

Electronic Supplementary Information for

Intrinsically Microporous Polymer-Based Hierarchical Nanostructuring of Electrodes via Nonsolvent-Induced Phase Separation for High-Performance Supercapacitors

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Experimental

1. Materials

5,5',6,6'-Tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, TCI, >97%) was purified by recrystallization from methanol (50 mL)/dichloromethane (950 mL). 2,3,5,6-tetrafluoroterephthalonitrile (TFTPN) was purified by sublimation at 150 °C under reduced pressure. Activated carbons such as MSP-20 and YP-50F were procured from Kansai Coke and Kuraray Chemical Co., respectively. Ketjen black was procured from Nippon Ketjen. Anhydrous tetrahydrofuran (THF, 99.9%), 1,2-dichlorobenzene (DB, 99%), potassium carbonate (K₂CO₃, 99.99%), and poly(vinylidene fluoride) (PVDF) were purchased from Sigma-Aldrich. Methanol and dichloromethane (99.5%) were purchased from Samchun chemicals. N,N-Dimethylformamide (DMF) was purchased from Burdick & Jackson. All solvents were used as received.

2. Synthesis of Polymers with Intrinsic Microporosity (PIM-1)

All the glassware was dried in an oven prior to use. Under a nitrogen atmosphere, a mixture of TTSBI (10.21 g, 30 mmol) TFTPN (6.00 g, 30 mmol) and anhydrous K₂CO₃ (8.29 g, 60 mmol) was dissolved in 210 mL of DMF in a 500 mL of two-neck round-bottomed flask equipped with a magnetic stirring bar. After two monomers were clearly dissolved, the flask was put into a pre-heated oil bath at 55 °C and then the reaction temperature was maintained for 3 days. The mixture was then cooled to room temperature and 420 mL of THF was added to the flask to remove low molecular weight residues. The resulting yellow polymer was dissolved in 300 mL of THF and re-precipitated in 1500 mL of methanol and 1500 mL of H₂O, respectively. The resulting powder was dried in a vacuum oven for 3 days. Yield: >74%. ¹H NMR (500 MHz, CDCl₃): δH (ppm) = 6.80 (2H, s), 6.41(2H, s), 2.46 - 2.04 (4 H, dd), 1.45-1.16 (12H, br);

Molecular mass: (Gel Permeation Chromatography, eluent = THF, against polystyrene standard : $M_n = 61\ 000$, $M_w = 128\ 000$, PDI = 2.1) Anal. Cald for $C_{29}H_{20}N_2O_4$ (wt%) : C, 75.64; H, 4.38; N, 6.08; O 13.90. Found: C, 74.2; H, 4.4, N, 6.2; O, 14.1.

3. Preparation of hierarchical porous carbon (cNPIM) monolith

cNPIM monolith was prepared by non-solvent induced phase separation (NIPS) process of PIM-1 solution. Briefly, PIM-1 powder (0.5 g) was dissolved in a mixture of DB (2.4 g) and THF (9.6 g) at 35 °C with a continuous stirring to form a 4 wt% homogeneous solution. The solution was then spread onto a clean flat glass plate. The thickness of the solution was adjusted using a doctor blade with 300 μm blade gap. The nascent casting solution was immersed in a non-solvent bath (methanol, 500 mL) at room temperature for 24 h. The film isolated was removed from the bath and then dried at ambient conditions for 48 h. The film was carbonized in a tube furnace at 1100 °C under H_2/N_2 atmospheres with a heating rate of 5 °C min^{-1} . Carbonized PIM-1 (cPIM) was formed using the same procedure except using NIPS process. In the case of cNPIM, carbonization at 1100 °C for 120 min hold time resulted in 80% loss of initial weight. For cPIM, carbonization at 1100 °C for 0, 120, and 180 min hold time resulted in 50, 60, and 80% loss of initial weight, respectively.

4. Characterization and calculation of the electrochemical performances

Morphologies of the cNPIMs were observed by a field emission scanning electron microscope (FE-SEM, Mira 3 LMU FEG, TESCAN) and a high-resolution transmission electron microscope (HR-TEM, G2 T-20S, TECNAI). The Brunauer–Emmett–Teller (BET) surface area and the pore size distribution (PSD) were obtained from N_2 adsorption-desorption isotherms at 77 K performed on a Micromeritics 3Flex instrument. Prior to BET surface area measurement, samples are degassed at for 30 min at 90 °C and for 24 h at 200 °C. The pore

size distribution (PSD) of carbonized PIM samples was calculated using Horvath-Kawazoe method. The total pore volume was based on single point adsorption total pore volume at $P/P_0 = 0.99$. ^1H -nuclear magnetic resonance (NMR, AVANCE, 700 MHz, Bruker) spectroscopy measurements were used to investigate the chemical structure. Number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) of PIM-1 were measured by size exclusion chromatography (SEC) in THF, using Shodex columns (KF-800 series) operating at 40 °C. Signals were detected with Wyatt WREX-06 (differential refractive index, RI) detector. Elemental analysis of PIM-1 was analyzed on a Thermo Scientific FLASH EA-2000 Organic Elemental Analyzers. Thermogravimetric analysis (TGA) was performed using a Pyris 1 (Perkin Elmer) thermal analyzer system at a heating rate of 10 °C min^{-1} from 25 to 1000 °C under a N_2 atmosphere). Electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) were performed using a Biologic SP-300 analytical equipment in three-and two-electrode modes in 1.0 M H_2SO_4 aqueous electrolyte. A saturated calomel electrode as a reference electrode, a Pt foil counter electrode, and the samples obtained as the working electrode were used in case of three-electrode configuration. For organic electrolyte system, two electrodes were assembled by using CR2032 coin-type cells with a Celgard® polypropylene separator in 1.0 M tetraethylammonium tetrafluoroborate (TEA/BF_4) in acetonitrile (ACN). Cell assembly was carried out in an argon-filled glovebox. The mass of electrode was approximately 0.8 mg cm^{-2} . The EIS test was performed in the frequency range from 100 kHz to 10 mHz at the amplitude of the sinusoidal voltage by applying a 5 mV signal. In the GCD profiles, the specific capacitance can be estimated using the following equation (in case of two-electrode mode):

$$C = 4I/[(\Delta V/\Delta t)m] \quad (2)$$

where I is the current applied, $\Delta V/\Delta t$ is the slope of the discharge curve after a IR drop at the beginning of the discharge curve, and m is the total mass of two electrodes.

The specific power (P , in $W\ kg^{-1}$) and energy (E , in $Wh\ kg^{-1}$) were calculated using the following equation:

$$P = E / \Delta t, \quad E = 0.5C(\Delta V)^2 / 3600M \quad (3)$$

where ΔV , Δt , M , and C are the potential window obtained from discharge curve after the IR drop, discharge time, the mass of electrodes (in kg), and the measured capacitance, respectively. The internal resistance was computed from the voltage drop at the beginning of each discharge:

$$R_{ESR} = \Delta V_{IR} / 2i \quad (4)$$

where ΔV_{IR} and i are the voltage drop between the first two points in the voltage drop at the top cutoff and applied current, respectively.

For comparison, different activated carbon (AC) electrodes such as MSP20 and YP50F were also prepared. Briefly, working electrodes were prepared by mixing ACs, Ketjen black, and 10 wt% of poly(vinylidene fluoride) (PVDF) in 1-methyl-2-pyrrolidone (NMP) at a mass ratio of 80:10:10 and then spreading onto graphite paper. The samples were dried for 24 h at 80 °C and then pressed under a pressure of 1 MPa at 25 °C. The mass of active materials was $\sim 1.6\ mg\ cm^{-2}$. A four-point probe station for measuring electrical properties was used. The electrical conductivity of each samples can be calculated as follows: $\sigma(S\ cm^{-1}) = 1 / (R_{sheet} \times t)$, where σ is the conductivity and t is the thickness of the sample.

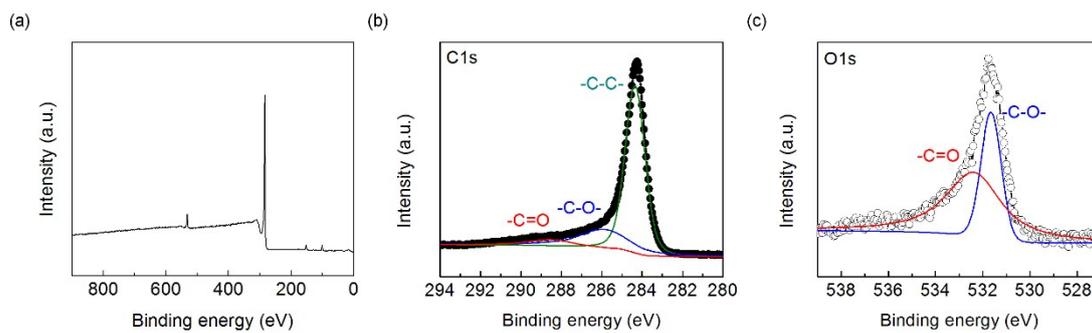


Fig. S1 XPS (a) survey, (b) C1s, and (c) O1s spectra of cNPIM.

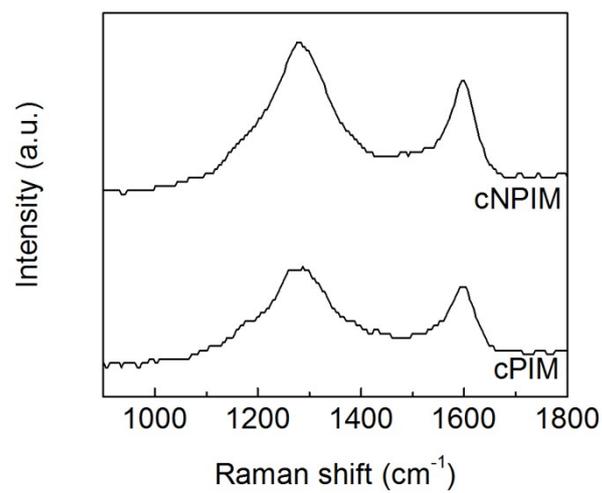


Fig. S2 Raman spectra of cPIM and cNPIM with peaks at 1350 and 1575 cm⁻¹ assigned to D and G bands, respectively.

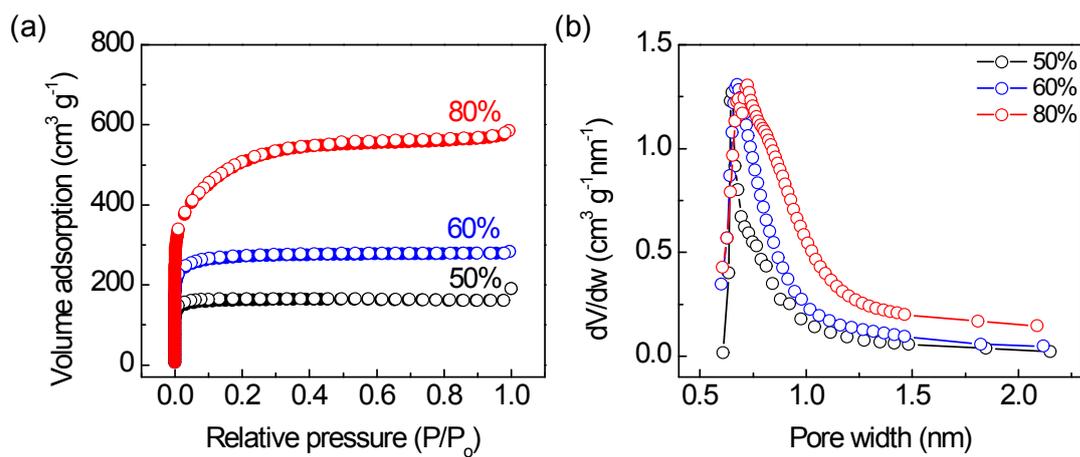


Fig. S3 (a) N₂ adsorption (filled)-desorption (open) isotherms and (b) pore size distribution as a function of degree of carbonization (%) for cPIMs with 50, 60, and 80% degree of carbonization.

Table S1 Pore characteristics of cPIM and cNPIM

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$) ^a	V_{micro} ($\text{cm}^3 \text{g}^{-1}$) ^b	V_{total} ($\text{cm}^3 \text{g}^{-1}$) ^a	APD (nm) ^c
cPIM	1840.7	1816.7	0.85	0.91	2.44
cNPIM	2101.1	1993.7	0.87	1.23	4.16

^aMicropore surface area and volume calculated from *t*-plot method. ^bTotal pore volume.
^cAverage pore diameter calculated from BJH desorption

Table S2 Comparison of the surface area and electrical conductivity of electrodes for SCs

	Surface area ($\text{m}^2 \text{g}^{-1}$)	Electrical conductivity (S cm^{-1})	Reference
Holey graphene	1560	10	[33]
Activated reduced graphene oxide (RGO) film	2400	58	[34]
RGO	778	1	[35]
Laser-scribed RGO	1520	17	[36]
Polyaniline/RGO	N/A	906	[37]
Repaired graphene oxide sheets/ multi-layered graphene balls 3D hybrids	527	186	[40]
Ag nanowires/3D-graphene foam/ ordered mesoporous carbon	484	762	[39]
Carbide-derived carbon	2000	160	[15]
Activated carbon	1644	1	[38]
Metal-organic framework	630	50	[41]
MOF-templated carbon	2872	N/A	[8]
MOF-templated carbon	3045	N/A	[12]
cNPIM	2101	150	This work

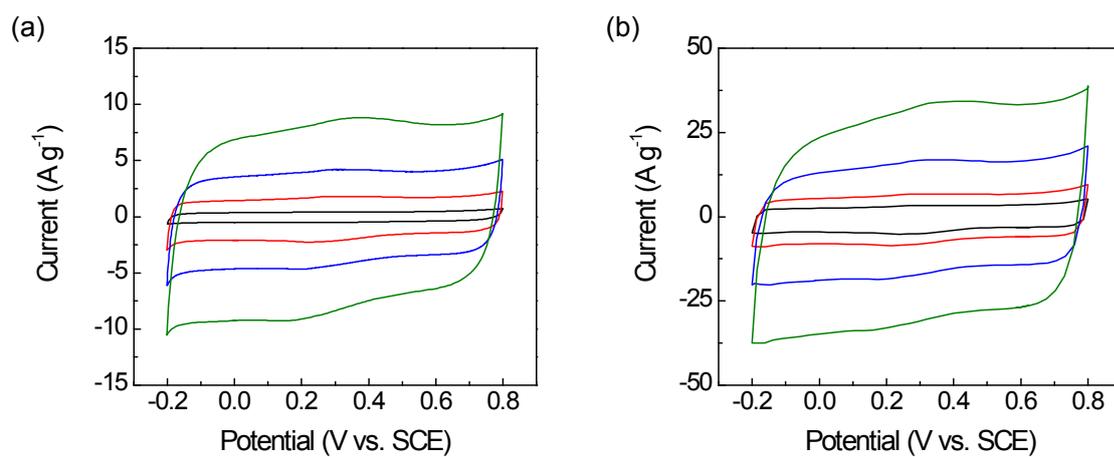


Fig. S4 Three-electrode CV curves of (a) cPIM and (b) cNPIM electrodes. Black, red, blue, and cyan lines correspond to 10, 20, 50, and 100 mV s^{-1} .

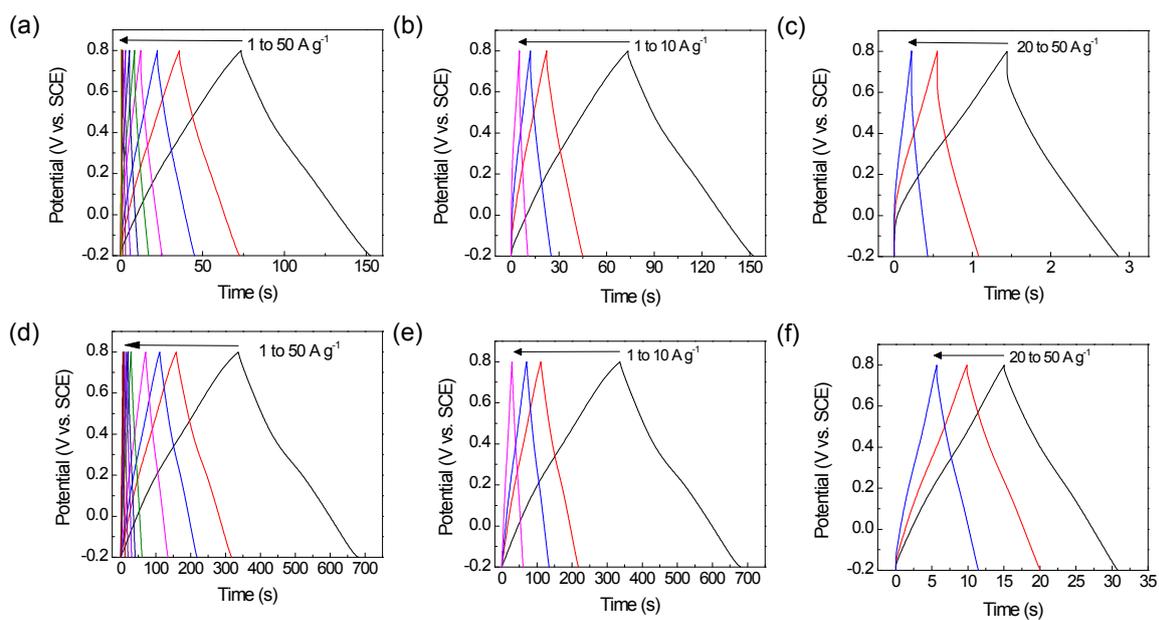


Fig. S5 Three-electrode GCD profiles of (a-c) cPIM and (d-f) cNPIM electrodes at different specific currents over the ranges of 1 to 50 A g⁻¹.

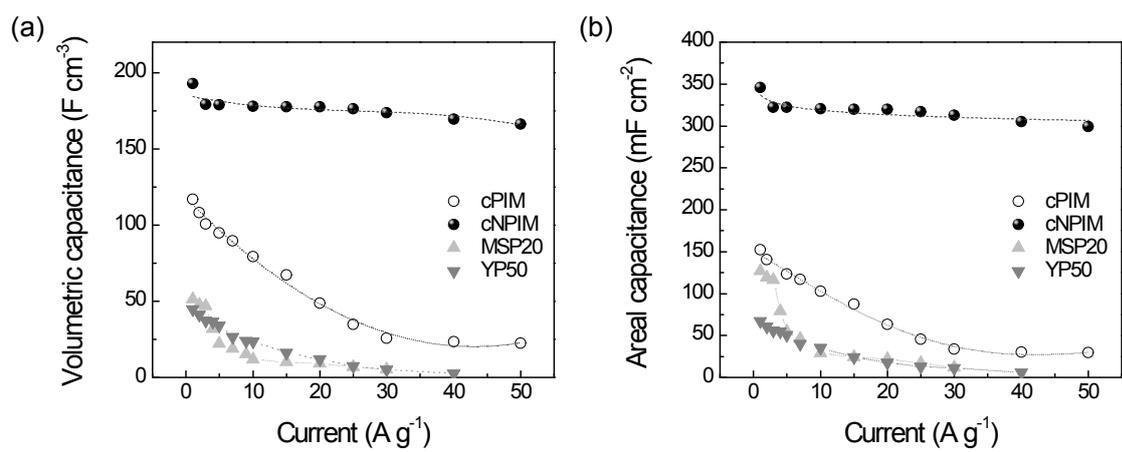


Fig. S6 In three-electrode system, (a) volume- and (b) area-based rate dependent capacitance for cNPIM electrodes.

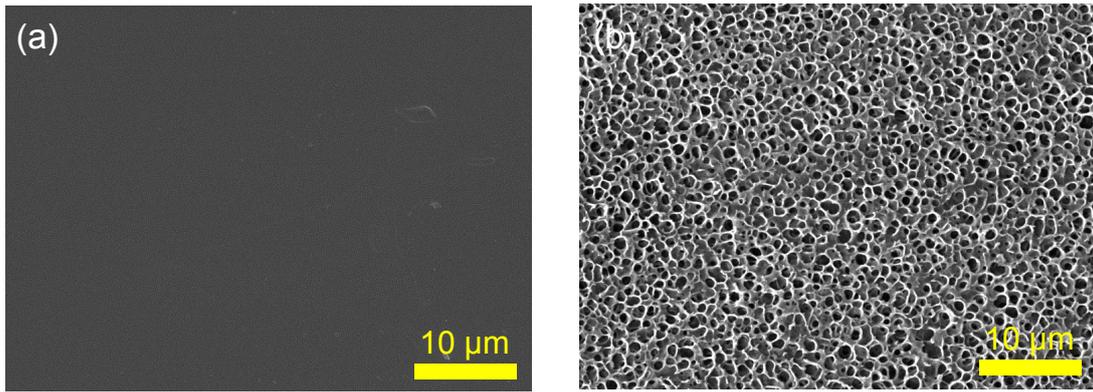


Fig. S7 SEM images of (a) solution cast and (b) NIPS-induced carbonized PI film.

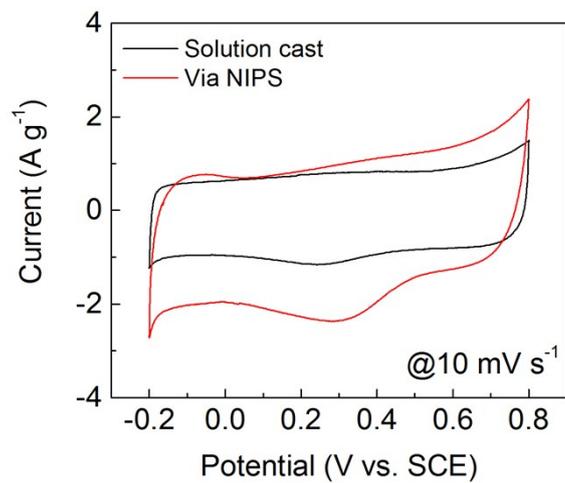


Fig. S8 CV curves of (a) solution cast and (b) NIPS-induced carbonized PI electrodes.

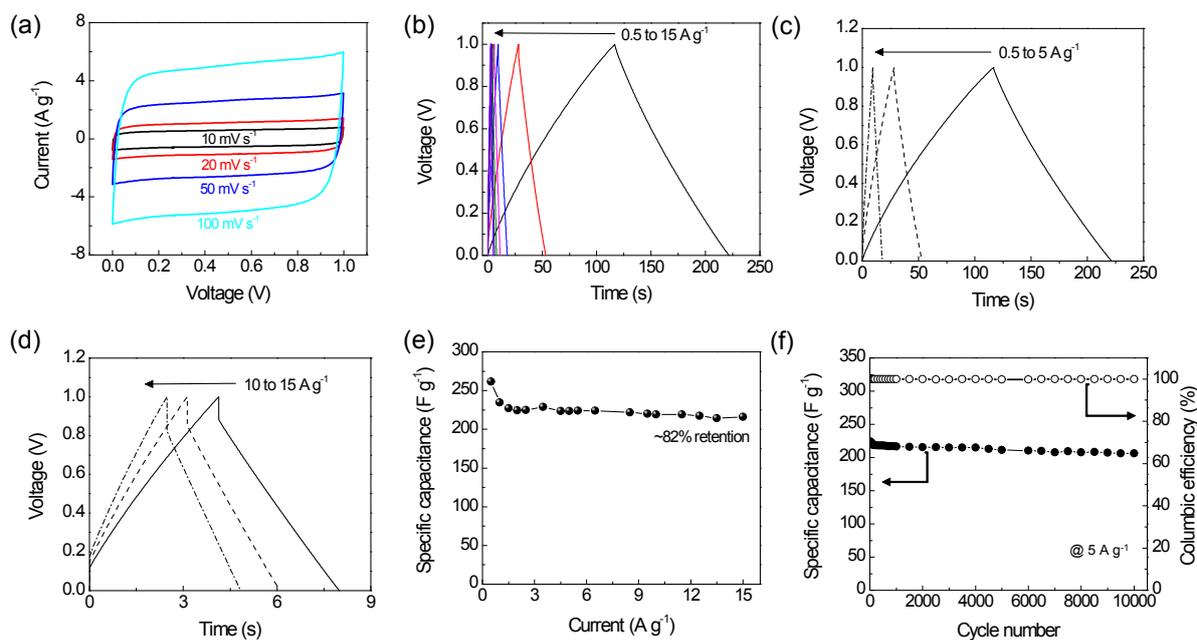


Fig. S9 In two-electrode configuration, (a) CV curves at different scan rates, (b-d) GCD profile at different specific currents, (e) rate dependent capacitances, and (f) long-term stability and Coulombic efficiency (over 10000 GCD cycles at a current of 5 A g⁻¹) of cNPIM electrodes.

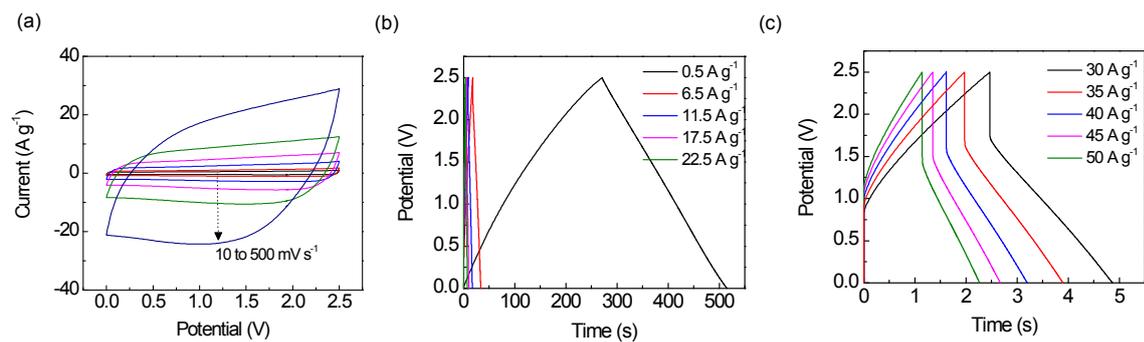


Fig. S10 Two-electrode (a) CV curves (at different scan rates) and (b,c) GCD curves (at different specific currents) of cNPIM in 1.0 M TEA/BF₄ in ACN.