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Supporting Information

Polyampholyte-doped Aligned Polymer Hydrogel as Anisotropic Electrolytes for Ultrahigh-Capacity Supercapacitor

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1. Materials

Polyacrylamide (PAM, non-ionic, Mw: 2 million-14 million), Acryamide (AAm), Sodium acetate anhydrous (NaAc), Sodium acetate trihydrate ($NaAc\cdot 3H_2O$), and Polytetrafluoroethylene preparation (PTFE, 60 wt%) were purchased from Aladdin Industrial Co., 2-acrylamido-2-methyl propane sulfonic acid (AMPS) was purchased from Alfa Aesar, (3-methacrylamidipropyl) trimethyl ammonium chloride (MAPTAC) was obtained from Evonik, N,N'-Methylenebisacrylamide (MBAA) was purchased from Shanghai Energy Chemical Co., Ltd. 2,2-Diethoxy Acetophenone (DEAP) was purchased from TCI (Shanghai) Development Co., Ltd. Activated carbon powder (YP80F, 2100 m^2/g) was purchased from Kuraray Co. Acetylene black was purchased from Shanghai 3F New Material Co., Ltd. Ammonium sulfate ($(NH_4)_2SO_4$) was purchased from Sinopharm Chemical Reagent Co., Ltd.

2. Preparation of hydrogel electrolytes

Typically, the aligned-AAm hydrogel was prepared by the following method: Firstly, 0.75 g AAm, 2.25 mg MBAA, 10uL DEAP were dissolved in 4.25 mL distilled water. Then a certain quality of PAM (0, 20, 40, 60, 80, 100 mg) and 3.5 g NaAc were added to the above solution with continuous stirring at 60 ℃ for 2 h, forming a precursor solution with high concentration of NaAc and certain concentration of PAM (0.0, 0.4, 0.8, 1.2, 1.6, 2.0 wt%). After cooling to room temperature without any disturbance, a $NaAc\cdot 3H_2O$ crystal as seed was placed on the surface of the above mixture to initiate crystallization of supersaturated $NaAc\cdot 3H_2O$, forming extensive rod-like “hot ice” template within the mixture (Video 1). Then the hydrogel with template was obtained by UV light polymerization for 30 min. The employed UV lamp of Maxima ML-3500C (Spectronics Corp, USA) with high intensity of 22.4 mw/cm^2 at 365 nm. The template was removed by washing hydrogel with excess distilled water ten times. At last, the hydrogel was socked in 1 M $(NH_4)_2SO_4$ solution for three days after being sliced in vertical direction with a thickness of 0.3 mm by a blade, and the aligned-AAm gel electrolyte was obtained.

The aligned-PA gel electrolyte was obtained by the same process except replacing 0.75 g AAm with 0.25 g AAm, 0.25 g AMPS and 250 uL MAPTAC.

The non-aligned gel electrolyte was prepared by the following method: 0.75 g AAm, 2.25 mg MBAA, 10uL DEAP were dissolved in 4.25 mL distilled water. Then a certain quality of PAM (0, 20, 40, 60, 80, 100 mg) was added to the above solution with continuous stirring at room temperature for 2 h, forming a precursor solution with certain concentration of PAM (0.0, 0.4, 0.8, 1.2, 1.6, 2.0 wt%). Then the hydrogel was obtained by UV light polymerization for 30min. At last, the hydrogel was socked in 1M $(NH_4)_2SO_4$ solution for three days after being sliced with a thickness of 0.3 mm by a blade, and the non-aligned gel electrolyte was obtained.

3. Characterizations

3.1. Optical microscope observation

The supersaturated precursor solution with certain concentration of PAM was dripped on a glass slide, and initiated to crystallize by a seed crystal at room temperature. The morphology and size of "hot ice" template were observed by optical microscope (AMG EVOS, America).

3.2. SEM Measurement

The gel sample was freeze-dried by refrigerated drying chamber (Scientz-10N, Ningbo, China) for two days. After that, the sample was sputter-coated with a thin layer of gold. Finally, the scanning electron microscope (Hitachi S-4800, JEOL, Tokyo, Japan) was employed to observe the surface structure of the samples at a voltage of 3 kV.

3.3. Rheological Measurement

The intrinsic viscosity of the precursor solution without NaAc was measured by Thermo Haake Rheostress RS6000 rheometer (Thermo Scientific, Karlsruhe, Germany) at 25 ℃. Steady rheological behaviors were performed ranging from 1 to

300 1/s. With the increase of PAM concentration from 0 wt% to 4 wt%, the intrinsic viscosity increases from 0.035 to 20.8 Pas.

3.4. Swollen Measurement

There is a swelling behavior when hydrogel is immersed in water. In order to evaluate it, the maximum swollen ratio was measured. Briefly, a non-aligned hydrogel with a known volume (V_0) was kept in distilled water, and measured the volume at intervals (V_t). The swollen ratio (ε) is defined as $\varepsilon = (V_t - V_0)/V_0$. After three days, the hydrogel reached maximum swollen ratio of 1.68.

3.5. FTIR measurement

The freeze-dried aligned-AAm gel and aligned-PA gel were measured by a Thermo Scientific Nicolet IS10 FTIR spectrometer in the wavenumbers range of 4000 to 400 cm^{-1} with KBr powder in a resolution of 0.4 cm^{-1}.

3.6. Mechanical measurement

The compressive stress-strain properties of hydrogel were measured by an electronic universal testing machine (UTM2502, Shenzhen Suns Technology CO., LTD.).The compressive test of the cylindrical samples, 13 mm in diameter and 6-10 mm in thickness, were carried out at the speed of 1 mm/min with 95% strain. And the compression recovery test was performed at a speed of 0.5 mm/min with 90% strain.

3.7. Ionic conductivity measurement

The ionic conductivity of hydrogel electrolytes were measured by AC impedance technique. In this experiment, the cylindrical electrolyte samples were sandwiched between two stainless steel electrodes and firm contact was ensured. The measurements were carried out by Metrohm Autolab PGSTA302N (The Netherlands) in the frequency range of 100 kHz to 10 Hz at room temperature. The intersection of the curve at the real part is taken as the bulk resistance of the hydrogel electrolyte (R_b), and the ionic conductivity of the sample is calculated according to the following equation:

$$\sigma = \frac{L}{AR_b} \qquad \text{[Equation S1]}$$

where L is the thickness of the hydrogel electrolyte and A is the electrode area.[1]

4. Electrochemical performances of solid state supercapacitors

4.1. Preparation of electrodes

The commercial activated carbon (YP 80F) was selected to prepare the electrodes of solid state supercapacitors as active material. Typically, the porous electrodes were prepared with a slurry mixture of activated carbon powder, PTFE binder (60%), and acetylene black (with a w/w ratio of 8:1:1). Then the mixture was spread on a titanium stainless steel collector. At last, the electrodes with mass loading of about 4 mg/cm^2 were obtained after being dried in a vacuum at 120 ℃ for 24 h.

4.2. Fabrication and characterization of solid state supercapacitors

The solid state supercapacitors were fabricated with the commercial activated carbon and hydrogel electrolytes. The cyclic voltammetry, chronopotentiometry and AC impedance measurements were measured by the Metrohm Autolab PGSTA302N coupled with a computer at room temperature. The cyclic voltammetry and galvanostatic charge–discharge curves were carried out at different scan rates and current densities, respectively. The cycling stability of the supercapacitors was performed at room temperature with a sweep charge and discharge rate at the current density of 1 $A\cdot g^{-1}$ for 10000 cycles by LAND CT2001A (Wuhan LAND Electronics CO., LTD).

The specific capacitance of the supercapacitor can be calculated from the cyclic voltammogram curves:

$$C_S = \frac{2S}{mv\Delta U} \qquad \text{[Equation S2]}$$

Where C_S is the specific capacitance, S is enclosed area of curves, m is the active material mass of the electrode, v is the potential scan rate, ΔU is the potential window.

C_S can also be calculated from the galvanostatic charge–discharge curves:

$$C_S = \frac{4I\Delta t}{m\Delta U} \qquad \text{[Equation S3]}$$

Where I is the discharge current, Δt is the discharge time, m is the active material mass of the electrode, ΔU is the voltage after *IR* drop.[2]

The energy density and power density are calculated using the following equations:

$$E = \frac{C_S \Delta U^2}{8} \qquad \text{[Equation S4]}$$

$$P = \frac{E}{\Delta t} \qquad \text{[Equation S5]}$$

Where E is the energy density, C_S is the specific capacitance calculated from Equation S3, ΔU is the voltage after *IR* drop, P is power density and Δt is the discharge time.[3]

References

[1] Liu, X. H.; Wu, D. B.; Wang, H. L.; Wang, Q. G., *Adv Mater* **2014,** *26* (25), 4370-4375.

[2] Yang, P. H.; Mai, W. J., *Nano Energy* **2014,** *8*, 274-290.

[3] Kang, Y. J.; Chun, S. J.; Lee, S. S.; Kim, B. Y.; Kim, J. H.; Chung, H.; Lee, S. Y.; Kim, W., *Acs Nano* **2012,** *6* (7), 6400-6406.

5. Figures

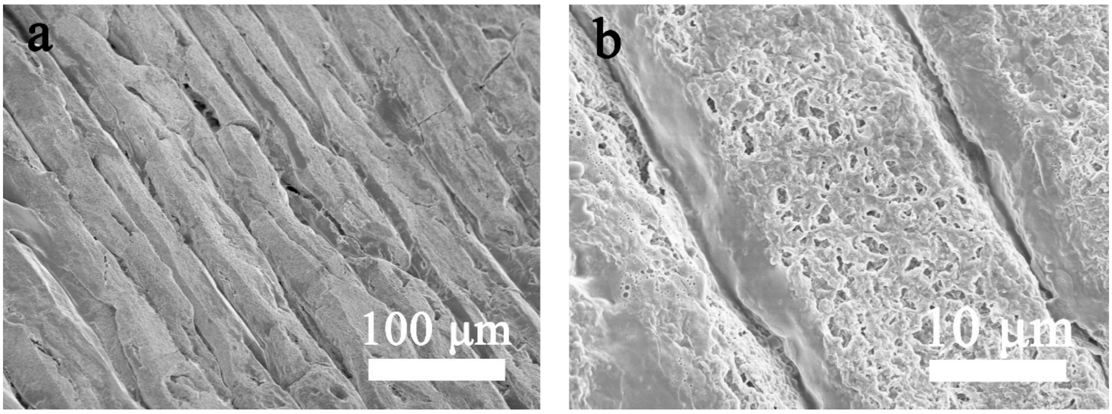

Fig.S1 SEM images of aligned NaAc·3H_2O crystal within freeze-dried gel.

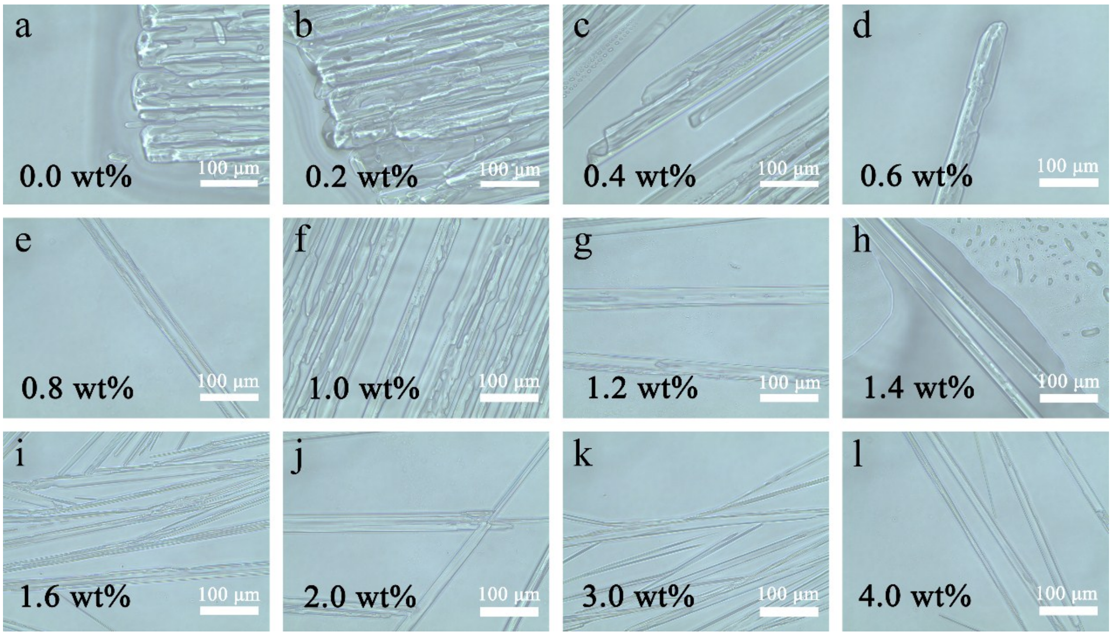

Fig.S2 Optical microscope images of the aligned NaAc·3H_2O crystals.

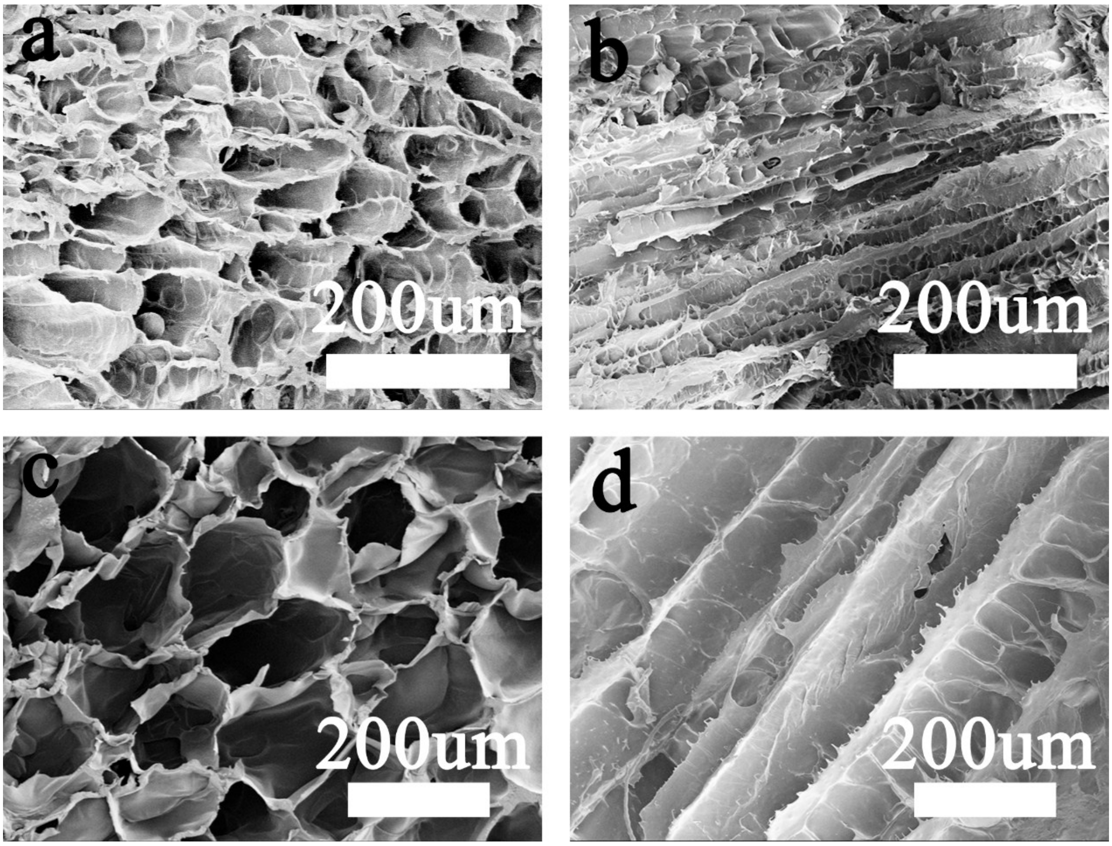

Fig.S3 (a) SEM image of the aligned pores within aligned-AAm-2 wt% gel at vertical-pore direction. (b) SEM image of the aligned pores within aligned-AAm-2 wt% hydrogel at parallel-pore direction. (c) SEM image of the aligned pores within aligned-AAm-0 wt% hydrogel at vertical-pore direction. (d) SEM image of the aligned pores within aligned-AAm-0 wt% hydrogel at parallel-pore direction.

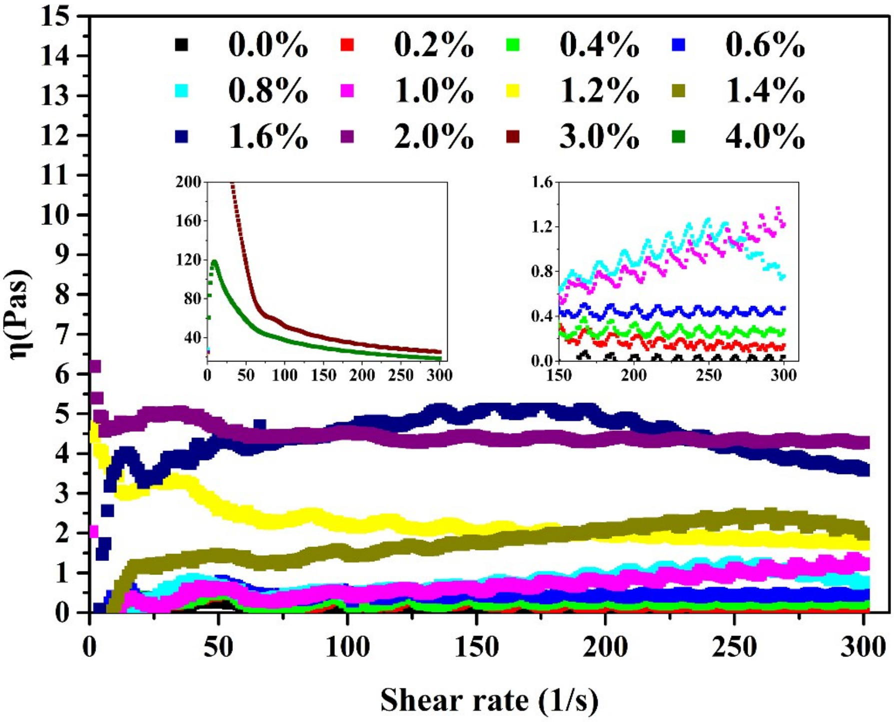

Fig.S4 The intrinsic viscosity of the precursor solution with different PAM concentration (0 wt%-4 wt%).

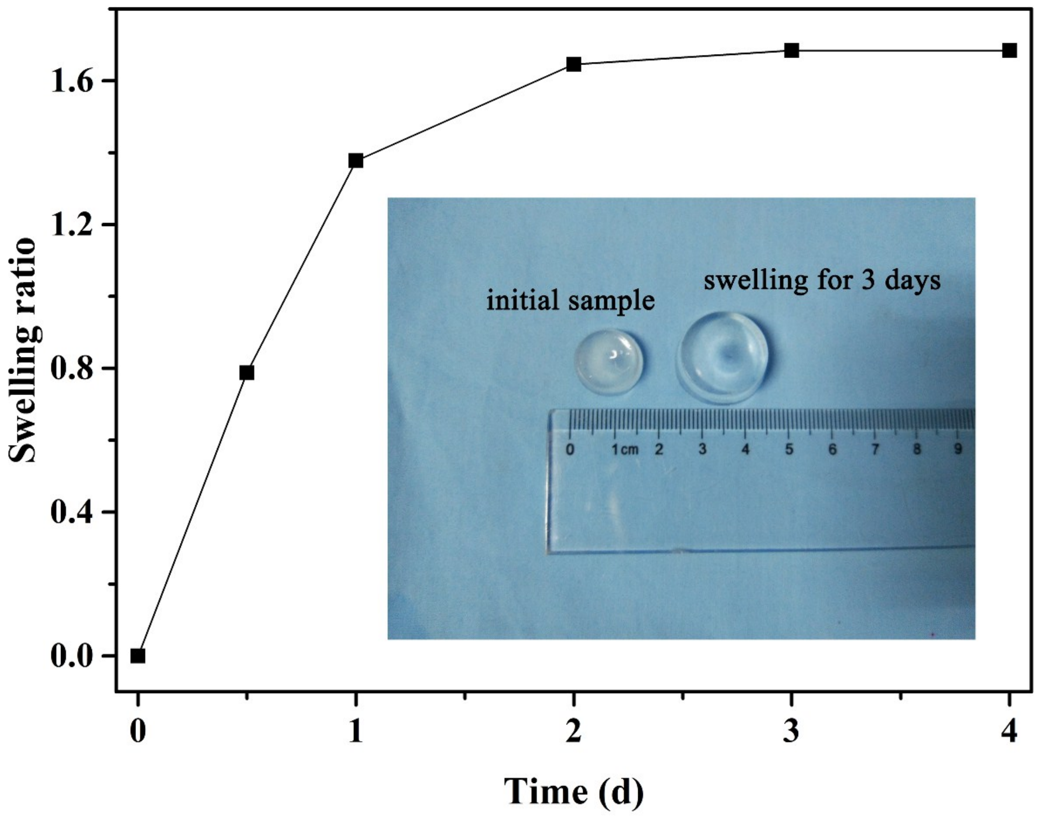

Fig.S5 The swelling behavior of the non-aligned-2 wt% hydrogel. Insert: the contrast of original hydrogel and the hydrogel immersing for 3 days.

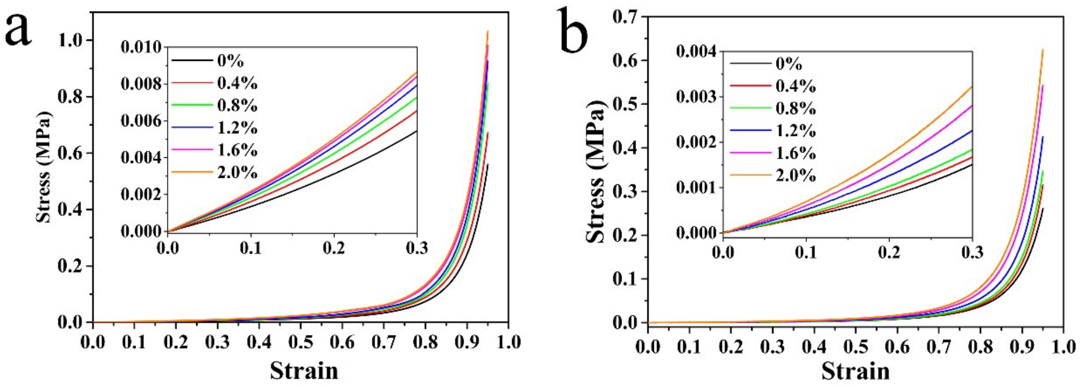

Fig.S6 (a) Compressive curves of the non-aligned hydrogel with different PAM contents. (b) Compressive curves of the aligned-AAm hydrogel with different PAM contents.

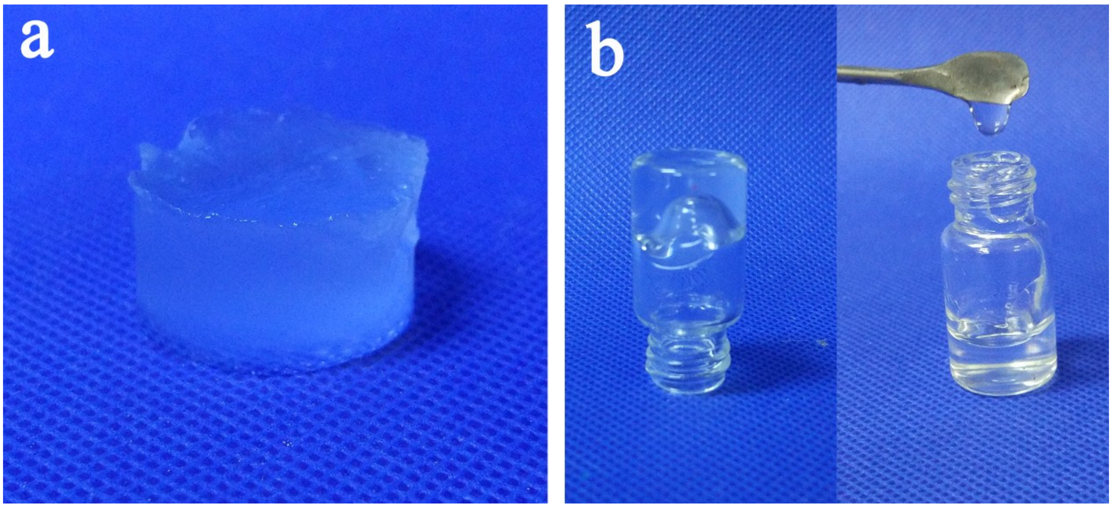

Fig.S7 (a) Photo of aligned-PA hydrogel. (b) Photo of PVA/H_3PO_4 gel.

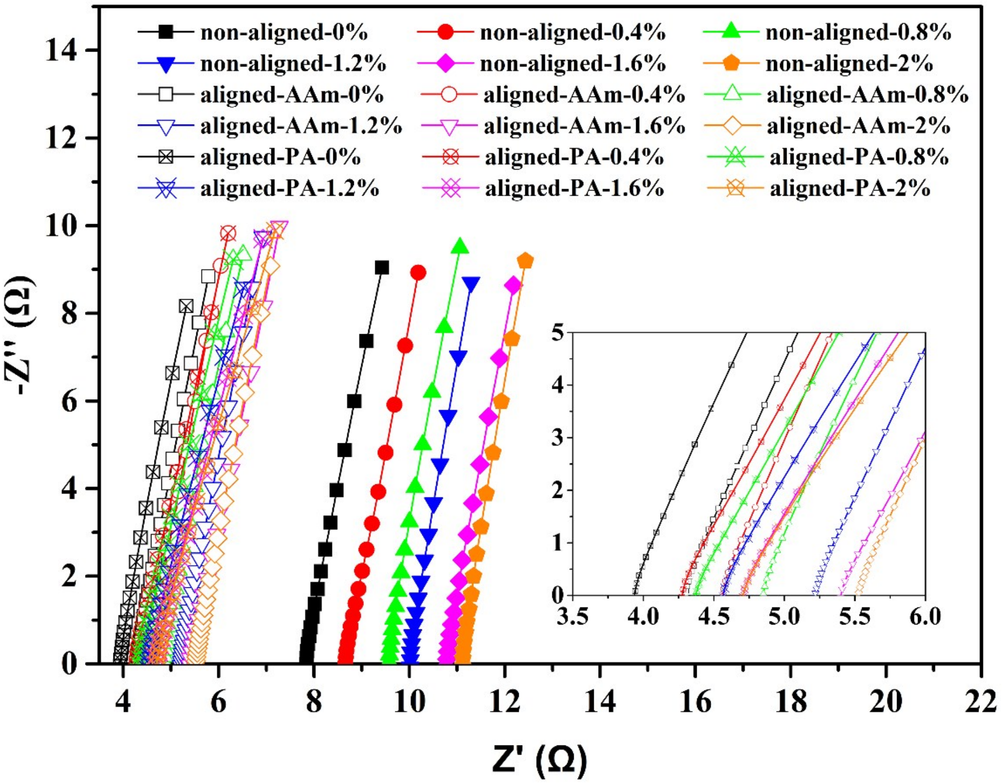

Fig.S8 The frequency dependent impedance plots of gel electrolytes with different structure.

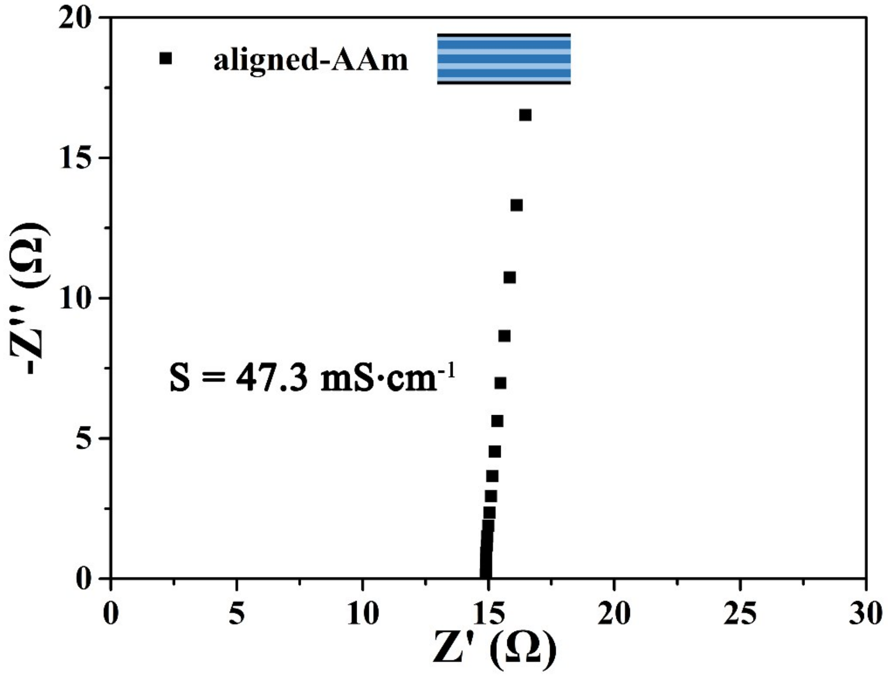

Fig.S9 The frequency dependent impedance plots and ionic conductivity of aligned-AAm-0 wt% gel electrolytes at parallel direction with size of 10×10×7 mm.

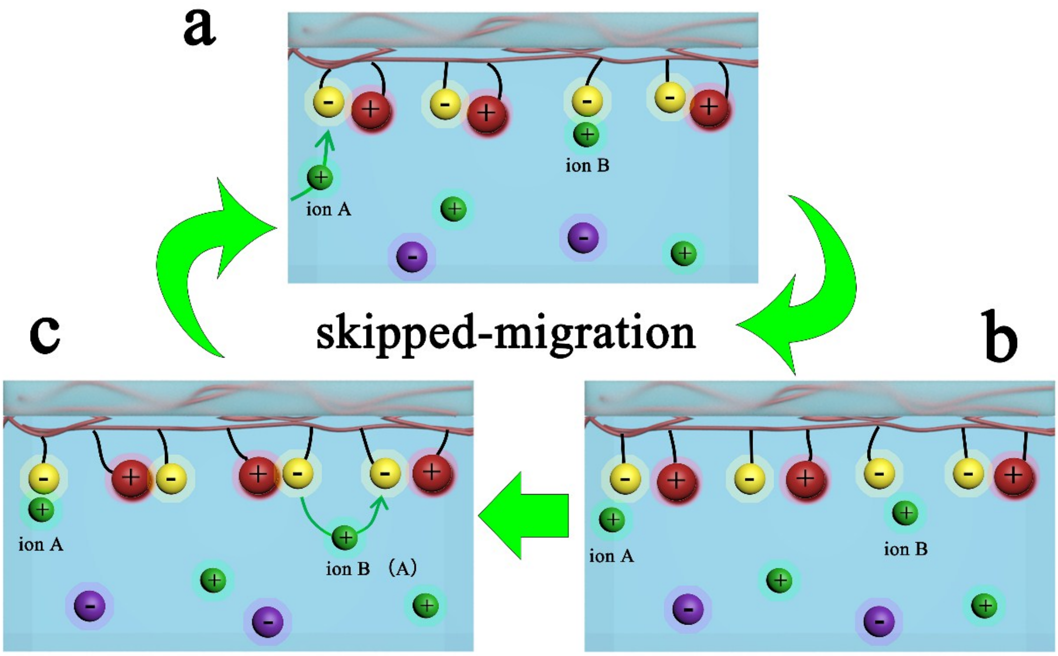

Fig.S10 Schematic of skipped-migration. (a) A free ion A is close to the ion pair of amphoteric groups on the polymer chain. (b) The primal charge balance is destroyed. (c) New balance is formed through the charge redistribution, and a new free ion B is released in the distance and next cycle is triggered simultaneously.

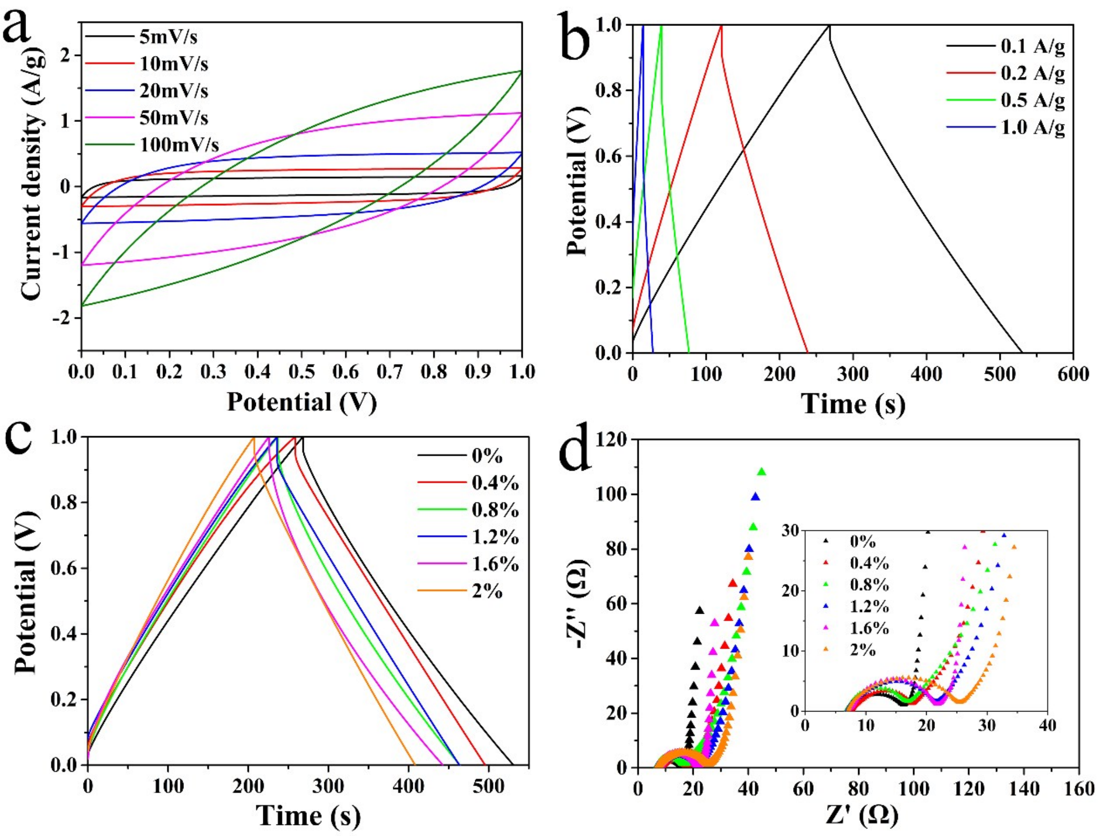

Fig.S11 (a) Cyclic voltammetry curves of non-aligned-0 wt% based supercapacitor at scan rate from 5 mV·s^{-1} to 100 mV·s^{-1}. (b) Galvanostatic charge–discharge curves of the non-aligned-0 wt% based supercapacitor at current density from 0.1 to 1.0 A·g^{-1}. (c) Galvanostatic charge–discharge curves of non-aligned based supercapacitors with different PAM concentration at 0.1 A·g^{-1}. (d) The Nyquist plots of non-aligned based supercapacitors with different PAM concentration.

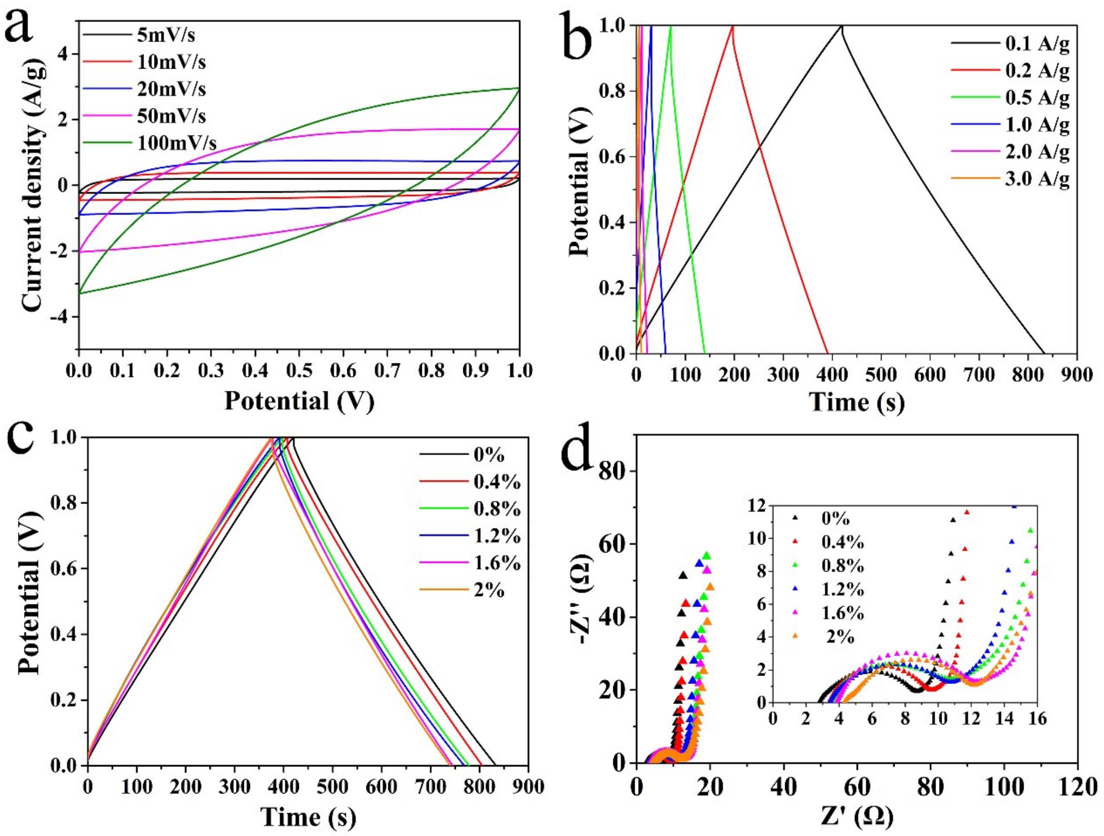

Fig.S12 (a) Cyclic voltammetry curves of aligned-AAm-0 wt% based supercapacitor at scan rate from 5 mV·s^{-1} to 100 mV·s^{-1}. (b) Galvanostatic charge–discharge curves of the aligned-AAm-0 wt% based supercapacitor at current density from 0.1 to 1.0 A·g^{-1}. (c) Galvanostatic charge–discharge curves of aligned-AAm based supercapacitors with different PAM concentration at 0.1 A·g^{-1}. (d) The Nyquist plots of aligned-AAm based supercapacitors with different PAM concentration.

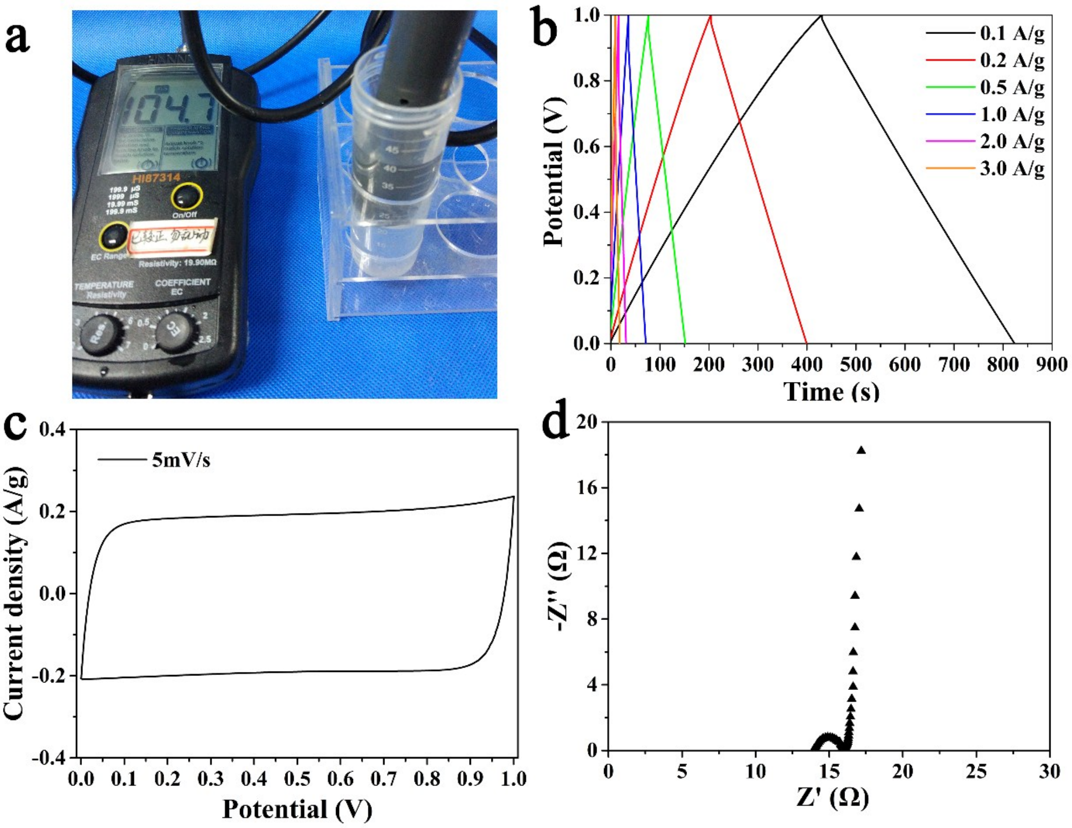

Fig.S13 (a) Ionic conductivity of 1 M $(NH_4)_2SO_4$ solution. (b) Galvanostatic charge–discharge curves of the liquid electrolyte based supercapacitor at current density from 0.1 to 3.0 $A\cdot g^{-1}$. (c) Cyclic voltammetry curve of liquid electrolyte based supercapacitor at 5 $mV\cdot s^{-1}$. (d) The Nyquist plots of liquid electrolyte based supercapacitor.

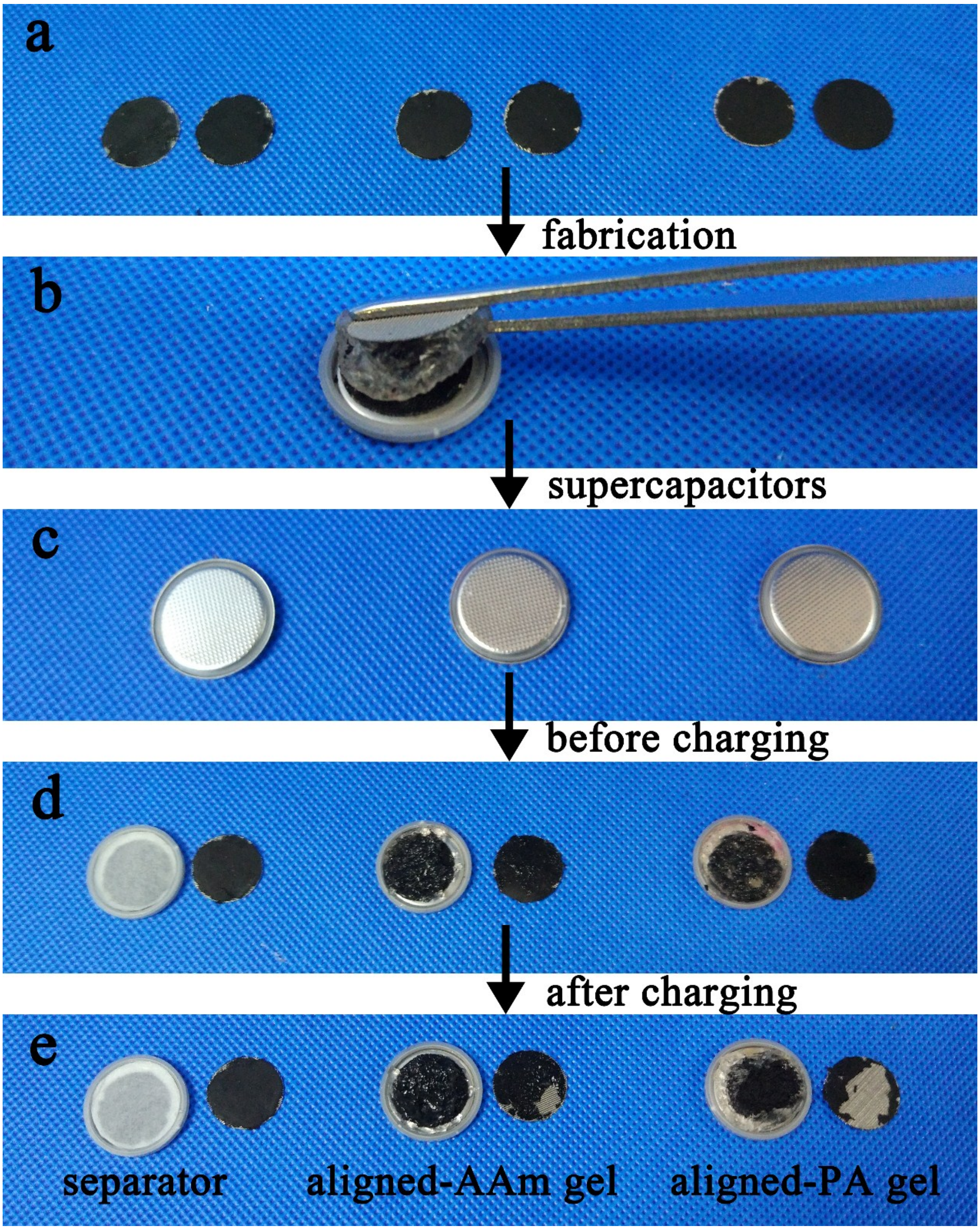

Fig.S14 Adhesion test. (a)The electrodes before fabricating with electrolytes. (b) The fabrication process. (c) The supercapacitors. (d) The electrodes of supercapacitors before charging. (e) The electrodes of supercapacitors after charging.