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Supporting Information

An Advanced Carbonaceous Porous Network for High-Performance Organic Electrolyte Supercapacitors

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Experimental

Preparation: Porous network structured polymer (PNSP) was prepared based on the phase separation of polystyrene via a Friedel-Crafts crosslinking reaction, as described in our previous report.[1] Briefly, 5 g of polystyrene was first dissolved in 100 ml of CCl_4. Meanwhile, 12 g of $AlCl_3$ was added to 100 ml of CCl_4 and then refluxed with magnetic stirring at 75 °C for 40 min. The obtained CCl_4 solution of polystyrene was added to the above mixture. Subsequently, the mixture was refluxed with magnetic stirring for 48 h at 75 °C. After that, a mixture solvent of 50 ml of 3.6% HCL and 150 ml of 95% ethanol was added, and the resulting precipitate was filtered off, washed, and dried at 100 °C. The as-prepared PNSP was subjected to semi-carbonization by heating at 500 ^{o}C for 3 h under N_2 flow with a heating rate of 5 °C/min. The resulting sample was referred to as semi-carbonized PNSP. After that, 1g of semi-carbonized PNSP was mixed with KOH aqueous solution containing 3 g

of KOH. 5 ml of ethanol was then added. The resulting mixture was dried at 110 °C, and then was carbonized in a tubular furnace at 900 °C for 3 h with a heating rate of 5 °C/min under N_2 flow. After cooled down to room temperature, the resultant material was washed with 36% HCl (10 ml) and distilled water (100 ml) three times, and dried, yielding the PNSC sample.

Characterization: The microstructure of the samples was investigated by a JSM-6330F scanning electron microscope (SEM) and JEM-2010HR transmission electron microscope (TEM). N_2 adsorption measurement was carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The BET surface area (S_{BET}) was analyzed by Brunauer-Emmett-Teller (BET) theory. The total pore volume (V_t) was estimated from the amount adsorbed at a relative pressure P/P_0 of 0.99. The micropore surface area (S_{mic}) and non-micropore (*i.e.*, meso- and macropore) surface area (S_{ext}) were determined by t-plot theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. The electrodes were prepared by mixing 84% carbon sample, 4% carbon black, 4% carboxymethyl cellulose and 8% styrene-butadiene rubber dispersed in ethanol/H_2O mixture solvent. The slurry of the mixture was coated on a Al foil. After coating, the electrodes were dried at 100 °C. The electrodes were cut into disks with diameter of 1 cm. A kind of sandwich-type coin supercapacitor consisting of the same carbon electrodes was then assembled in a glove box. Before each assembling, both the two electrodes and the separator were soaked in 1 M tetraethylammonium tetrafluoroborate ($(C_2H_5)_4NBF_4$)/propylene carbonate (PC) organic electrolyte. The

electrochemical measurements were characterized with the assembled coin-type supercapacitor. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using an IM6e electrochemical workstation. The galvanostatic charging-discharging behavior was characterized by BT2000 (ARBIN Instruments).

Table S1 Textual characteristics of typical samples

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_t (cm^3/g)
PNSC	2653	579	2074	1.73
AC	2269	752	1518	1.15

Note: S_{BET}, S_{mic}, S_{ext} and V_t represent BET surface area, micropore surface area, non-micropore (*i.e.*, meso- and macropore) surface area, and total pore volume, respectively.

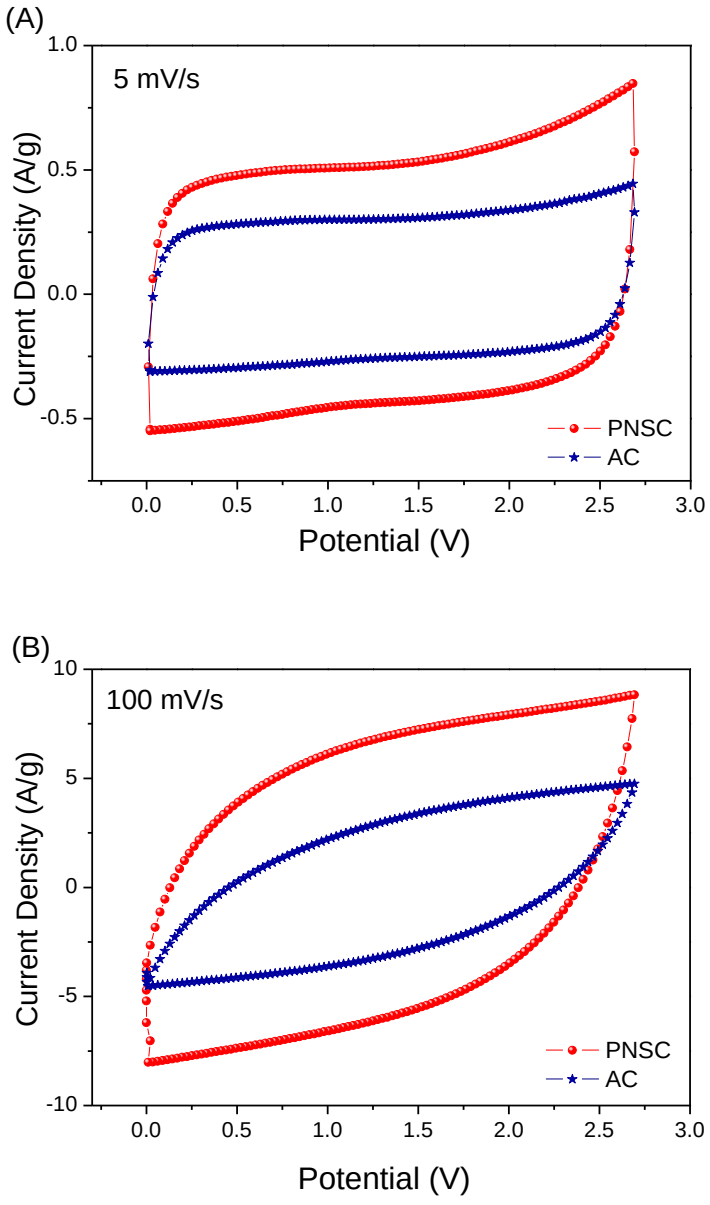

Fig. S1 Cyclic voltammograms at various sweep rates for PNSC and AC.

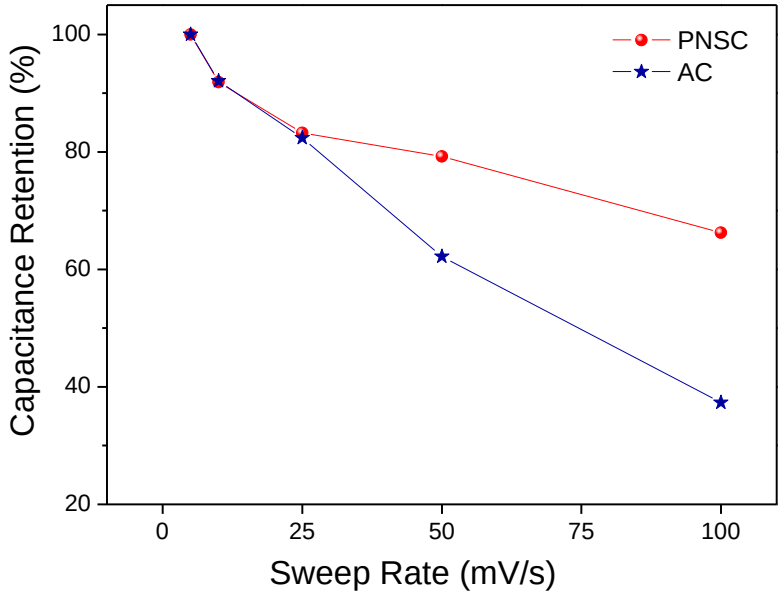

Fig. S2. The mass specific capacitance retention ratios as a function of sweep rates from 5 to 100 mV/s for PNSC and AC.

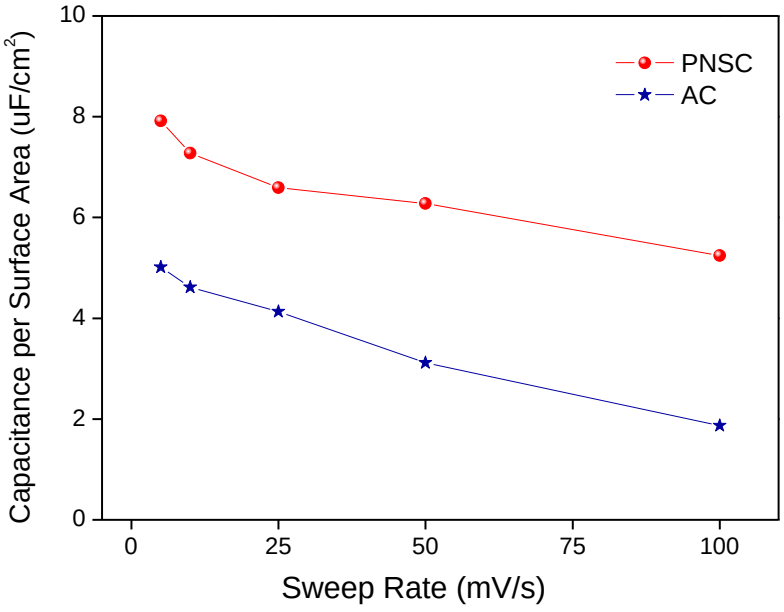

Fig. S3 The capacitance per surface area at various sweep rates for PNSC and AC.

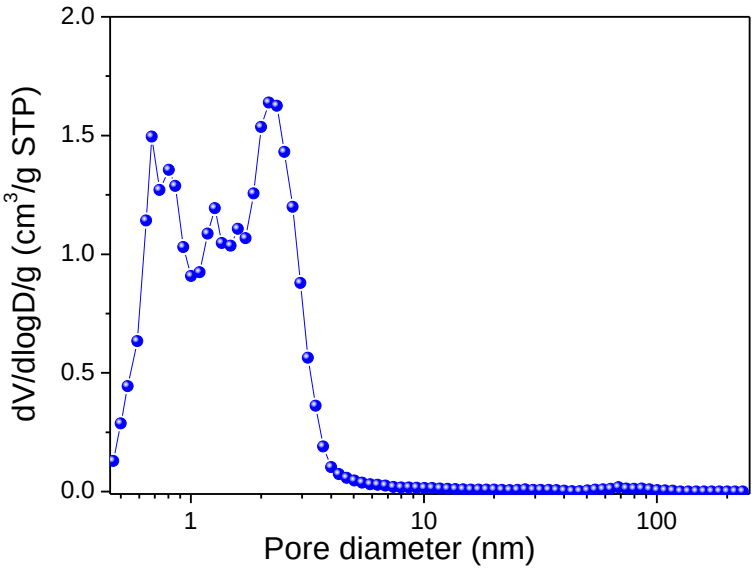

Fig. S4 DFT pore size distribution of AC.

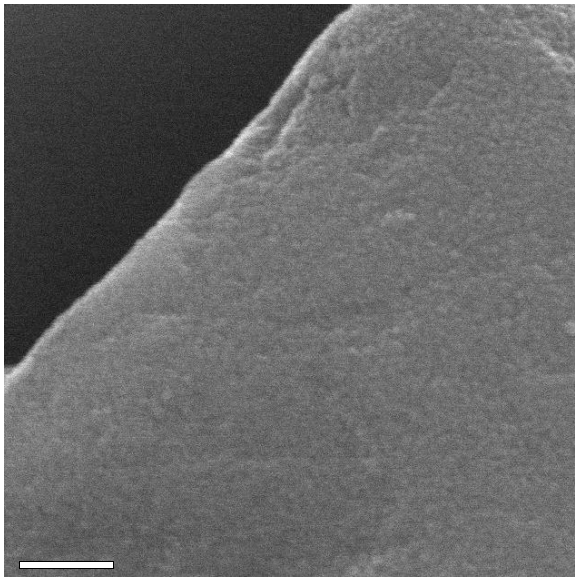

Fig. S5 SEM image of AC.

Reference

1. C. Zou, D. Wu, M. Li, Q. Zeng, F. Xu, Z. Huang and R. Fu, *J. Mater. Chem.* , 2010, **20**, 731.