Electronic Supplementary Information

High-energy supercapacitors based on hierarchical porous carbon with an ultrahigh ion-accessible surface area in ionic liquid electrolytes

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Experimental

Sample preparation: Hierarchical porous polystyrene (HPP) was prepared according to our previously reported template-free method by constructing carbonyl crosslinking bridges between polystyrene (PS) chains (*J. Mater. Chem.*, 2010, 20, 731-735). Briefly, anhydrous $AlCl_3$ was first added to CCl_4 and then refluxed with magnetic stirring at 75 °C. CCl_4 solution of PS was then added to the above mixture. The overall ratio of PS: $AlCl_3$: CCl_4 was 5 g: 12 g: 200 ml. Subsequently, the mixture was refluxed with magnetic stirring for 48 h at 75 °C to undergo the $AlCl_3$-catalyzed Friedel–Crafts reaction of PS and CCl_4. After that, the reaction was terminated by adding ethanol–water solution, and then the product was filtered off, washed with ethanol–water solution containing hydrochloric acid and then distilled water, followed by drying at 110 °C. The as-prepared HPP was semi-carbonized at 500 °C for 3 h in N_2 flow with a heating rate of 5 °C min^{-1}, and then cooled down, leading to the semi-carbonized sample HPP-500. After that, approximately 1g of HPP-500 was

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mixed with KOH pellets at a KOH/HPP-500 mass ratio of 6/1 and 20 ml ethanol was added to completely dissolve the KOH pellets. The mixture was dried at 110 °C and then carbonized in a tubular furnace at 900 °C for 3h with a heating rate of 5 °C min^{-1} under flowing nitrogen. After cooled down to room temperature, the resultant material was taken out, washed with 10% HCl and distilled water three times, and dried at 110 °C for 6 h, leading to formation of ultrahigh surface area HPC (UHSA-HPC). For comparison, the unactivated control sample PS-HPC was also prepared with the same procedure but without adding KOH.

Material characterization: The microstructure of the samples was investigated by a Hitachi S4800 scanning electron microscope (SEM), a JEM-2010HR transmission electron microscope (TEM), and a Micromeritics ASAP 2010 surface area and porosity analyzer. Before N_2 adsorption measurements, the samples were degassed for more than 10 h at 250 ^{o}C. The BET surface area was analyzed by Brunauer-Emmett-Teller (BET) theory. The total pore volume was estimated from single point adsorption at a relative pressure P/P_0 of ~0.99. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing.

Electrochemical characterization: The carbon electrodes in the form of round sheet were obtained by pressing a mixture film of 92 wt% carbon sample and 8 wt% polytetrafluorethylene into an aluminium grid current collector. The ionic liquid 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) was used as electrolyte. A kind of sandwich-type button supercapacitor consisting of the same carbon electrodes was assembled in the glove box (H_2O and O_2 <1 ppm). Before each assembling, the electrodes and separators were soaked in [bmim][PF_6] electrolyte for about 8 h in the glove box. All electrochemical measurements were performed with the assembled two-electrode button supercapacitor cells at 60 ^{o}C. Galvanostatic charge-discharge tests were executed at various current densities over a voltage range of 0-4V using an Arbin instrument. The calculation formula of C_m is: $C_m=2It/(m\Delta V)$,

where C_m is the specific capacitance of carbon sample, I the charge-discharge current, m the mass of carbon sample in each electrode, ΔV the discharge voltage, and t the discharge time. The energy density (E) and power density (P) are obtained, respectively, by the equations reported in the reference (*Angew. Chem. Int. Ed.* 2008, 47, 373-376): $E=CU^2/2$ and $P=IU/2$, where C, U, and I are the gravimetric capacitance for the two-electrode supercapacitor cell by galvanostatic charge-discharge test, the cell voltage (i.e., 4 V), and the current density, respectively. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) (excitation signal: 5 mV; frequency range: 0.01-10000 Hz) were carried out using an IM6ex electrochemical workstation.

Table S1 Specific mass capacitance and energy density at various current densities for UHSA-HPC and PS-HPC.

Sample	Specific mass capantiance (F/g)			Energy density (Wh/kg)		
	100 mA/g	200 mA/g	500 mA/g	100 mA/g	200 mA/g	500 mA/g
PS-HPC	28	19	7	16	11	4
UHSA-HPC	191	161	114	106	89	63