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 ℃ 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_4NBF_4-AN) electrolyte for 1 h to obtain the stretchable ACM/Et_4NBF_4-AN organic QPE.

Characterization: The swelling ratio of the crosslinked ACM membrane was calculated according to the following equation: $swelling\ ratio = (D_w - D_d)/D_d \times 100\%$, where D_d and D_w are the diagonal length of dry and swollen membranes, respectively. The ACM/Et_4NBF_4-AN electrolyte uptake was calculated according to following equation: $electrolyte\ uptake = (W_w - W_d)/W_d \times 100\%$, 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_4NBF_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_4NBF_4-AN QPE was obtained by the blocking stainless steel (SS)//ACM/Et_4NBF_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 (σ) was calculated from the bulk resistance (R_b, Ω) according to following equation: $\sigma = L/(R_b \times S)$, where L is the thickness (cm) of the ACM/Et_4NBF_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 × 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：

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

where ρ_0 is the resistivity measurement of sheet samples, $G(\frac{W}{S})$ is the thickness correction function which can be obtained by looking up related tables, W is the thickness of sheet samples (μm), S is the probe spacing (1 mm), $D(\frac{d}{S})$ is the correction function of the sample shape and measurement site. For a rectangular sheet sample of 4 × 2 mm, its corresponding $D(\frac{d}{S})$ 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, F cm^{-3}) was calculated by using the following formula:

$$C_s = I\Delta t/(VU)$$

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

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

$$C_{cell} = I\Delta t/(VU)$$

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

The energy density (E_{cell}, mW h cm^{-3}) and the power density (P_{cell}, 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} (F cm^{-3}) is the volumetric specific capacitance of the two-electrode cell, U (V) is the potential window excluding IR drop, Δt (s) is the discharge time.

Results and discussions

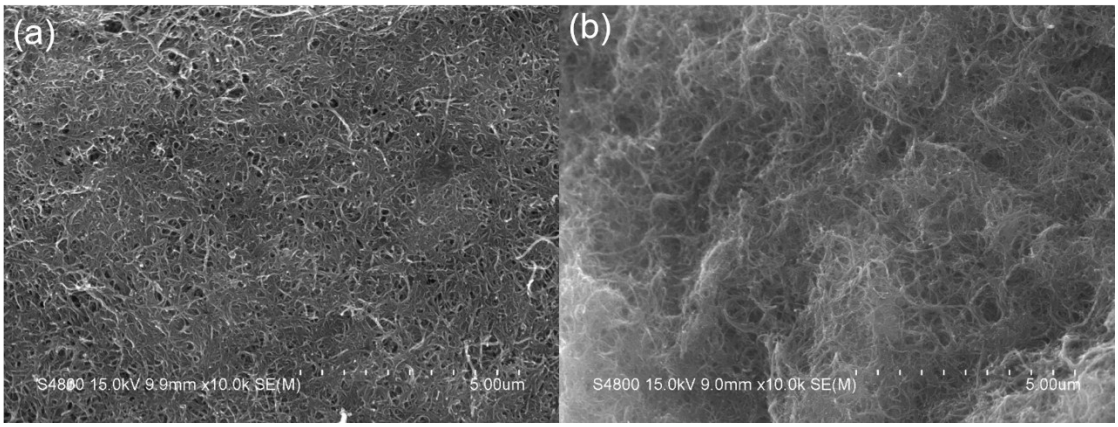

Fig. S1 Surficial FE-SEM images of ACM/MWCNTs films containing (a) 35 wt% MWCNTs and (b) 50 wt% MWCNTs.

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

Samples	Element content (%)		
	C	N	O
Crosslinked ACM	67.7	5.6	26.7
ACM/MWCNTs	66.3	6.5	27.2
ACM/MWCNTs@PDAA	75.8	9.4	14.8

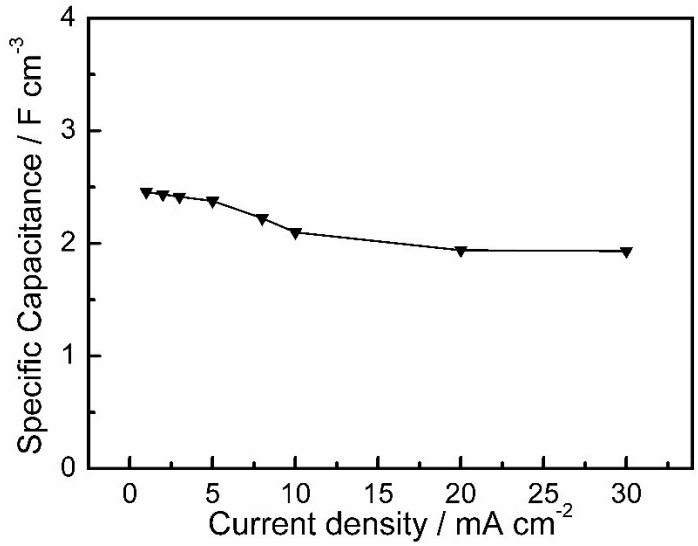

Fig. S2 Specific capacitances versus current densities for ACM/MWCNTs film electrode.

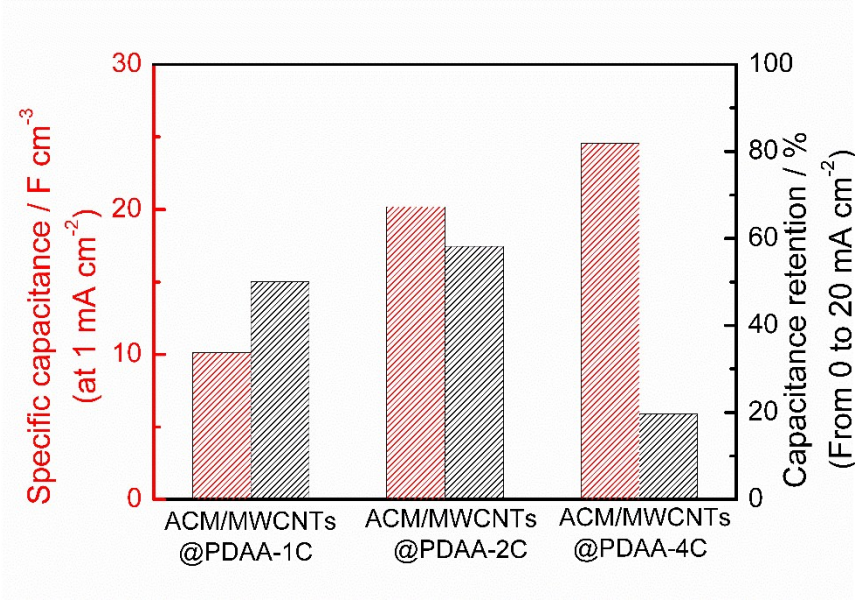

Fig. S3 Specific capacitance (at 1 mA cm^{-2}) and capacitance retention (from 0 to 20 mA cm^{-2}) versus ACM/MWCNTs@PDAA films with various polymerization charge densities (1, 2 and 4 C cm^{-2}).

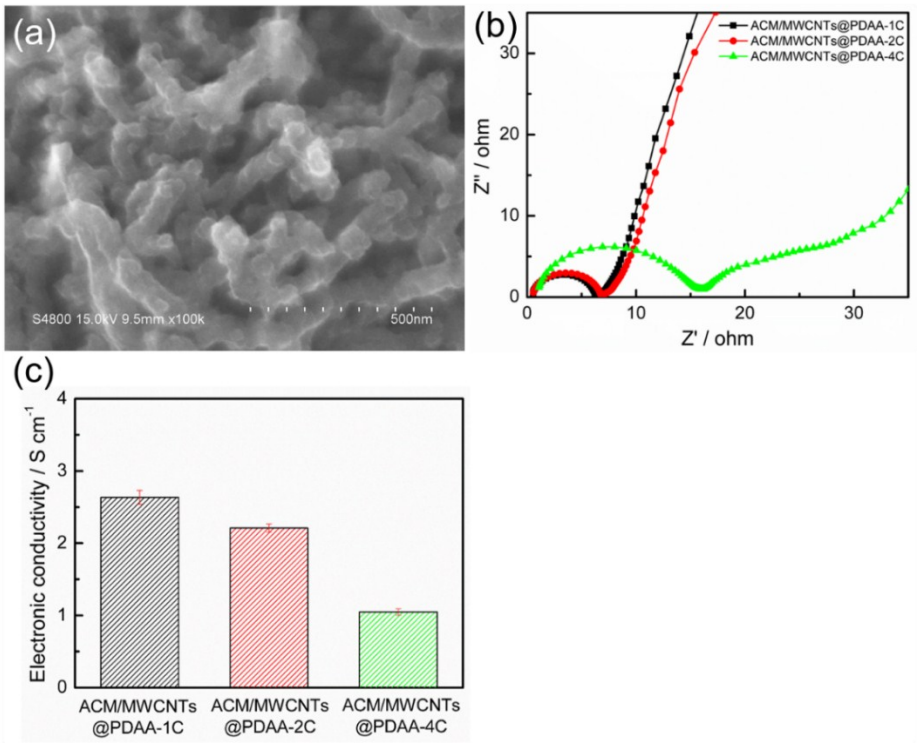

Fig. S4 (a) FE-SEM image of ACM/MWCNTs@PDAA grown for 4 C cm^{-2}. (b) Nyquist plots and (c) Electronic conductivity of ACM/MWCNTs@PDAA films grown for 1, 2 and 4 C cm^{-2}.

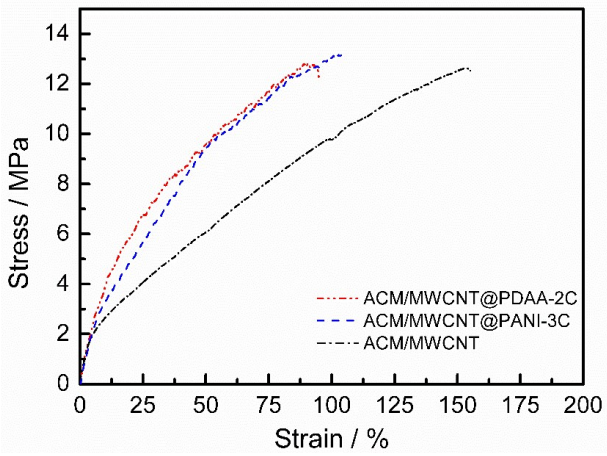

Fig. S5 Stress-strain curves of ACM/MWCNTs, ACM/MWCNTs@PDAA grown for 2 C cm^{-2} and ACM/MWCNTs@PANI grown for 3 C cm^{-2}.

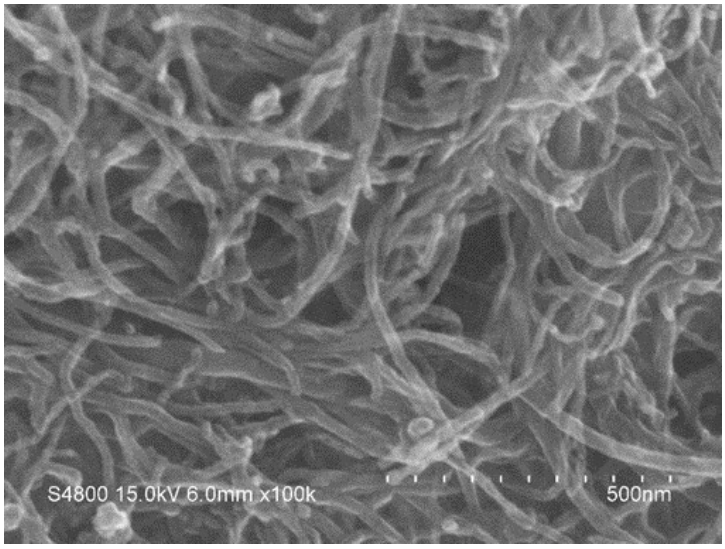

Fig. S6 FE-SEM image of ACM/MWCNTs@PANI film (grown for 3 C cm^{-2}).

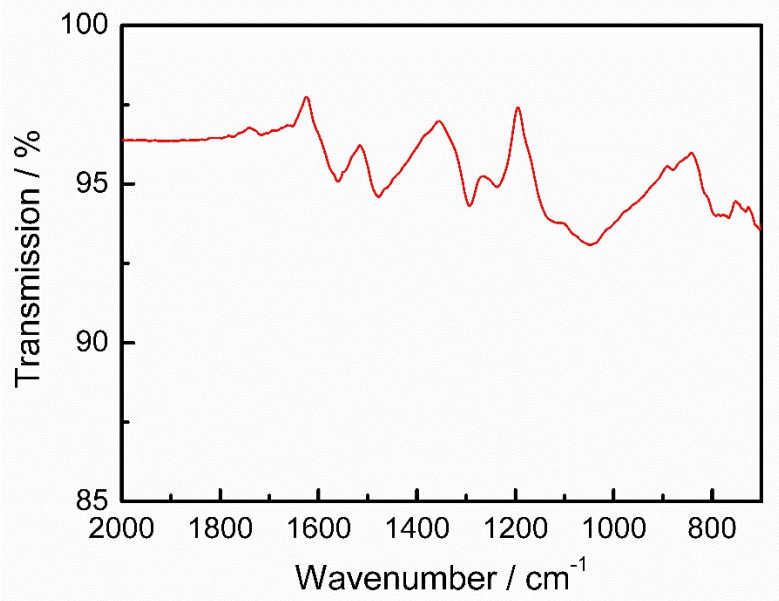

Fig. S7 FTIR spectrum of ACM/MWCNTs@PANI film (grown for 3 C cm^{-2}).

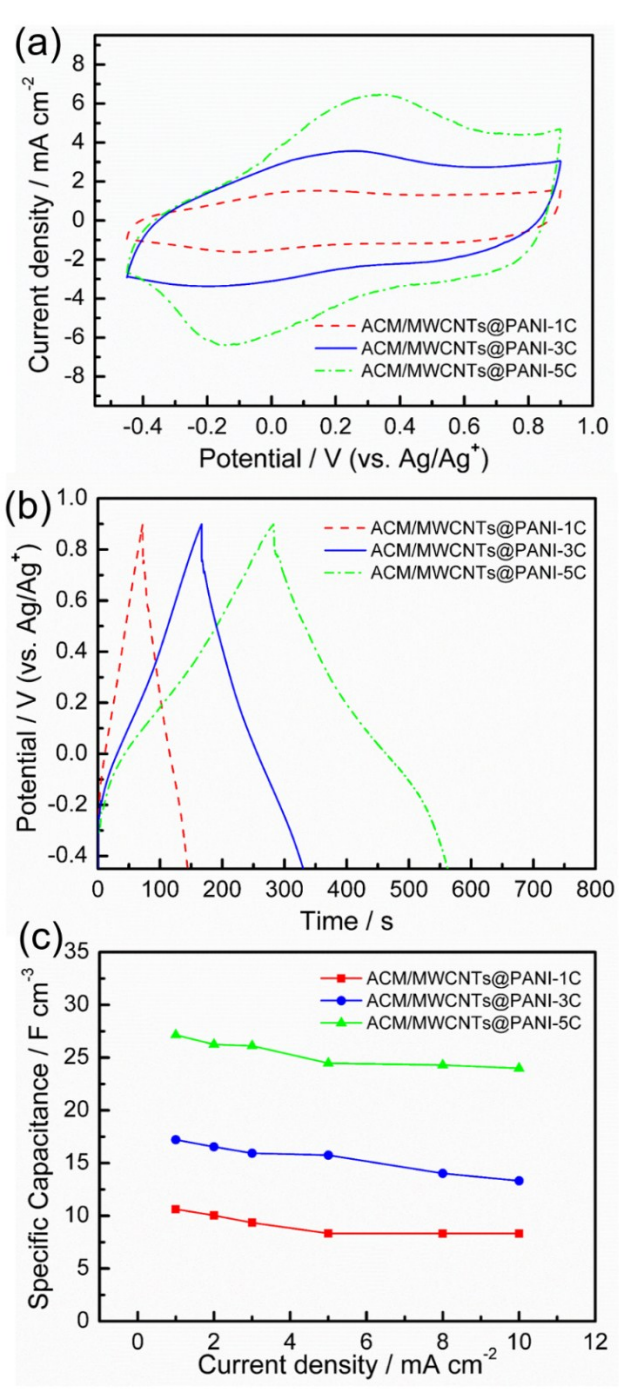

Fig. S8 (a) Cyclic voltammograms at 10 mV s^{-1}, (b) Galvanostatic charge/discharge curves at 2 mA cm^{-2} and (c) specific capacitance as a function of current densities from 1 to 10 mA cm^{-2} of ACM/MWCNTs@PANI film electrodes with various polymerization charge densities (1, 3 and 5 C cm^{-2}) in a three-electrode mode.

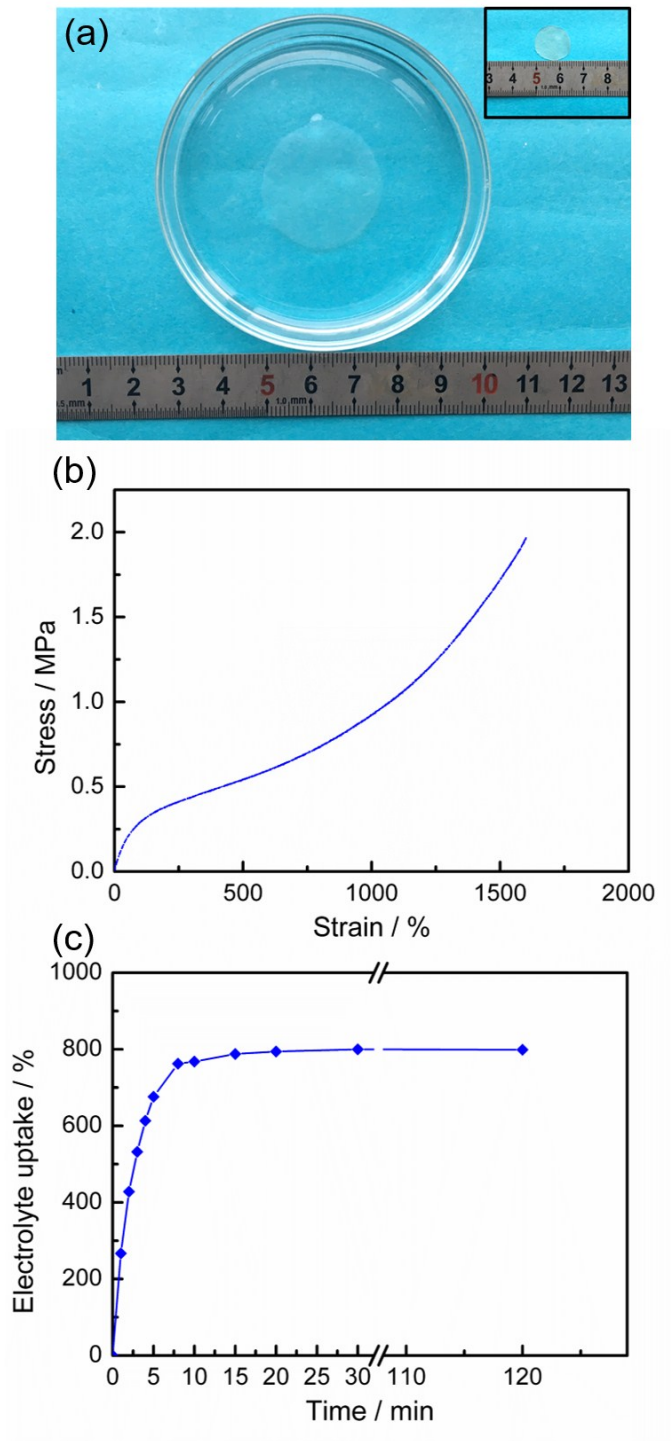

Fig. S9 (a) ACM membrane cross-linked with 4 wt% DETA after immersing in acetonitrile at 50 ℃ (The inserted photo shows the membrane before immersion). (b) Stress-strain curves and (c) Electrolyte uptake versus various immersion time for cross-linked ACM membrane with 4 wt% DETA.

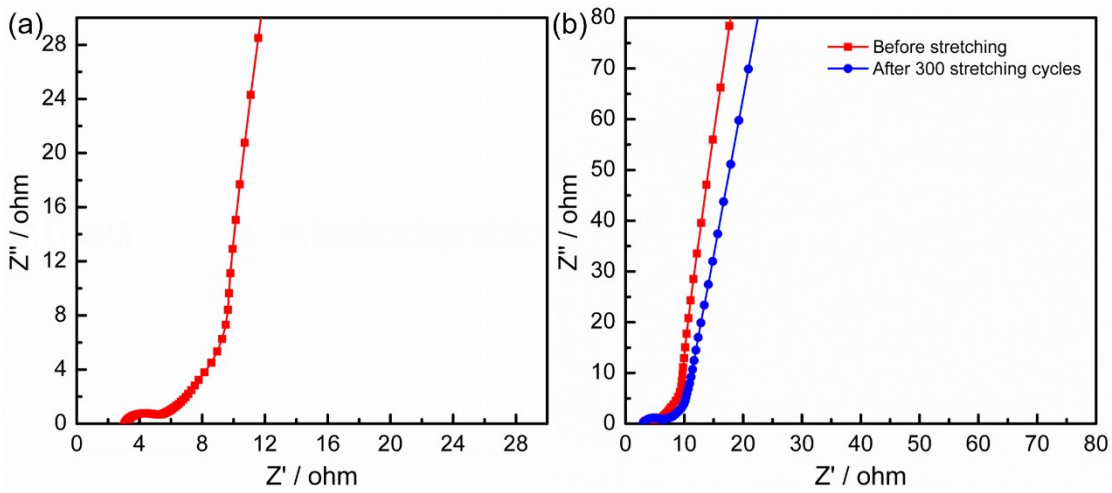

Fig. S10 Nyquist plots of ACM/MWCNTs@PANI//ACM/Et_4NBF_4-AN//ACM/MWCNTs@PDAA *o*ASSC (a) under static condition and (b) before and after 300 stretching cycles.