Supplementary Information for

High-performance stretchable supercapacitors based on intrinsically stretchable acrylate rubber/MWCNTs@conductive polymer composite electrodes

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Experimental Section

Preparation of ACM organic quasi-solid-state polymer electrolyte (QPE): The cross-linked acrylate rubber (ACM) membranes were prepared by the chemical cross-linking method. Typically, ACM and diethylenetriamine (DETA) were dissolved separately in acetone. 4 wt% (with respect to the weight of ACM) DETA solution were then added into the ACM solution. After mechanical stirring for 8 h, the slightly yellow homogenous solutions were obtained. Then the homogenous solutions were let stand

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for 20 min for deaeration and then cast onto PTFE plates. After drying completely at 
room temperature, the cross-linked ACM membranes were cured at 80 °C for 48 h. Then 
the uncross-linked part of ACM membranes was removed by extraction with acetone 
in a Soxhlet apparatus. Finally, the cross-linked ACM membranes were immersed in 
tetraethylammonium tetrafluoroborate-acetonitrile (Et$_4$NBF$_4$-AN) electrolyte for 1 h to 
obtain the stretchable ACM/Et$_4$NBF$_4$-AN organic QPE.

**Characterization:** The swelling ratio of the crosslinked ACM membrane was 
calculated according to the following equation: \[ \text{swelling ratio} = \frac{(D_w - D_d)}{D_d} \times 100\% \], 
where \( D_d \) and \( D_w \) are the diagonal length of dry and swollen membranes, respectively.
The ACM/Et$_4$NBF$_4$-AN electrolyte uptake was calculated according to following 
equation: \[ \text{electrolyte uptake} = \frac{(W_w - W_d)}{W_d} \times 100\% \], where \( W_d \) is the dry weight of 
the crosslinked ACM membrane dried in a vacuum oven at 60 °C, and \( W_w \) is the wet 
weight of the crosslinked ACM membrane immersed in Et$_4$NBF$_4$-AN. The mechanical 
properties of the crosslinked ACM membranes were evaluated with a Zwick Roell 
testing system at a tensile speed of 100 mm min$^{-1}$. The ionic conductivity of the 
ACM/Et$_4$NBF$_4$-AN QPE was obtained by the blocking stainless steel 
(SS)/ACM/Et$_4$NBF$_4$-AN//SS model device using electrochemical impedance 
spectroscopy (EIS) with an AC amplitude of 5 mV from $10^5$ to 1 Hz. The ionic conductivity (\( \sigma \)) was calculated from the bulk resistance (\( R_b \), \( \Omega \)) according to following 
equation: \[ \sigma = \frac{L}{(R_b \times S)} \], where \( L \) is the thickness (cm) of the ACM/Et$_4$NBF$_4$-AN 
organic QPE, \( S \) is the effective contact area (cm$^2$), and \( R_b \) is obtained from the Nyquist plot.
Calculating the electronic conductivity of film electrodes: The conductivities of samples were determined by SX 1934 four-probe instrument using tailored rectangular film electrodes of $4 \times 2$ mm. Firstly, the thickness of the sheet sample was measured by electronic digital display micrometer. Then the conductivity of the sheet sample can be obtained according to the equation as follows:

$$\rho = \rho_0 G\left(\frac{W}{S}\right) D\left(\frac{d}{S}\right)$$

where $\rho_0$ is the resistivity measurement of sheet samples, $G\left(\frac{W}{S}\right)$ is the thickness correction function which can be obtained by looking up related tables, $W$ is the thickness of sheet samples ($\mu$m), $S$ is the probe spacing (1 mm), $D\left(\frac{d}{S}\right)$ is the correction function of the sample shape and measurement site. For a rectangular sheet sample of $4 \times 2$ mm, its corresponding $D\left(\frac{d}{S}\right)$ is 0.4301. Based on all above, the conductivities of all film electrode samples were obtained.

Calculating PDAA weight content of the ACM/MWCNTs@PDAA film based on TGA data: We used the mass residuals of ACM/MWCNTs, PDAA (71 wt% according to our previous work) and ACM/MWCNTs@PDAA at 800 °C for calculating the PDAA weight content ($X$) of the ACM/MWCNTs@PDAA composite film grown for 2 C cm$^{-2}$. According to the TGA curves (Figure 3d), the weight residuals of ACM/MWCNTs and ACM/MWCNTs@PDAA were read to be about 43 wt% and 50 wt%, respectively. The PDAA weight content ($X$) of the composite can be calculated by using the following equation: $0.43(1-X) + 0.71X = 0.50$. Thus, the PDAA weight content ($X$) of ACM/MWCNTs@PDAA was calculated to be 25 wt%.
Data analysis of electrochemical measurements: The specific capacitance of the three-electrode system \((C_s, \text{ F cm}^{-3})\) was calculated by using the following formula:

\[
C_s = \frac{I \Delta t}{VU}
\]

where \(I (\text{A})\) is the discharge current, \(\Delta t (\text{s})\) is the discharge time, \(V (\text{cm}^3)\) is the volume of the stretchable film electrode, and \(U (\text{V})\) is the potential window excluding IR drop.

The volumetric specific capacitances of the two-electrode cell configuration \((C_{cell}, \text{ F cm}^{-3})\) was calculated by using the following equations:

\[
C_{cell} = \frac{I \Delta t}{VU}
\]

where \(I (\text{A})\) is the discharge current, \(\Delta t (\text{s})\) is the discharge time, \(V (\text{cm}^3)\) is the total volumes of two electrodes and organic QPE, \(U (\text{V})\) is the potential window excluding IR drop.

The energy density \((E_{cell}, \text{ mW h cm}^{-3})\) and the power density \((P_{cell}, \text{ W cm}^{-3})\) for the two-electrode cell can be evaluated by using the following equations:

\[
E_{cell} = 0.5C_{cell}U^2/3.6
\]

\[
P_{cell} = 3.6E_{cell}/\Delta t
\]

in which \(C_{cell} (\text{F cm}^{-3})\) is the volumetric specific capacitance of the two-electrode cell, \(U (\text{V})\) is the potential window excluding IR drop, \(\Delta t (\text{s})\) is the discharge time.
Results and discussions

Fig. S1 Surficial FE-SEM images of ACM/MWCNTs films containing (a) 35 wt% MWCNTs and (b) 50 wt% MWCNTs.

Table S1 XPS results of crosslinked ACM, ACM/MWCNTs and ACM/MWCNTs@PDAA films for element content.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Element content (%)</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
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<tr>
<td>Crosslinked ACM</td>
<td>67.7</td>
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<tr>
<td>ACM/MWCNTs</td>
<td>66.3</td>
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<tr>
<td>ACM/MWCNTs@PDAA</td>
<td>75.8</td>
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**Fig. S2** Specific capacitances versus current densities for ACM/MWCNTs film electrode.

**Fig. S3** Specific capacitance (at 1 mA cm$^{-2}$) and capacitance retention (from 0 to 20 mA cm$^{-2}$) versus ACM/MWCNTs@PDAA films with various polymerization charge densities (1, 2 and 4 C cm$^{-2}$).
Fig. S4 (a) FE-SEM image of ACM/MWCNTs@PDA grown for 4 C cm$^{-2}$. (b) Nyquist plots and (c) Electronic conductivity of ACM/MWCNTs@PDA films grown for 1, 2 and 4 C cm$^{-2}$.

Fig. S5 Stress-strain curves of ACM/MWCNTs, ACM/MWCNTs@PDA grown for 2 C cm$^{-2}$ and ACM/MWCNTs@PANI grown for 3 C cm$^{-2}$. 
**Fig. S6** FE-SEM image of ACM/MWCNTs@PANI film (grown for 3 C cm$^{-2}$).

**Fig. S7** FTIR spectrum of ACM/MWCNTs@PANI film (grown for 3 C cm$^{-2}$).
Fig. S8 (a) Cyclic voltammograms at 10 mV s⁻¹, (b) Galvanostatic charge/discharge curves at 2 mA cm⁻² and (c) specific capacitance as a function of current densities from 1 to 10 mA cm⁻² of ACM/MWCNTs@PANI film electrodes with various polymerization charge densities (1, 3 and 5 C cm⁻²) in a three-electrode mode.
Fig. S9  (a) ACM membrane cross-linked with 4 wt% DETA after immersing in acetonitrile at 50 °C (The inserted photo shows the membrane before immersion). (b) Stress-strain curves and (c) Electrolyte uptake versus various immersion time for cross-linked ACM membrane with 4 wt% DETA.
Fig. S10 Nyquist plots of ACM/MWCNTs@PANI//ACM/Et$_4$NBF$_4$-AN//ACM/MWCNTs@PDA A oASSC (a) under static condition and (b) before and after 300 stretching cycles.