"All-in-Gel" Design for Supercapacitors towards Solid-State Energy Devices with Thermal and Mechanical Compliance

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Materials and Fabrication

The long single-walled carbon nanotubes (SWCNTs-l) (Purity: more than 90%, Outer Diameter: 1-2 nm, Inner Diameter: 0.8-1.6 nm, length: 5-30 μm), the short single-walled carbon nanotubes (SWCNTs-s) (Purity: more than 90%, Outer Diameter: 1-2 nm, Inner Diameter: 0.8-1.6 nm, length: 1-3 μm), the Multi-walled carbon nanotubes (MWCNTs) (Purity: more than 95%, Diameter: 8 nm, length: 10-30 μm) were purchased from Nanjing XFNANO Materials Tech Co., Ltd. $EMIMBF_4$ was purchased from Center for green chemistry and catalysis

Lanzhou. The DMAA and DEAP (2,2-Diethoxyacetophenone) was purchased from TCI (Shanghai) Development Co., Ltd, MBAA was purchased from Energy Chemical.

To prepare Bucky gel, firstly, SWCNT (40 mg) and $EMIMBF_4$ (100 mg) was ground for 15 min in an agate mortar. The bucky gel thus obtained was transferred to a mixture of PVdF(HFP) (83.85 mg) and 4-methyl-2-pentanone (MP) (2.5 mL). Then, acetylene black (10 mg) was added to this mixture to improve the conductivity of the gel. After the solvent (MP) was evaporated at 80 °C, mass ratio of the residual solid composite material was 4:10:1:8 (CNT, $EMIMBF_4$, AB, PVdF(HFP)).

The Buckygel electrode slurry was coated on the upper surface of the prepared ionogel electrolyte. The resulting material was then put into the vacuum drying oven at room temperature to remove the volatile solvent for 2 hours. After finishing following step, the lower surface of the prepared cylinder-shape electrolyte was also coated.

Characterization

The morphology and the microstructure of the Bucky-gel electrode and the ionogel electrolyte was observed with SEM (Hitachi S-4800). The mechanical performance of the ionogel is tested with the Tensile testing machine (Suns UTM2502). The CV, GCD and EIS testing of the supercapacitor was tested with an electrochemistry workstation (Auto Lab, PGSTA302N), while the cycling stability experiment is carried out by the other machine (Land). The performance of the all in gel supercapacitor under extreme high and low temperature is achieved with the electrothermal dry oven (from 30 ºC to 100 ºC) and the Circulating cooling thermostat regulator. The rheology and thermal stability performance was tested with Rotating rheology analyzer (Thermo Scientific HAAKE RS6000) Thermogravimetric Analyzer (TA TGAQ500).

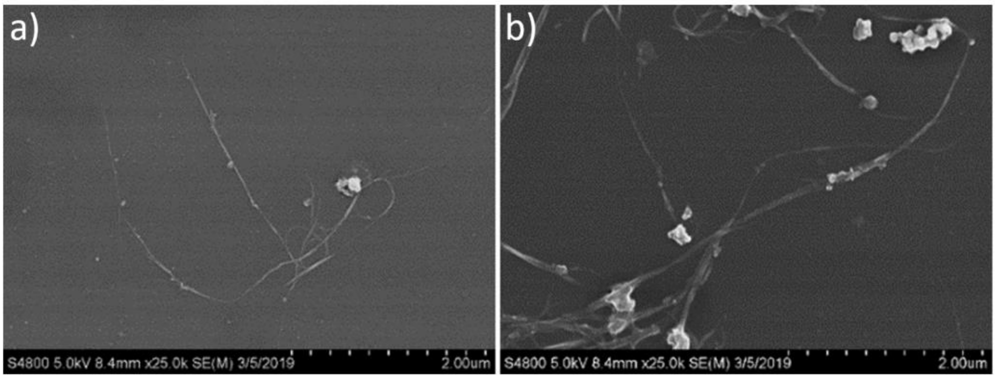

Fig. S1 a) SEM image of SWCNTs-l before grinding; b) SEM image of SWCNTs-l after grinding.

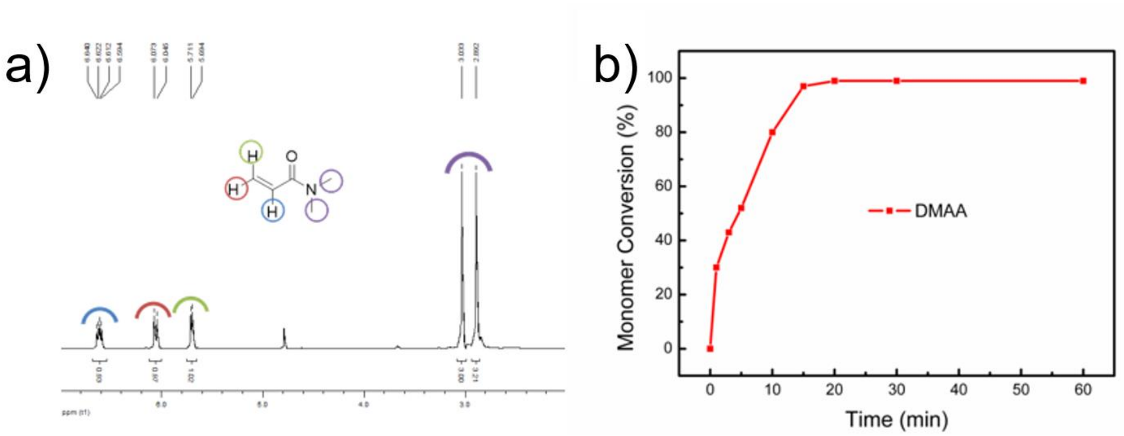

Fig. S2 a) ^{1}HNMR of the monomer DMAA in the precursors. b) DMAA monomer conversion curves with different UV radiation time.

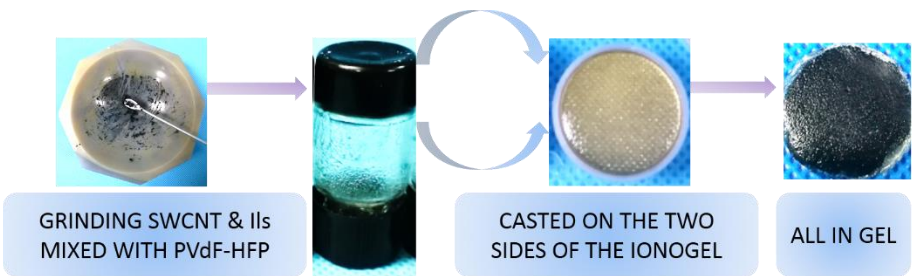

Fig. S3 Bucky gel preparation and device fabrication process.

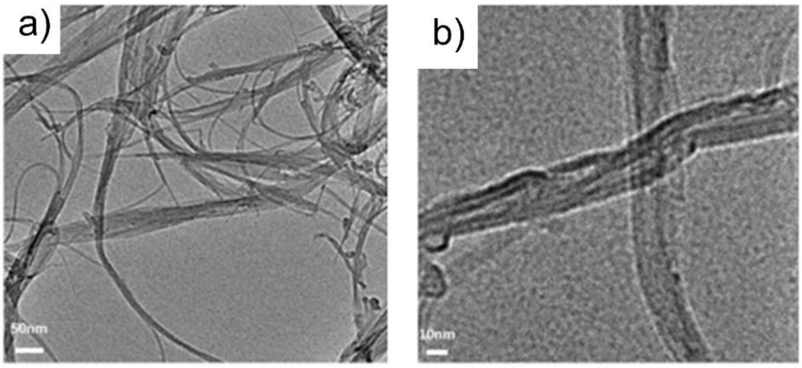

Fig. S4 TEM images of the L-Bucky gel electrode with scale bar a) 50nm and b) 10nm.

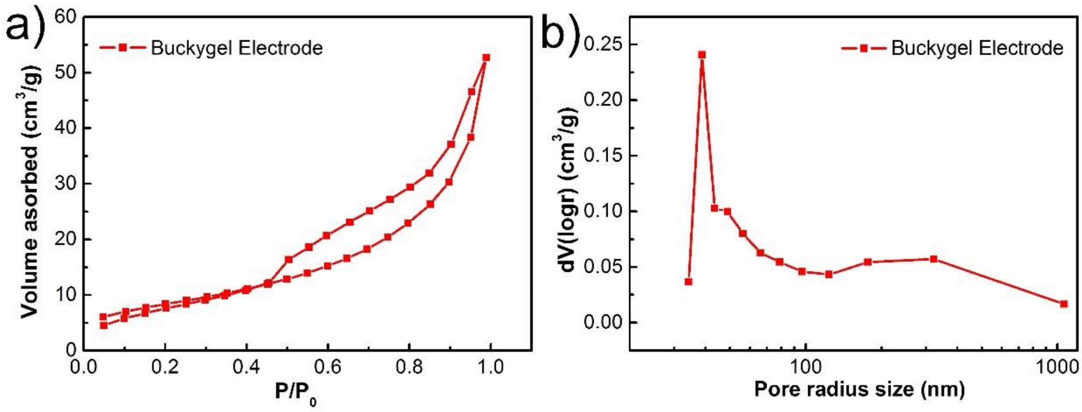

Fig. S5 a) N2 adsorption–desorption isotherms of the Bucky gel electrode; b) pore size distributions of the Bucky gel electrode.

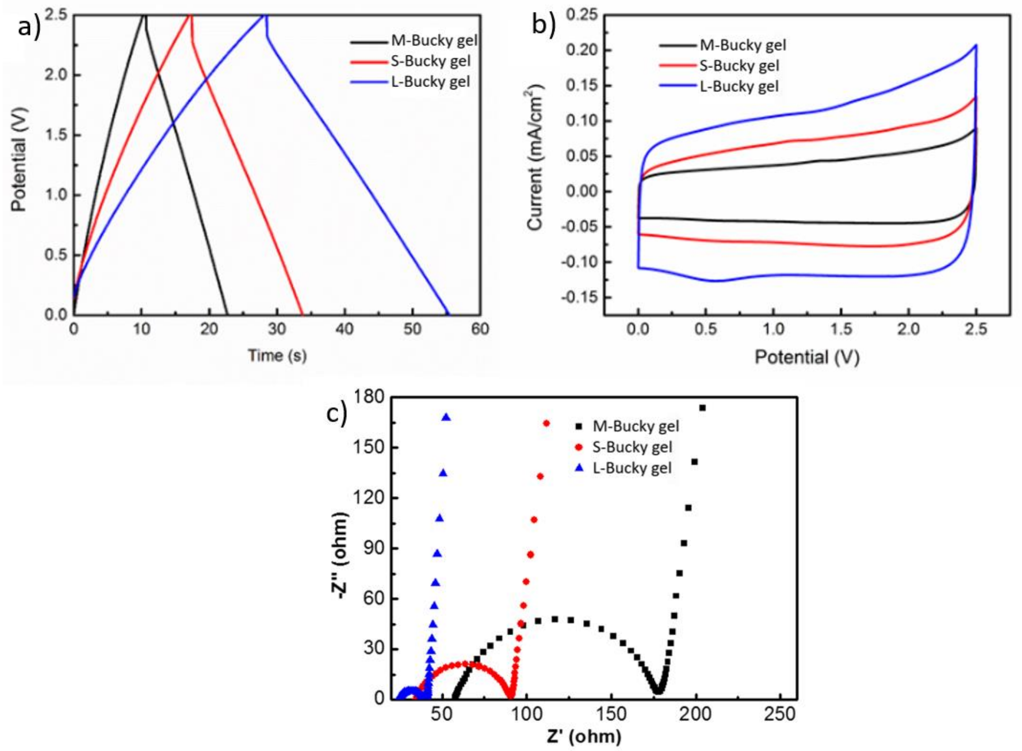

Fig. S6 Galvanostatic charge-discharge curves at 1.0 mA/cm^2 (a) cyclic voltammetry curves at a scan rate of 10 mV/s (b) and impedance (c) of XG-ionogel based supercapacitors with different electrodes of M-Bucky gel, S-Bucky gel and L-Bucky gel. The same mass is applied for all selected electrodes.

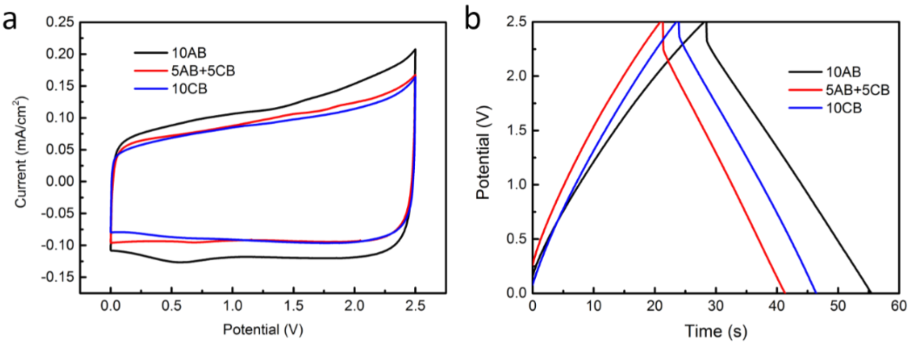

Fig. S7 (a) Cyclic voltammetry curves at a scan rate of 10 mV/s and (b) galvanostatic charge-discharge curves at 1.0 mA/cm^2 of XG-ionogel based supercapacitors applying L-Bucky gel electrodes with different mass ratio of conductive additives.

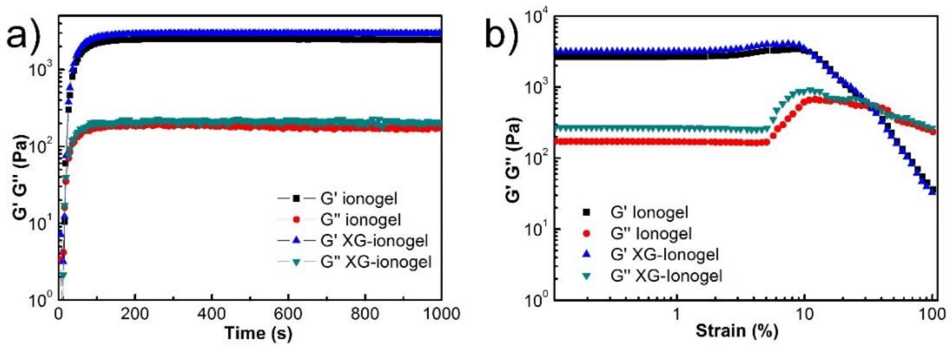

Fig. S8 a) Dynamic frequency sweeps of the precursors under UV irradiation. b) The changes of storage moduli (G') and loss moduli (G'') with various strains of the ionogel and XG-ionogel.

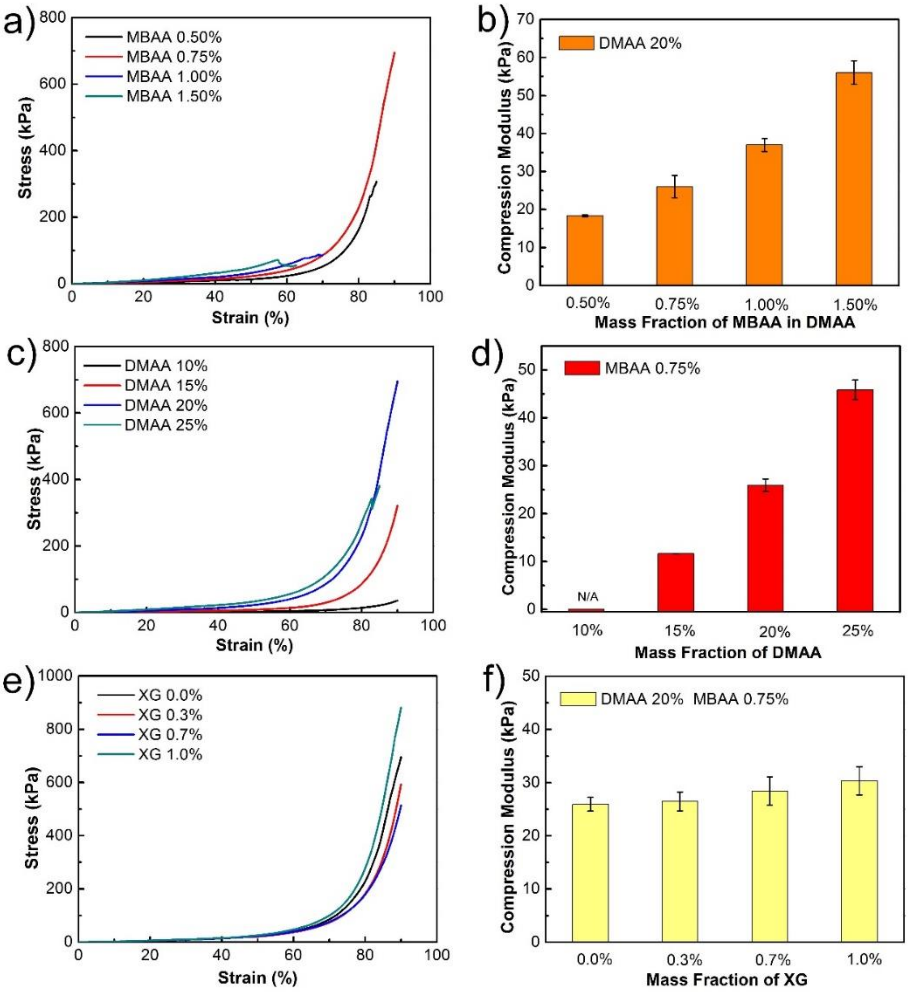

Fig. S9 a) Compression curves to determine the best content of MBAA crosslinker with the ionogels under 90% strain when the content of the monomer is 20% . b) Compression Modulus of ionogels with different content of MBAA. c) Compression curves of the ionogels with different monomer concentrations (MBAA 0.75 wt% in DMAA) and their calculated Young's modules (d). e) Compression properties of the composite ionogels with different XG concentrations (20 wt% DMAA with 0.75 wt% MBAA) and their calculated Young's modules (f).

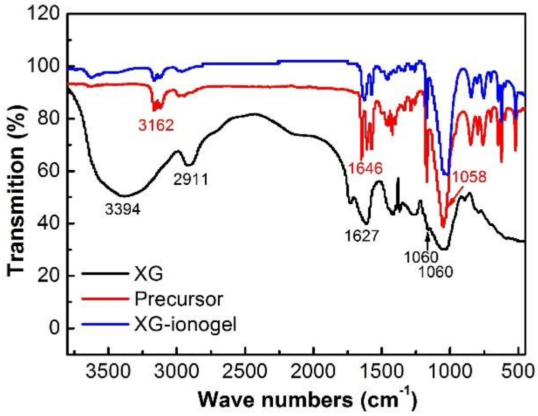

Fig. S10 FT-IR spectrum of the XG, precursor and XG-ionogel.

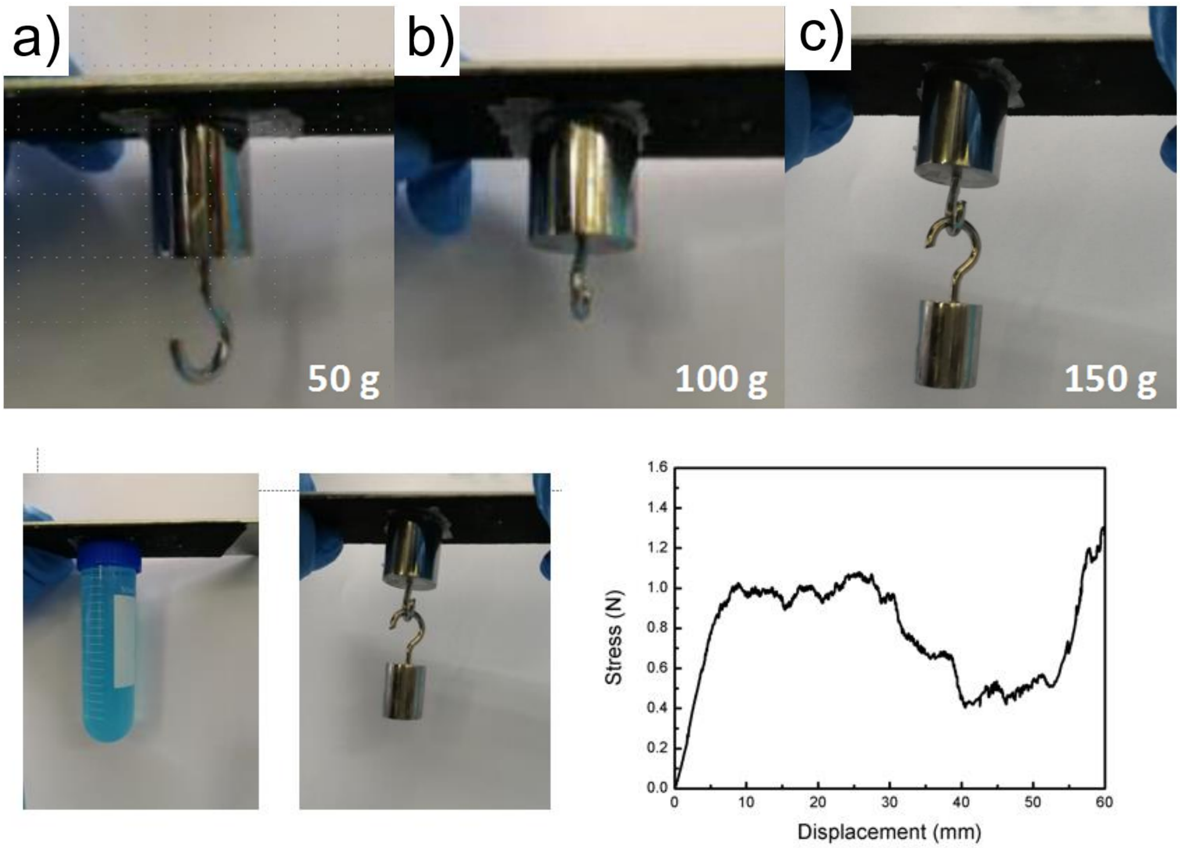

Fig. S11 Peel Adhesion Test of Ionogels with carbon cloth materials

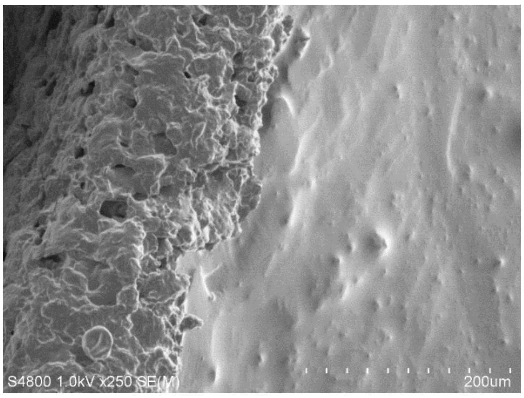

Fig. S12 Enlarged SEM image of the interface between L-Buckey gel electrode and ionogel electrolyte.

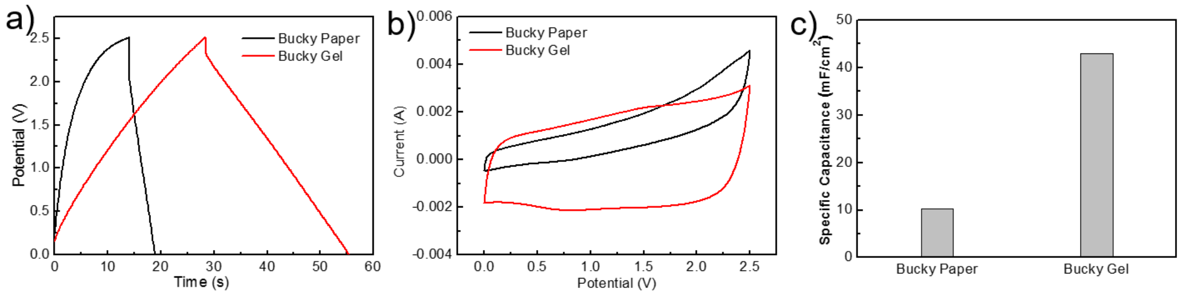

Fig. S13 XG-ionogel based supercapacitor applying Bucky paper and L-Bucky gel as electrodes at room temperature. a) Galvanostatic charge-discharge curves with different current density at 1.0 mA/cm^2. b) Cyclic voltammetry curves at 50 mV/s. c) Their calculated specific capacitance at 1.0 mA/cm^2.

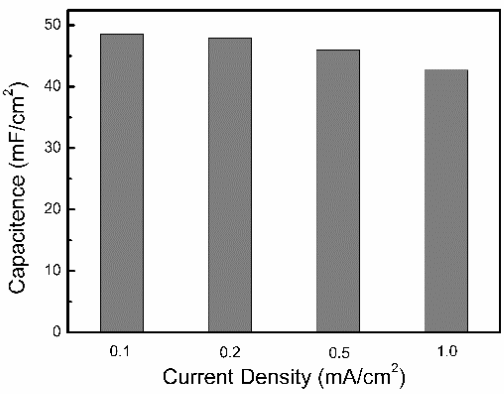

Fig. S14 The calculated specific capacitance of all-in-gel supercapacitor at room temperature and different current densities.

Table S1. Nomination of electrode materials

Sample	Materials	Nomination of the electrode materials
1	MWCNT	M-Bucky gel
2	SWCNT-s	S-Bucky gel
3	SWCNT-l	L-Bucky gel

Table S2. Nomination of electrode materials with with different mass ratio of conductive additives

Sample	Mass of the AB (mg)	Mass of the CB (mg)
10 CB	0	10
5 AB+5 CB	10	0
10 AB	5	5

Table S3. The calculated specific capacitance at different current densities from 0.1-1.0 mA/cm^2.

Current Desity (mA/cm2)	Csp (mF/cm2)
0.1	48.52
0.2	47.94
0.5	45.92
1.0	42.65

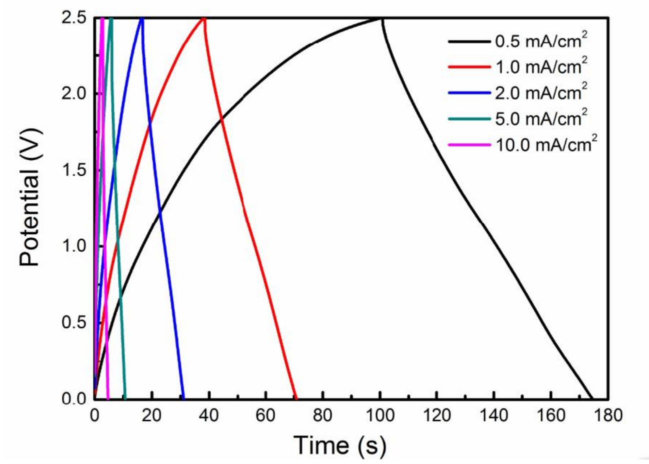

Fig. S15 The charging/discharging curves of all-in-gel supercapacitor at room temperature and different current densities.

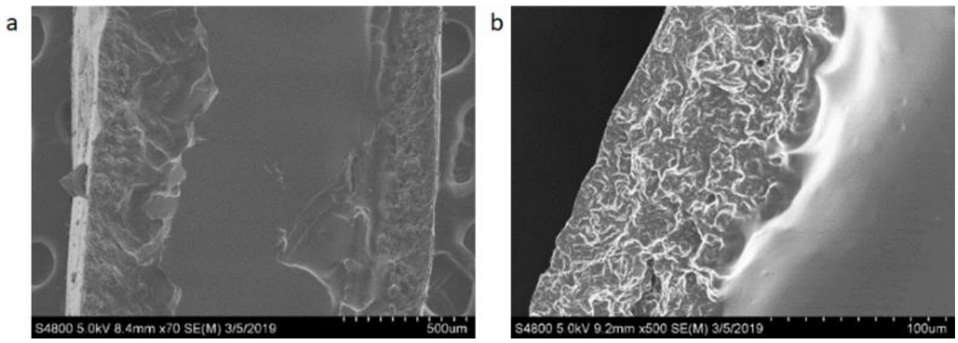

Fig. S16 SEM images of the interface between Bucky gel electrode and ionogel electrolyte after cycling tests.

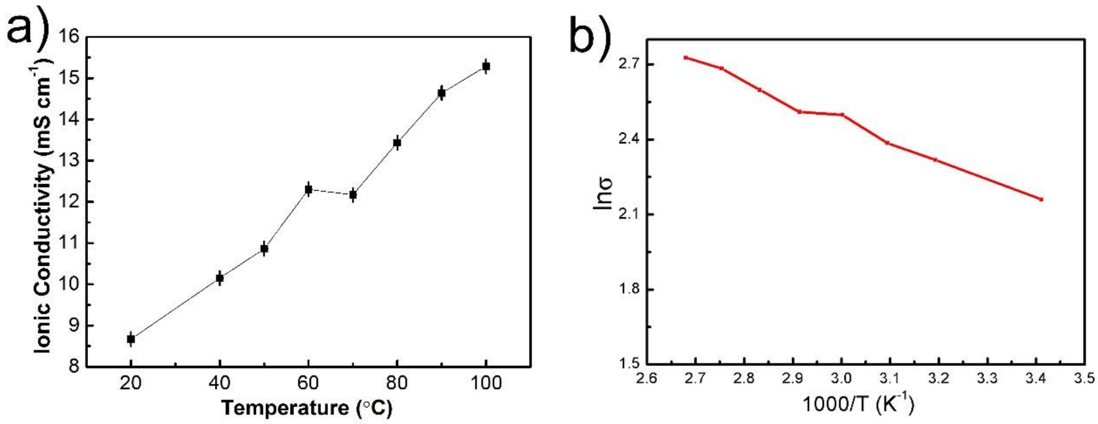

Fig. S17 a) The temperature dependent ionic conductivities of the XG-ionogel. b) The Arrhenius plots of the temperature dependent ionic conductivity.

Table S4 Comparision of the performances of various ionogel based supercapacitors.

Gel Type	Conductivity	Strain %	Capacitance	Cycle (device)	Thermal	REF
PDMS-ionogels	3 mS/cm	e.m.60 kPa, 30 %, 5000 cycles	Not available	-	Up to 200°C	S1
(PANI)–SWCNTs–sponge	-	60% strain, 100 cycles	216 F/g @0.64 A/g	1000	-	S2
Ionogel-in-mask TiO2 hybrid gel electro-lyte	3.5 mS/cm at 25C	y.m 2.6kPa	177 F/g at 200 °C, 143/Fg at 25 °C, current density of 1 A/g 26 F/g at 25 °C, current density of 15 A/g	-	25 °C to 200 °C	S3
inorganic gel polymer electrolyte	0.2 mS/cm at 40C, 10 ms/cm at 60C	e.m.0.935 MPa	90 F/g	-	-	S4
Ionogel Electrolyte	1.5 mS/cm, 20C	-	20 F/g (80 F/g per electrode)	10,000	-	S5
carbon nanofiber-Ionic Liquid-Rich Ionogel	5.7 mS/ cm at 25 °C	-	153 F/g	20000	−15 to ∼300 °C	S6

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