene ring.⁵ According to reported work,⁶ two kinds of resonant structures of PEDOT (*i.e.* the

benzoid and quinoid form) determine the electronic property of PEDOT:PSS. The benzoid (insulating or semiconducting) form possesses a π -electron localized structure, while the quinoid (conducting) form has a delocalized state of π -electrons.⁶ The band (centered at 1430 cm⁻¹) of pure PEDOT:PSS can be deconvoluted into two vibrations at 1436 and 1417 cm⁻¹, indicating a mixture of both benzoid and quinoid resonant form (Fig. S2d). In contrast, after introducing ANFs into PEDOT:PSS, the major resonant form of PEDOT in pristine ANFs/PEDOT:PSS film is quinoid form, even full quinoid resonant form in ANFs/PEDOT:PSS film. The increase of conducting form (quinoid form) in the film indicates the enhancement of electrical conductivity.



Fig. S3 Current-voltage (*I-V*) measurements on ANFs/PEDOT:PSS film under a various geometric state (normal, bending and twisting) were carried out between -0.5 V and 0.5 V at a scan rate of 100 mV s⁻¹.



Fig. S4 (a) Photograph of solution collected after vacuum filtration through nylon membrane of PEDOT:PSS aqueous solution (left) and ANFs/PEDOT:PSS dispersion (right). (b) UV absorption spectra of PEDOT:PSS aqueous solution with different concentration. (c) The absorbance versus the concentration of PEDOT:PSS.

In Fig. S4a, the color of filtrate collected after vacuum filtration through nylon membrane of ANFs/PEDOT:PSS dispersion is colorless, while that of PEDOT:PSS aqueous solution (1.3 mg mL⁻¹) is dark blue, implying a vast majority of PEDOT:PSS permeating the nylon membrane. We measured the content of PEDOT:PSS in the filtrate by standard absorptive value method, as shown in Fig. S4b. The absorption peaks at 225 nm are ascribed to the aromatic ring of PSS.³ The equation for the UV absorbance versus the concentration of PEDOT:PSS is given as follows:

$$Abs = 0.0299C_{PEDOT:PSS} + 0.0858$$
(1)

Based on the above-mentioned measurements, the content of PEDOT:PSS in the filtrate is calculated as 0.64 mg mL⁻¹. Compared with the color of filtrate, we assume that there is an strong interaction between ANFs and PEDOT:PSS.



Fig. S5 CV curves of ANFs/PEDOT:PSS film with/without DMSO-treatment collected at scan rate of 200 mV s⁻¹.



Fig. S6 CV curves of the flexible all-solid-state SC collected in different operating potential windows at the scan rate of 100 mV s^{-1} .

It can be seen from Fig. S6 that the flexible device shows rectangular-like CV curves when the operating potential window expands from 0-1.0 V to 0-1.6 V. When the operating potential window reaches 0-1.8 V, oxygen evolution is occurred.⁷ Therefore, the operating potential of the flexible device can reach as high as 1.6 V.



Fug. S7 Electrochemical tests of DMSO-treated PEDOT:PSS film-based all-solid-state SCs. (a) CV curves of the SCs recorded at different scan rate of 50, 100, 200, 400, and 500 mV s⁻¹. (b) GCD profiles of the SCs recorded at different current density of 0.1, 0.2, 0.5, 0.8, and 1.0 A cm⁻³. (c) Volumetric capacitance as a function of current density. (d) Energy density and power density Ragone plot of the SCs. (e) Nyquist plot of the SCs. (f) Cycling stability of the SCs at a relatively high current density of 1.0 A cm⁻³ at room temperature.

In Fig. S7a, redox peaks during the anodic and cathodic sweeps are clearly observed, which are related to the electron-transfer pseudocapacitive processes of $PEDOT^{0}/PEDOT^{+}$ (0.48 and 0.28 V) with the assistance of H⁺ given below:⁸

$$PEDOT^{+} \cdot PSS^{-} + H^{+} + e^{-} \leftrightarrow PEDOT^{0} \cdot PSS^{-} \cdot H^{+}$$
(2)

With an increase of scan rate, the redox current peaks increase linearly, indicating a surface-controlled electrochemical process and good pseudocapacitive behavior.⁵ In Fig. S7b, the GCD profiles are nearly symmetrical with linear slop, suggesting that the DMSO-treated PEDOT:PSS film has excellent electrochemical reversibility. The volumetric capacitance of the SCs was calculated and the corresponding results are shown in Fig. S7c. When the entire volume of the device (including the volume of PVA/H₂SO₄ gel) is taken into account, the volumetric capacitance of the device is 7.5 F cm⁻³ at a current density of 0.1 A cm⁻³, and decreases to 6.8 F cm⁻³ at a current density of 2.0 A cm⁻³, which are better than those of DMSO-treated PEDOT:PSS film-based SC. The volumetric energy and power densities normalized with respect to the entire device volume for the SC are present in the Ragone plot of the Fig. S7d. The maximum of energy density for the flexible device is found to be 2.68 mW h cm⁻³ at a power density of 80.7 mW cm⁻³. Moreover, the device could still maintain an energy density

of 2.42 mW h cm⁻³ at a high power density of 1816 mW cm⁻³. Fig. S7e exhibits the Nyquist plot of the solid-state SC. The ESR of the SC is 2.2 Ω cm⁻², demonstrating a rapid diffusion of ions. The long-term charge/discharge cycling test at a current density of 1.0 A cm⁻³ were carried out at room temperature, shown in Fig. S7f. It can be seen that the cycling stability of the device is poor as the capacitance retention with only 51.0%, which is uneconomic for practical application.



Fig. S8 Volumetric Ragone plot of ANFs/PEDOT:PSS film-based SC.



Fig. S9 The device for investigating the impact resistance of the flexible SC.

All-solid-state SC (0.6 cm \times 2.0 cm) with conductive Ag wire welded at both end was fabricated for electrochemical test. The flexible SC was fixed on white foam and installed in the middle of polymethyl methacrylate box. Then a glass funnel was fixed on white foam above the SC to leak sand. The dried sand used in this experiment was commercial product for sand painting. The leaking rate of sand was controlled in the range of 700-800 cm³ h⁻¹. Meantime, an air blower (rated power: 30 W, revolving speed: 2800 r min⁻¹, air speed: ~12 m s⁻¹) was fixed perpendicular to the glass funnel, so as to let sand fly for continuously striking the surface of the SC (around the red mark). To investigate the impact resistance of the flexible SC, we used CV test at a scan rate of 100 mV s⁻¹, and the corresponding result can be seen in Fig. 6e.



Fig. S10 CV curves of ANFs/PEDOT:PSS film-based flexible SCs collected at 0 °C (a) and -20 °C (b). GCD profiles of ANFs/PEDOT:PSS film-based flexible SCs obtained at 0 °C (c) and -20 °C (d).

References

- 1 J. Fan, Z. Shi, L. Zhang, J. Wang and J. Yin, *Nanoscale*, 2012, 4, 7046-7055.
- D. Antiohos, G. Folkes, P. Sherrell, S. Ashraf, G. G. Wallace, P. Aitchison, A. T.
 Harris, J. Chen and A. I. Minett, *J. Mater. Chem.*, 2011, 21, 15987-15994.
- 3 Y. Xia, K. Sun and J. Ouyang, *Adv. Mater.*, 2012, **24**, 2436-2440.
- 4 S. H. Lee, J. S. Sohn, S. B. Kulkarni, U. M. Patil, S. C. Jun and J. H. Kim, *Org. Electron.*, 2014, **15**, 3423-3430.
- 5 J. Zhao, S. Xu, K. Tschulik, R. G. Compton, M. Wei, D. O'Hare, D. G. Evans and X. Duan, *Adv. Func. Mater.*, 2015, **25**, 2745-2753.
- 6 A. G. MacDiarmid, Angew. Chem. Int. Ed., 2001, 40, 2581-2590.
- N. Yu, H. Yin, W. Zhang, Y. Liu, Z. Tang and M.-Q. Zhu, *Adv. Energy Mater.*, 2016, 6, 1501458.
- 8 G. Cai, P. Darmawan, M. Cui, J. Wang, J. Chen, S. Magdassi and P. S. Lee, *Adv. Energy Mater.*, 2016, **6**, 1501882.