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Supplementary Information

Elastic Ionogels with Freeze-aligned Pores Exhibit Enhanced Electrochemical Performances as Anisotropic Electrolytes of All-solid-state Supercapacitors

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1. Materials

1-N-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$), 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide (BMIMTFSI), and 1-butyl-3-methylimidazolium terafluoroborate ($BMIMBF_4$) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. TiO_2 was procured from Dekedaojin (Beijing) Co., Ltd. Poly (ethylene glycol) methacrylate (PEGMA, Mn=500) and Poly (ethylene glycol) dimethacrylate (PEGDA, Mn=700) were procured from Sigma Chemical Co., Ltd. Acetylene black and polytetrafluoroethylene (PTFE, 60 wt% aqueous dispersion) were obtained from Shanghai 3F New Material (Shanghai) and Aladdin Chemistry Co., Ltd.

2. The preparation of ionogels

Typically, 10 mg of PEGMA (PEGDA) was added to a stirred suspension of TiO_2 (5 mg) in ionic liquid (895 mg). After 30 minutes, the suspension turned to a uniform solution. The precursor was directional freezing at the moving rate of 2 mm/min with the help of a precision bath circulator and tensile-compressive tester. Afterwards, the preparation of the ionogel can be realized by the self- triggerd UV light polymerization for 2.5 hours at -18 ℃ refrigerator. The UV lamp was cold point light-source (Shanghai Huijun Science＆Technology Devel Opment Co., Ltd), which could produce a high intensity of 99.8 mw/cm^2 at 365 nm. A tensile-compressive tester was used to prepare the aligned ionogel. The precursor was directionally frozen in low temperature solvent (-18 ℃) at the rate of 2 mm/min. The low temperature was controlled by a thermostatic bath (Ningbo Tianheng Instrument Factory, THD-4006H) with the solvent of ethanol. Then the precursor can transfer from a liquid state to a solid state. To obtain the aligned ionogel with further frozen treatment, we frozen the precursor in liquid nitrogen after its first freezing process. Afterwards, the aligned ionogel can be prepared via UV light polymerization for 2.5 hours with an ambient temperature of -18 ℃. Also the non-aligned ionogel was prepared through UV light polymerization for 2.5 hours at -18 ℃ but without the directional freezing process.

3. Pre-treatments and characterizations

3.1 Pre-treatment of Scanning Electron Microscope (SEM) samples

The ionogel samples for SEM analysis were firstly put into acetone for long maceration periods of ten days (the acetone was changed two times a day). Then the acetone was changed to water. After that, the samples were cut into small cubes and dried via vacuum-freeze drying (Freezing Dryer, Scientz–10N, Ningbo Scientz Biotechnology Co., Ltd.). The samples with dry polymer structures were obtained after the vacuum-freeze drying treatment. Then, the above samples were coated with a thin layer of gold by the conductive coating process (with a thickness of about 5 nm). Finally, the polymer structures of the samples were observed by scanning electron microscope (S-4800, Hitachi High-Technologies Corporation, Tokyo, Japan) at the voltage of 1 kV.

3.2 Electron Paramagnetic Resonance (EPR) measurement

The EPR test was monitored by the EPR Spectrometer (A300, Bruker Instruments, Inc.) and operated at 9.873 GHz (modulation frequency: 100 kHz; microwave power, 20 mW; receiver gain: 4×10^5; modulation amplitude: 0.5 G). The feasibility of the UV light initiated free radical reaction can be proved by spin trapping and electron paramagnetic resonance technique. The monomer radical can promote the long-lived propagating radical which can be seen in the EPR spectrum of the $BMIMPF_6$ solution of TiO_2-NPs and PEGMA/PEGDA after UV irradiation. The precursor mixture was firstly placed in the EPR tester and irradiated by UV light with an average intensity of 25.0 mw/cm^2 at 365 nm). The spectrum recorded the signals after 6 minutes.

3.3 Mechanical Measurement

The compressive measurements of the ionogels were monitored by a tensile-compressive tester (FR-108B, Farui Co.). The ionogel samples were set on the lower plate, after that, the samples were compressed by the upper plate at the speed of 1 mm/min. The ionogels with 0.1 wt%

and 1 wt% TiO_2 were tested with 12 mm in diameter and 2 mm in thickness because they can hardly be shaped. Others were tested with 12 mm in diameter and 10 mm in thickness. Besides, every test was repeated for three times.

3.4 Rheological Measurement

The rheological experiments were performed on a Thermo Haake Rheostress RS6000 rheometer (Thermo Scientific, Karlsruhe, Germany) with parallel-plate geometry (with diameter of 20 mm and a gap of 1 mm). To understand the gelation kinetics, the storage modulus (G') and loss modulus (G'') were monitored as a function of time. The dynamic time sweep of the precursor containing 89.5 wt% $BMIMPF_6$, 0.5 wt% TiO_2-NPs, and 10 wt% monomers was initiated under UV light (23.5 mw/cm^2 at 365 nm) at a fixed strain of 1% and a constant frequency of 1 rad s^{-1}. To further confirm the gelation behavior of the samples, the frequency-dependent storage modulus (G') and loss modulus (G'') were carried out by a rheometer. The frequency sweep curves of the ionogels through cryopolymerization with TiO_2 contents of 0.25 wt% and 0.5 wt% were tested with a frequency range from 1 to 100 rad s^{-1} and a fixed strain of 1%. However, the samples with too little or too much TiO_2 were very weak in mechanical strength. As for the aligned ionogel, the frequency sweep curves was carried out at a fixed strain (γ = 1%) with a frequency range from 1 to 100 rad s^{-1}.

3.5 Thermogravimetric Trace (TGA)

The reaction mixtures were obtained with different reaction time, and about 5 mg of the above samples was put in a hermetically sealed aluminum oxide pan. The experiments were carried out under nitrogen atmosphere at the heating rate of 15 ℃/min with the temperature range from room temperature to 600 ℃. Because of the negligible vapor pressure of the ionic liquid, for our ionogels where the ionic liquid is the solvent and is thermal stable, the mass loss of volatiles below 250 ℃ can be attributed to the unreacted monomers which can be detected by TGA.[1,2] Therefore, the TGA measurement can be used as effective method to monitor the conversion of the cryopolymerization reaction of ionogel which involves no volatile compositions. Therefore, the conversion of the monomers for our ionogel can be estimated by TGA method.

3.6 Brunauer–Emmett–Teller (BET) Measurement

The nitrogen adsorption–desorption isotherms of carbon nanocages were measured at 77 K by an automatic adsorption instrument (TRISTAR3000, MICROMERITICS). The average pore diameters and specific surface areas were calculated according to Brunauer–Emmett–Teller (BET) equation. Additionally, the pore size distribution was obtained by Barrett–Joyner–Halenda (BJH) method.

3.7 Mercury Intrusion Measurement

Because the N_2 adsorption measurements cannot measure big pores that are much larger than 20 nm, the pore size and distribution were complemented by Hg porosimetry (AutoPore IV 9500).

The porosity was obtained by utilizing ethanol to go into the pores. The ethanol was used as the displacement liquid because it can easily penetrate into the polymer pores without inducing shrinkage or swelling as a nonsolvent of the polymers.[3] The porosity was measured according to the following equation:

$$\text{porosity}(\%) = \frac{volume\ occupied\ by\ ethanol}{voclume\ of\ polymer + volume\ occupied\ by\ ethanol}$$

4. Electrochemical properties of ionogel electrolytes

4.1 Preparation of Electrodes

Carbon nanocages were prepared and used as electrode materials. The electrodes were prepared with the mixture of carbon nanocage powder, polyvinylidene fluoride (PVDF, 2.5 wt% emulsion), and acetylene black with a w/w ratio of 80:10:10. The electrodes were dried in vacuum at 120 ℃

for 24 h (with a mass loading of about 1 mg cm^{-2}). The titanium plating stainless steel wire (500 mesh) was selected as current collector. Finally, the electric double layer supercapacitor can be fabricated using two electrodes and an ionogel electrolyte.

4.2 Electrochemical Measurements

Cyclic voltammetry, alternating current impedance sectroscopy, and chronopotentiometry were monitored by a Metrohm Autolab PGSTA302N potentiostats-galvanostats (The Netherlands). The non-aligned and aligned ionogels were prepared with the same precursors. The difference is the freezing treatment, the non-aligned ionogels (without directionally freezing process) and aligned ionogels (with directionally freezing process). The ionogels were fabricated and tested as electrolytes of supercapacitors. All of the ionogels were placed in vacuum oven at 120 °C for 24 hours to remove the possible absorbed water before the fabrication.

All the comparable properties were obtained under the same conditions, including the same electrodes, the same test conditions, etc. All the tests about the aligned ionogels were performed with the vertical direction. Only in the anisotropic resistivity measurements, the vertical direction was named aligned-2 and parallel direction was named aligned-1. And the electrochemical property of the ionic liquid based supercapacitor was obtained in pure ionic liquid electrolyte without separator.

The supercapacitors were fabricated in button batteries with the force of about 0.2 N, cross-sectional area =2 cm^2, and ionogel thickness=100 um. All of the supercapacitors were hold for 12 h before testing. To measure the mechanical and electrochemical robustness, the supercapacitors were packaged in a square with polyethylene terephthalate film (2 cm * 1 cm).

In the low temperature tests, every sample was first put in -18 ℃ refrigerator. The high temperature behaviour of the supercapacitor was performed in the oven, and the device was hold for 1 h before the test at various temperatures.

In AC impendence tests, the supercapacitors were assembled in button batteries (area=2 cm^2, ionogel thickness=100 um). AC impedance measurements were employed to measure ionic conductivity of the ionogels. The ionogel electrolytes were SS/electrolyte/SS (stainless steel electrode: SS) sandwiched structured coupled with a polytetrafluoroethylene (PTFE) spacer which can provide a circular hole to hold the ionogel electrolyte. The tested samples were placed in a water-controlled furnace. The non-aligned and aligned samples are in the same sizes through comparative experiments. The AC impendence tests were measured over the frequency range of 100 kHz to 0.1 Hz.

The conductivity of the electrolyte is calculated according to the Equation:

$\sigma=l/(AR_b)$

where R_b is the resistance of the bulk electrolyte, l is the thickness of the gel and A is the area of electrode covered by gel.[4]

For porous gels, the resistance (R) can be described as

$$R=\tau\rho l/A \qquad \text{[Equation S1]}$$

where τ is the tortuosity and $\tau > 1$, ρ is the resistivity, l is the length, and A is the cross-sectional area.[5]

The tortuosity of the non-aligned ionogel ($\tau_{non\text{-}aligned}$) was assumed to be larger than the vertical aligned ionogel ($\tau_{aligned\text{-}2}$), resulting in resistances $R_{non\text{-}aligned} > R_{aligned\text{-}2}$.

5. References

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6. Figures

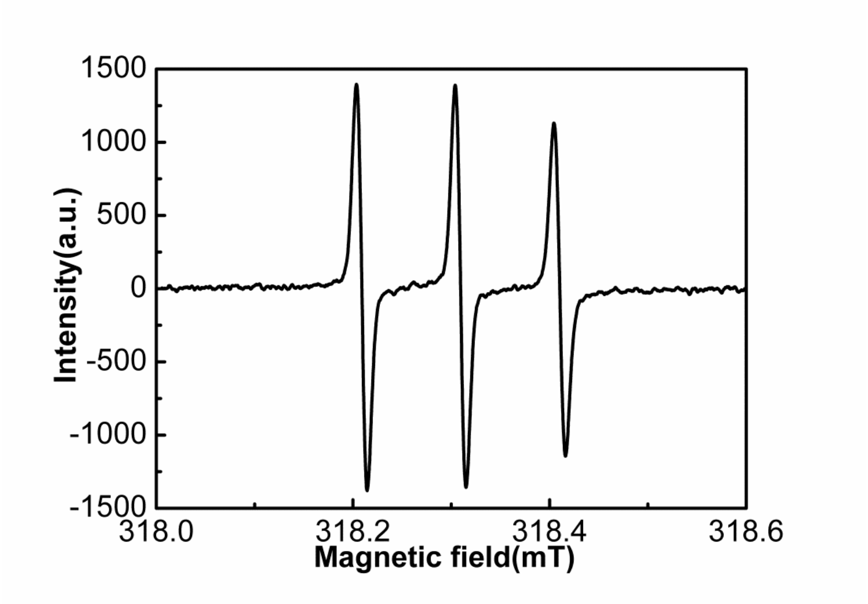

Figure S1. EPR spectra of the precursor solution of 89.5 wt% $BMIMPF_6$, 0.5 wt% TiO_2, and PEGMA (with 5 wt% PEGDA) under UV irradiation at the time of six minutes.

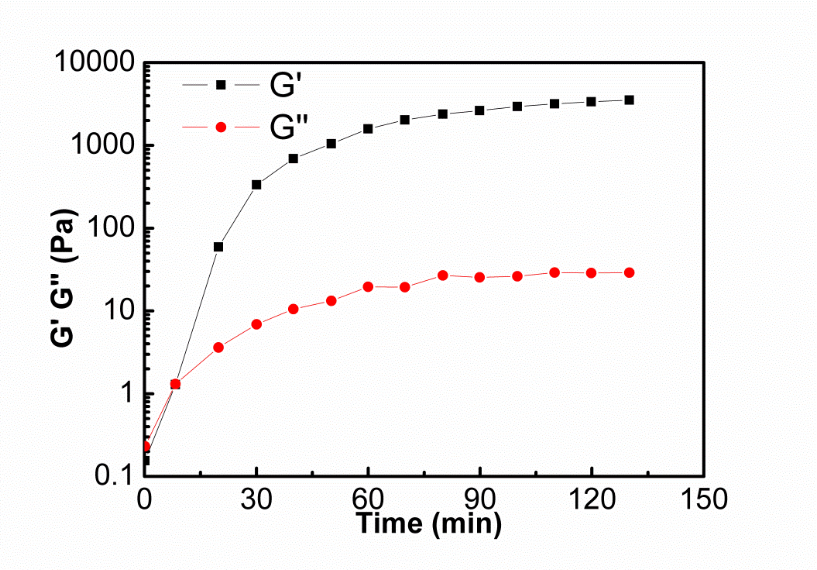

Figure S2. Dynamic time sweeps of a gelation system containing 89.5 wt% $BMIMPF_6$, 0.5 wt% TiO_2, and 10 wt% PEGMA (with 5 wt% PEGDA) at a strain of 1% and a frequency of 1 rad s^{-1} under UV irradiation

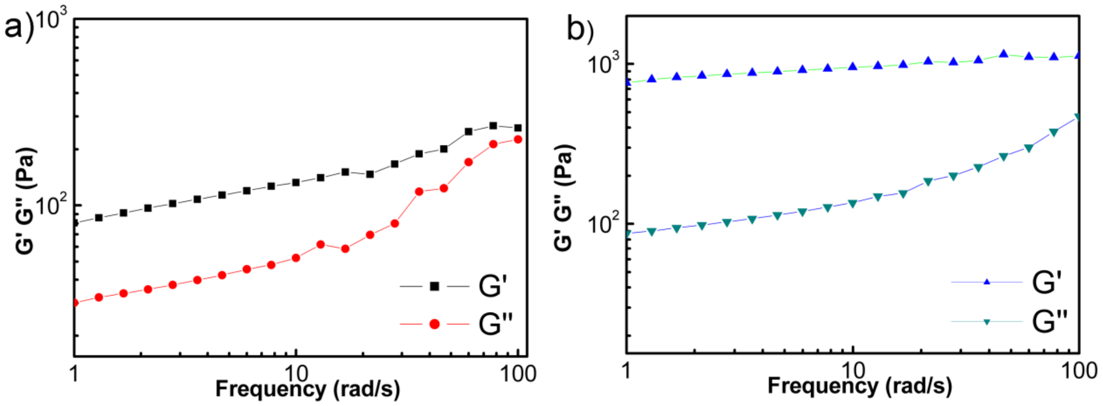

Figure S3. The frequency sweep curves of the ionogels through cryopolymerization with various TiO_2 contents at a fixed strain of 1%: a) 0.25 wt%; b) 0.5 wt%.

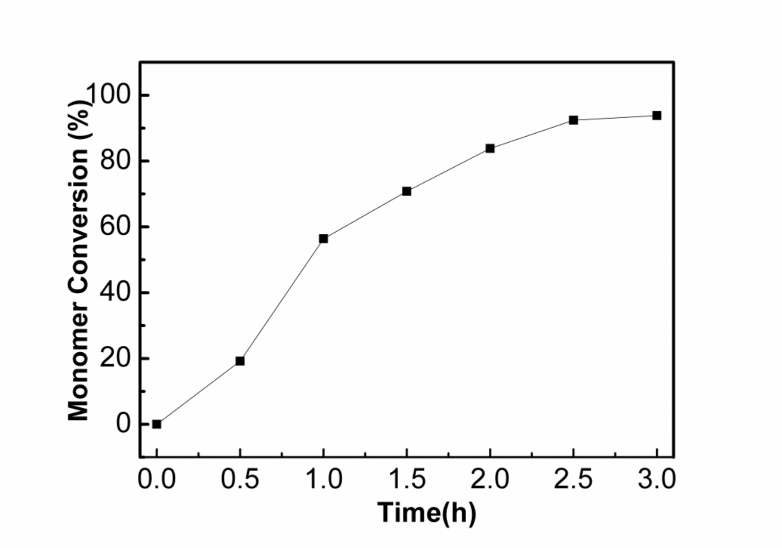

Figure S4. The time-dependent monomer conversion in the $BMIMPF_6$-based system calculated using TGA method.

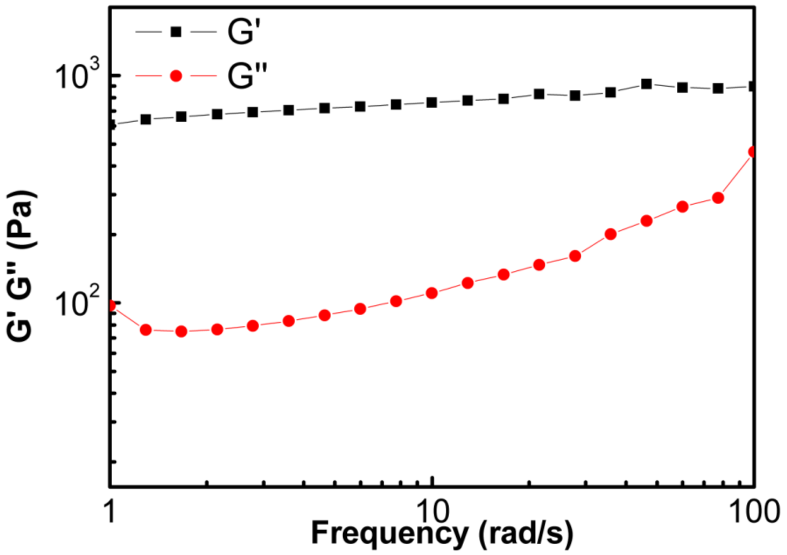

Figure S5. The frequency sweep curves of the aligned ionogel electrolyte at a fixed strain (γ = 1%).

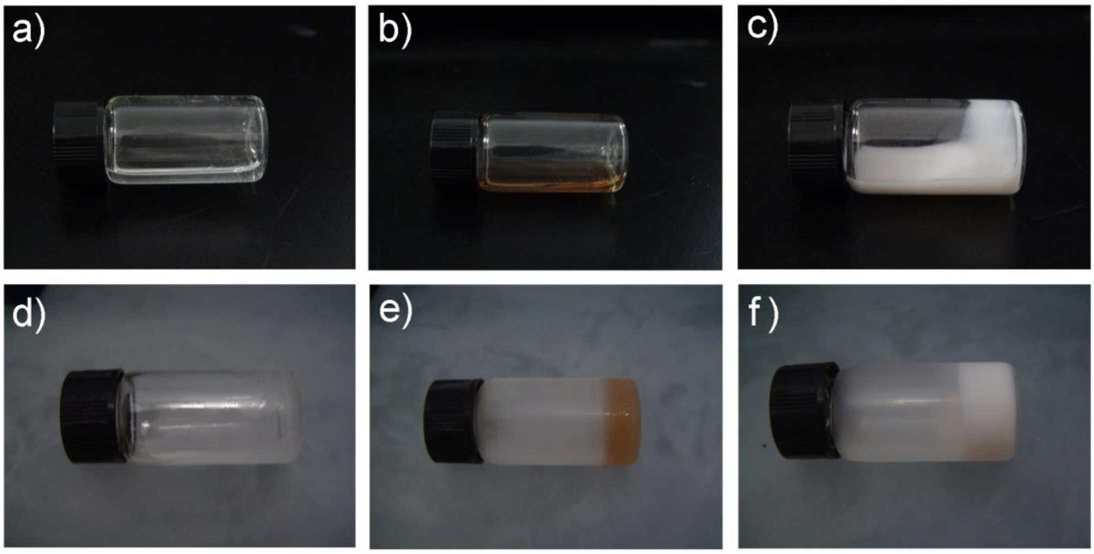

Figure S6. Photographs of the samples at room temperature (25 ℃): a) pure $BMIMPF_6$, b) PEGMA (with 5 wt% PEGDA), c) precursor solution of 89.5 wt% $BMIMPF_6$, 0.5 wt% TiO_2, and 10 wt% PEGMA (with 5 wt% PEGDA); at low temperature (-18 ℃): d) pure $BMIMPF_6$, e) PEGMA (with 5 wt% PEGDA), f) precursor solution.

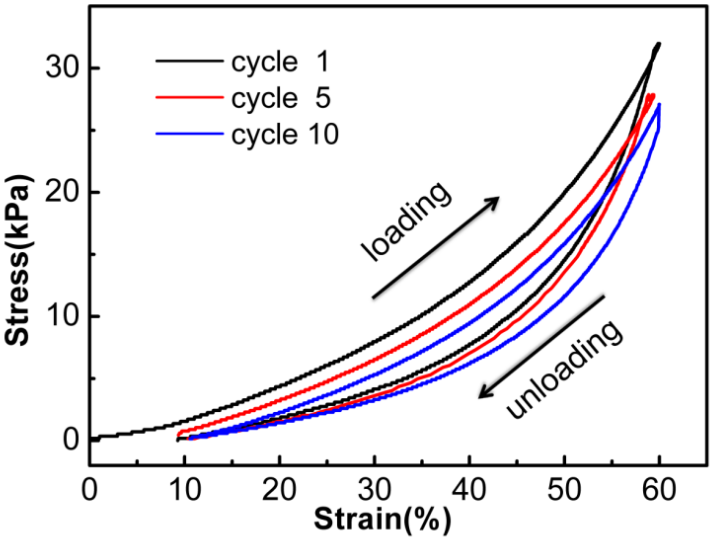

Figure S7. Compression recovery of the ionogel with 0.5 wt% TiO_2 through 10 cycles with 60% strain.

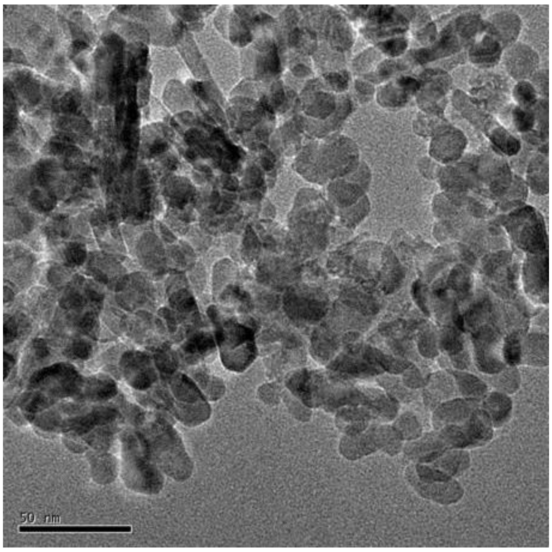

Figure S8. TEM of the TiO_2 nanoparticles (the average size of the TiO_2 nanoparticles is 25 nm).

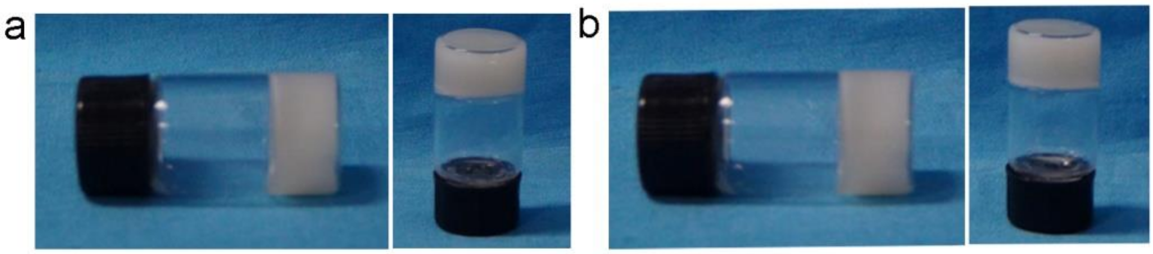

Figure S9. Photographs of the ionogels during a laid-out time of seven days. a) non-aligned ionogel and b) aligned ionogel.

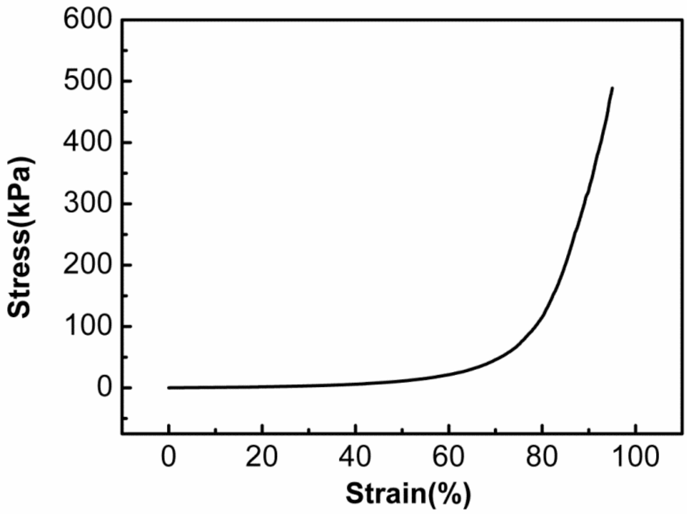

Figure S10. Compressive curve of the ionogel with aligned structures prepared by cryopolymerization.

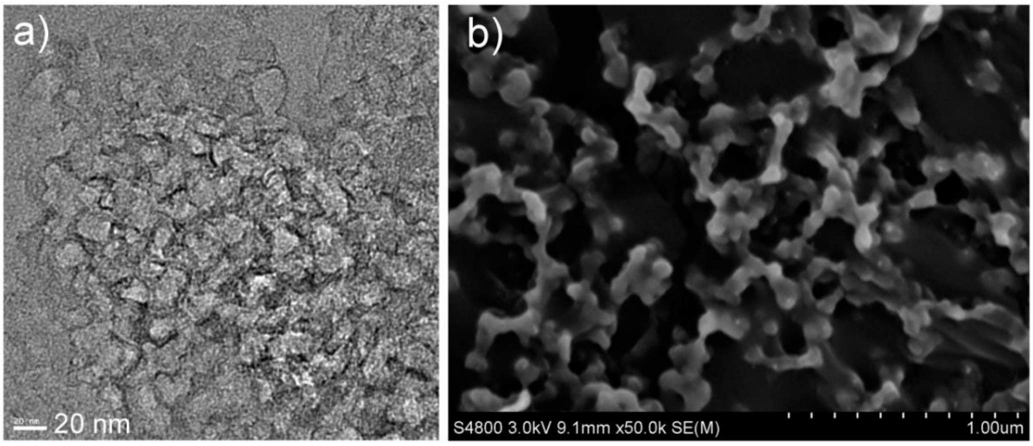

Figure S11. a) Typical TEM image of the carbon nanocages; b) SEM image of the carbon nanocages.

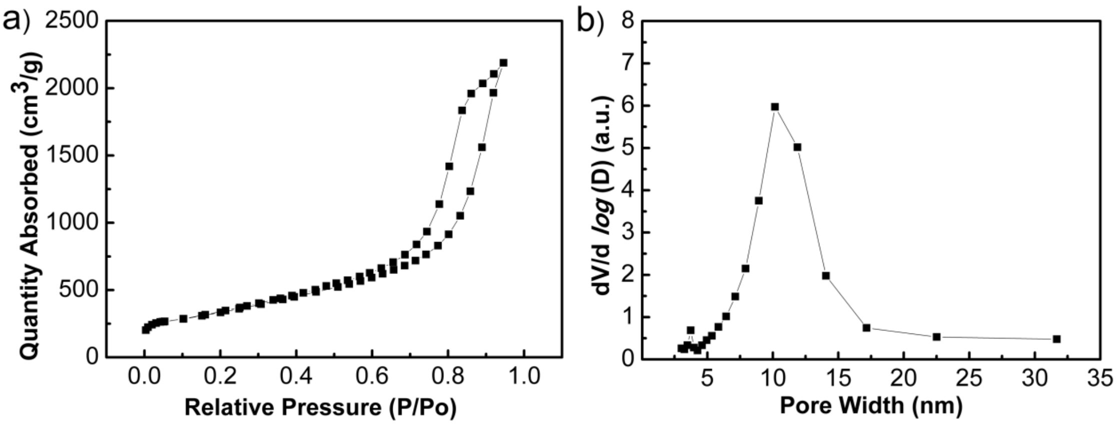

Figure S12. a) N_2 adsorption–desorption isotherms of the carbon nanocages; b) pore size distributions of the carbon nanocages.

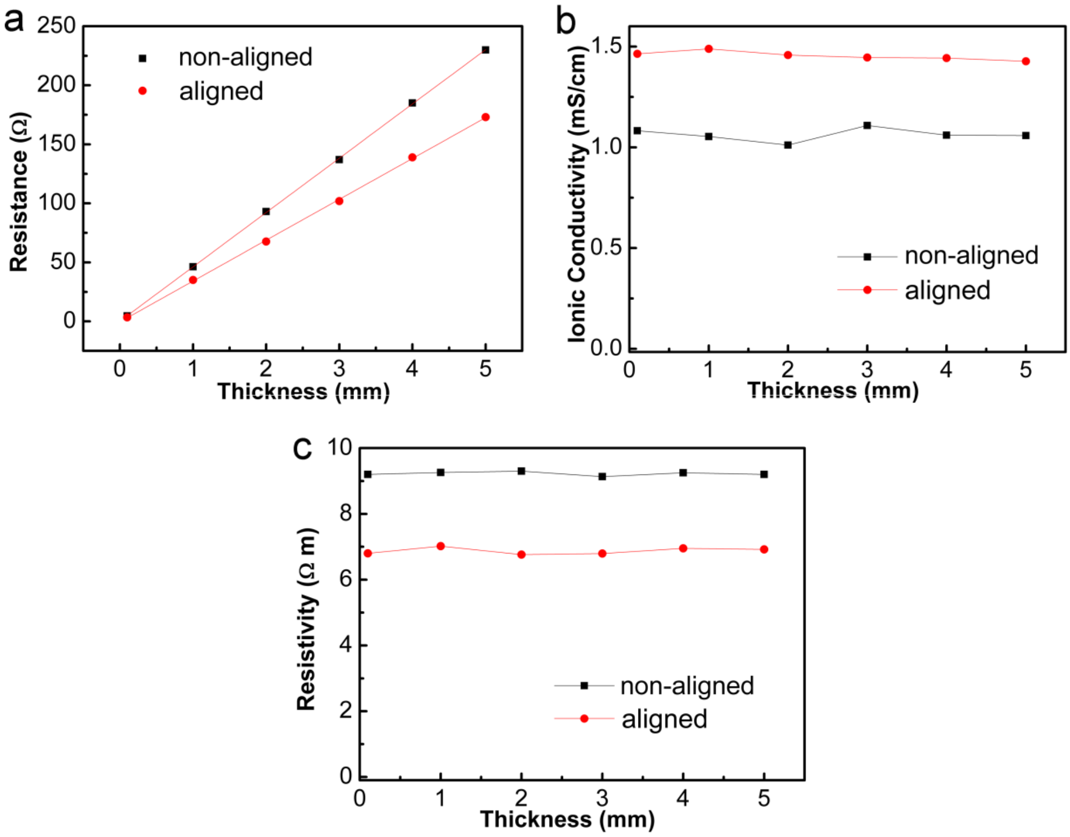

Figure S13. The electrochemical properties of the non-aligned and aligned ionogels with various thickness: a) resistance, b) ionic conductivity, and c) resistivity.

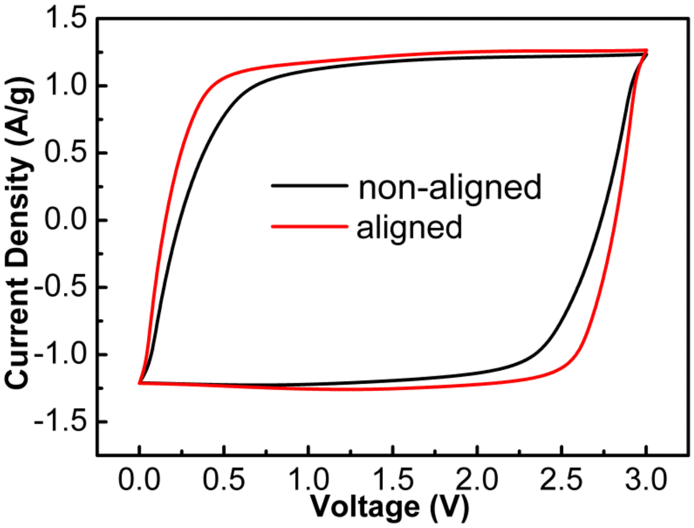

Figure S14. Cyclic voltammetry behaviors of the non-aligned and aligned ionogel electrolyte based supercapacitors tested at 25 mV/s.

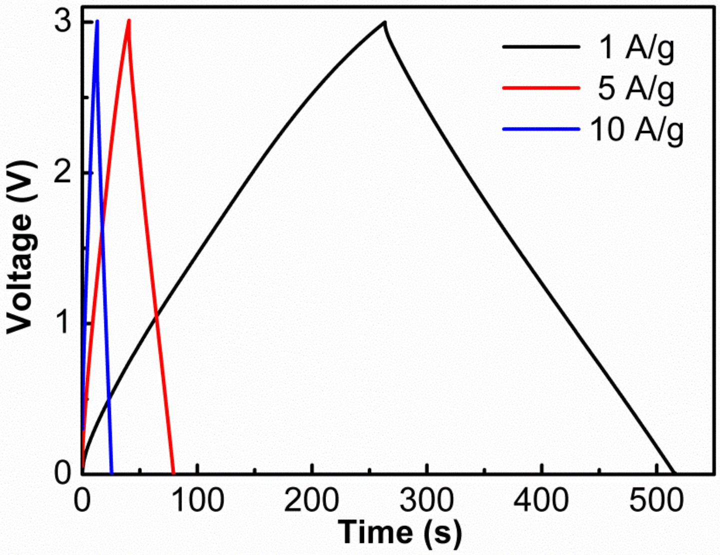

Figure S15. The charging and discharging behaviors of the aligned-ionogel based supercapacitor at various current densities of 1A/g, 5 A/g and 10 A/g.

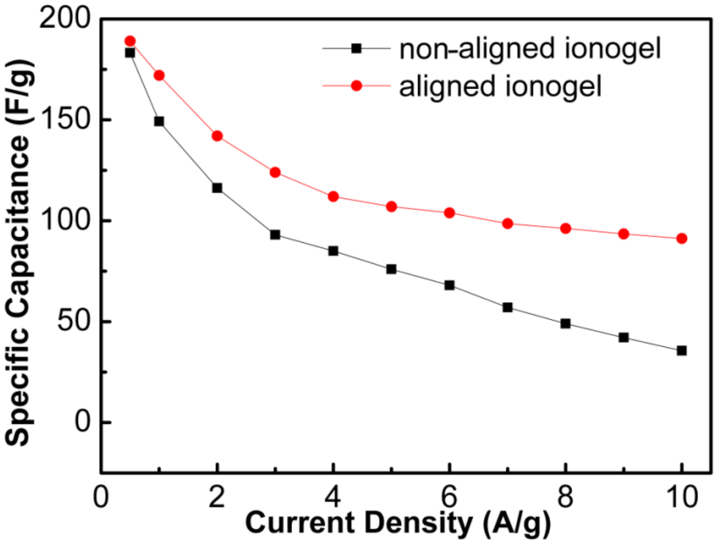

Figure S16. The correlation of specific capacitance with various current densities for BMIMTFSI-ionogel-electrolyte based supercapacitors.

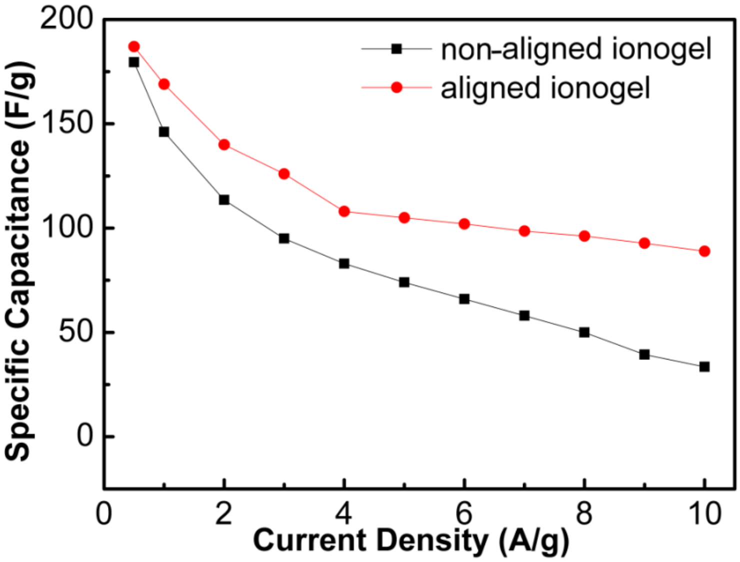

Figure S17. The correlation of specific capacitance with various current densities for $BMIMBF_4$ ionogel based supercapacitor.

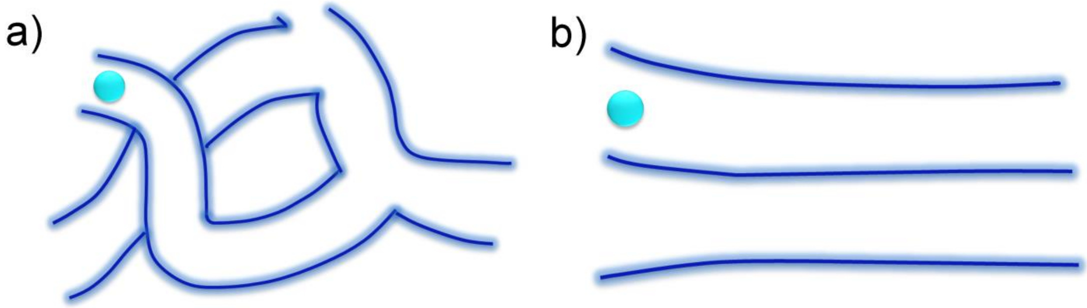

Figure S18. The mechanism of the ion transport under action of electric field in non-aligned and aligned porous networks.

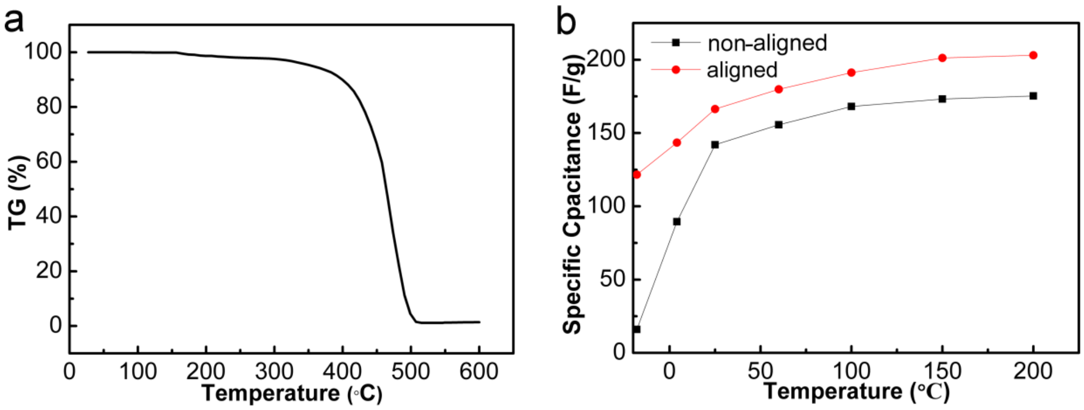

Figure S19. a) TGA curve of the ionogel. b) Capacitive performance of the non-aligned and aligned ionogel based supercapacitors at a wide temperature range from -18 °C to 200 °C.

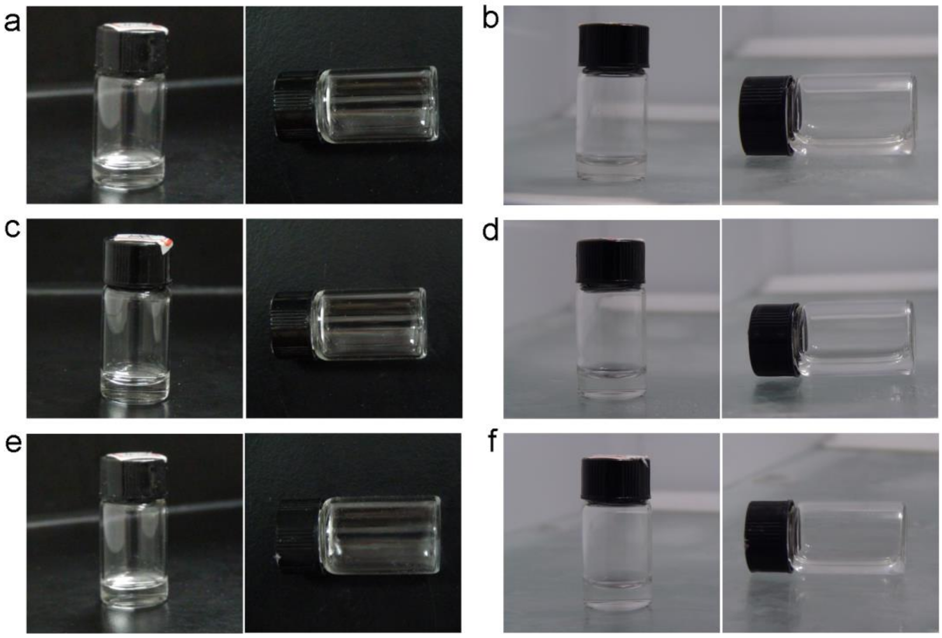

Figure S20. Photographs of the ionic liquids placed vertical and horizontal at various temperatures. a) BMIMPF$_6$ at room temperature; b) BMIMPF$_6$ at -18 °C; c) BMIMBF$_4$ at room temperature; d) BMIMBF$_4$ at -18 °C; e) BMIMTFSI at room temperature; f) BMIMTFSI at -18 °C.

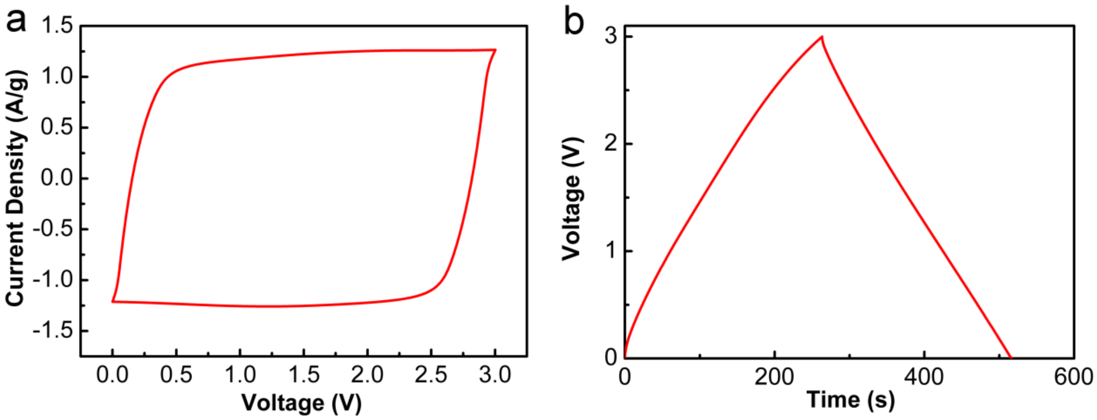

Figure S21. Room-temperature electrochemical properties of the aligned ionogel prepared with further frozen treatment. a) Cyclic voltammetry curve of the ionogel electrolyte based supercapacitors. b) Galvanostatic charge–discharge curve of the ionogel electrolyte based supercapacitors.

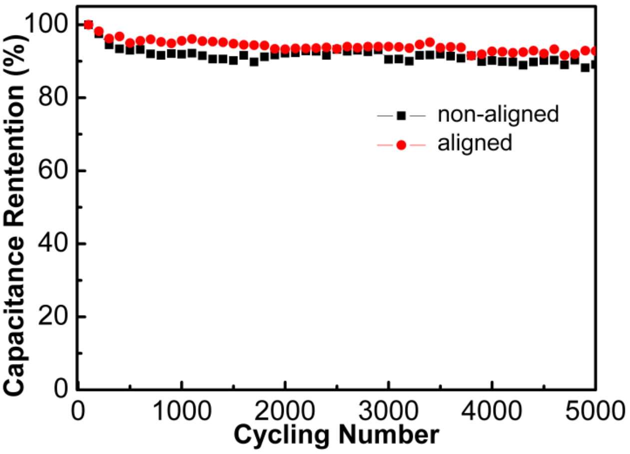

Figure S22. The operation stability of non-aligned and aligned ionogel based supercapacitors at the current density of 0.25 A/g and room temperature in carbon nanocage electrodes through 5000 cycles.

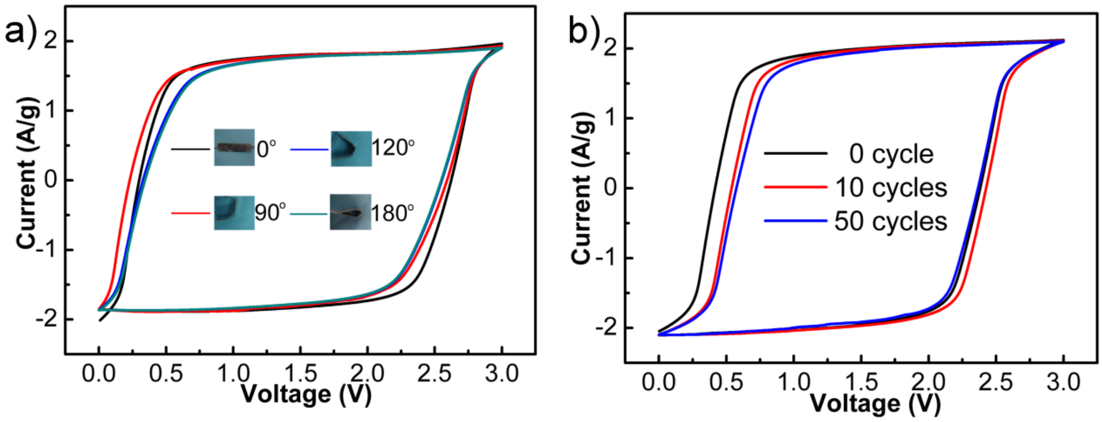

Figure S23. Electrochemical performances of the aligned ionogel based supercapacitors: c) the cyclic voltammetry curves at 40 mV s^{-1} and various bending angles; d) the cyclic voltammetry curves at 50 mV s^{-1} after differerent bending cycles.