Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Title: A sulfonated polyaniline with high density and high rate Na-storage performances as a flexible organic cathode for sodium ion batteries

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Supporting Information

Experimental Section

Material preparation: The PANS polymer was synthesized via chemical oxidative copolymerization. A typical experimental procedure was to add ammonium persulfate (10 mmol in 1 M HCl 10 mL) dropwise into a mixed solution of 40 mL 1 M HCl containing aniline (2 mmol) and o- aminobenzenesulfonic acid (10 mmol) to initiate the polymerization. The reaction was carried out at 0-5 ^{o}C for 12 h. The copolymer was obtained by filtering and rinsing the precipitate with ethanol for several times, and then immersing in a mixture of 20 mL 0.4 M NaOH solution and diluted hydrazine hydrate for 4 h with stirring, and adding the solution slowly to a large excess of acetone thus giving the sodium polyaniline salt. To prepare the PANS/C nanoparticles, the as-prepared PANS polymer was ball-milled with Ketjen Black (KB) for 12 h at a weight ratio of 3:1.

Structural Characterization: The morphology of the obtained samples were characterized using field-emission scanning electron microscopy (Zeiss SIGMA FESEM). The structure of as-prepared polymer were determined by X-ray diffraction (XRD) using a PANalytical Multi-Purpose Diffractometer equipped a Cu K_{α} Radiation (λ=1.5406Å). Fourier transformed infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 FTIR spectrometer with KBr pellets. The specific surface area were determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption measurement on TriStar II 3020. X-ray photoelectron spectroscopy tests were carried out on a KRATOSXSAM800 instrument with the magnesium source Mg

K α 1253.6 eV operated at 12.5 kV and 16 mA. Elemental analysis of the chemical composition of the polymer were characterized on Vario Micro cube elemental analyzer (EA). ICP-AES analysis were performed with IRIS Intrepid III XSP.

Electrochemical Measurements: The electrode performance of PANS was characterized on 2025 type coin cells with a PANS film as a cathode and a sodium disk as anode, separated with a Cellgard 2400 separator. The PANS cathode consisted of 80% wt. ball-milled PANS/C, 10% wt. Super P and 10% wt. PTFE. To test the capacity contribution from the carbon addictive (KB) in the cathode, the electrode performance of KB electrode was carried on 2025 type coin cells with a KB film as a cathode and a sodium disk as anode. The KB film consisted of 90% wt KB, 10% wt PTFE. The electrolyte is 1 mol L^{-1} $NaPF_6$ in a mixture of ethylene carbonate, diethyl carbonate (EC/DEC =1:1 by volume, Shinestar battery materials co. Ltd, China). Cyclic voltammograms were measured on a CHI 660d electrochemical workstation (Shanghai, China) at a scan rate of 0.1 mV s^{-1} and the charge-discharge experiments were conducted on a Land CT.

1 SEM imagine of the bulk PANS

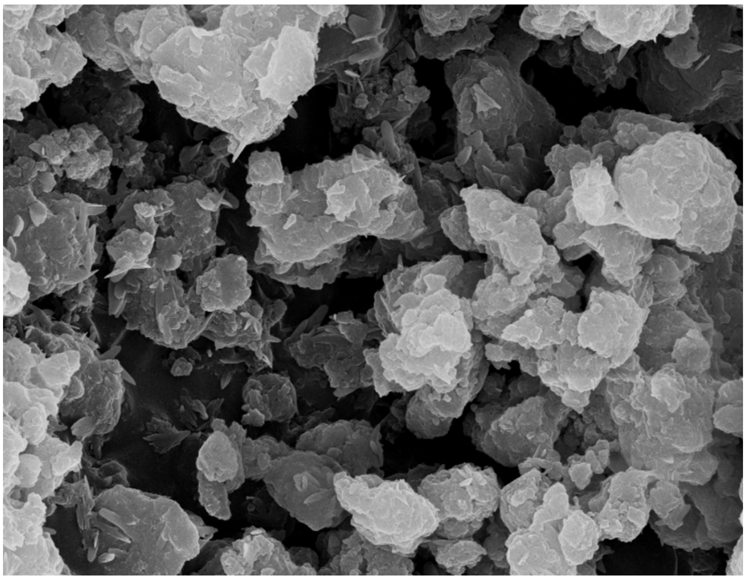

Fig. S1 SEM imagine of the as-prepared PANS

2. Nitrogen adsorption/desorption isotherms of the polymer

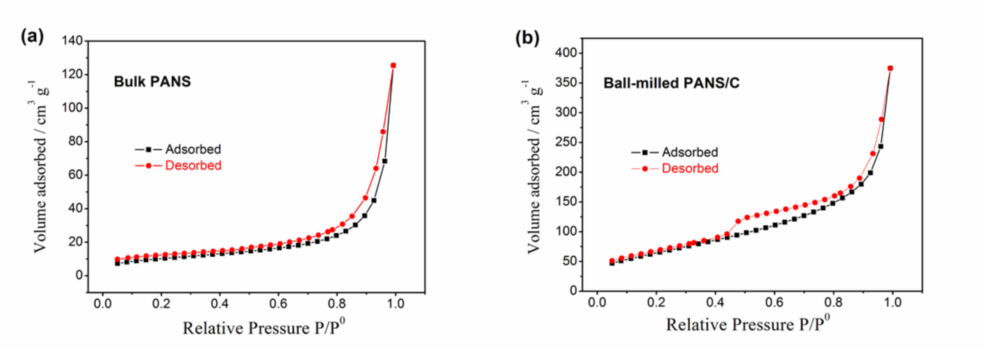

Figure S2. Nitrogen adsorption/desorption isotherms of as-prepared PANS（a） and the ball-milled PANS/C nanoparticles(b)

The specific surface area of bulk PANS and PANS/C is calculated to be 37.1, 235.4 m^2 g^{-1}, respectively.

3. XRD patterns of the as-prepared PANS

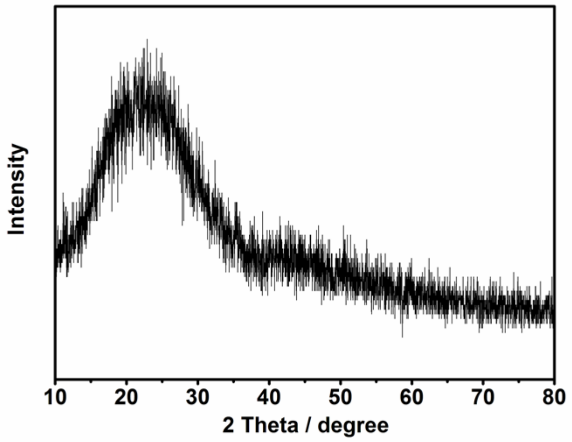

Figure S3. XRD patterns of the as-prepared PANS.

4. **X-ray photoelectron spectra of the as-prepared PANS**

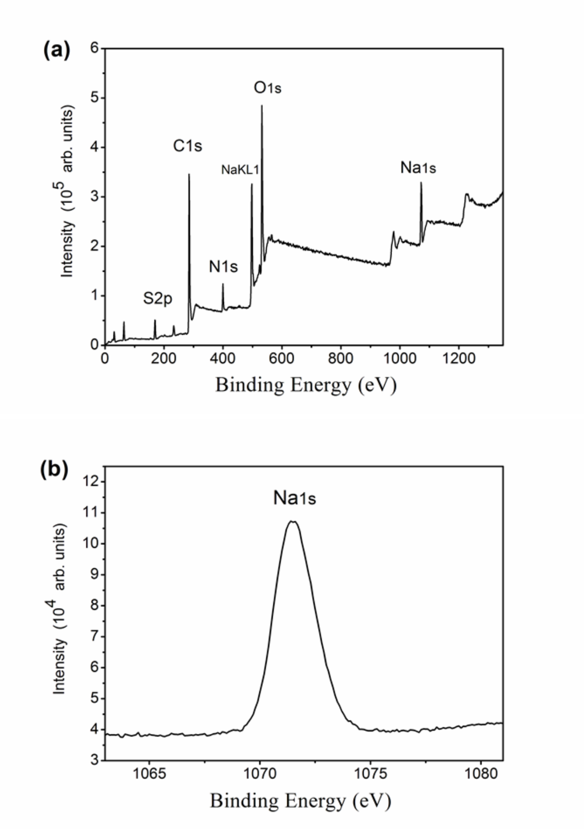

Figure S4. (a) X-ray photoelectron spectra of the as-prepared PANS polymer; (b) high resolution image of Na 1s band in (a)

The binding energy for Na 1s electrons appears at 1071.4 eV, which confirms Na in the presence of -SO_3Na state, indicating the -SO_3Na group bound to the polyaniline backbone.

5. **Elemental composition information of the as-prepared PANS**

Table S1. Elemental analysis results of the as-prepared PANS

Element	C.	H	N.	S	Na	O
% wt.	50.55	4.510	8.32	9.516	8.417	18.687

Based on the elemental composition analysis and ICP characterization, the composition of PANS polymer can be calculated to be $[C_6H_4N.\ C_6H_4NSO_3Na]_n$, indicating a ~ 50% sulfonation degree.

6. Electrochemical performances of the carbon addictive (KB) electrode

CV curves of the carbon addictive (KB) measured in a voltage range of 1.8 to 3.7 V at a scan rate of 0.1 mV s^{-1}Electrochemical performances of the carbon addictive (KB) electrode

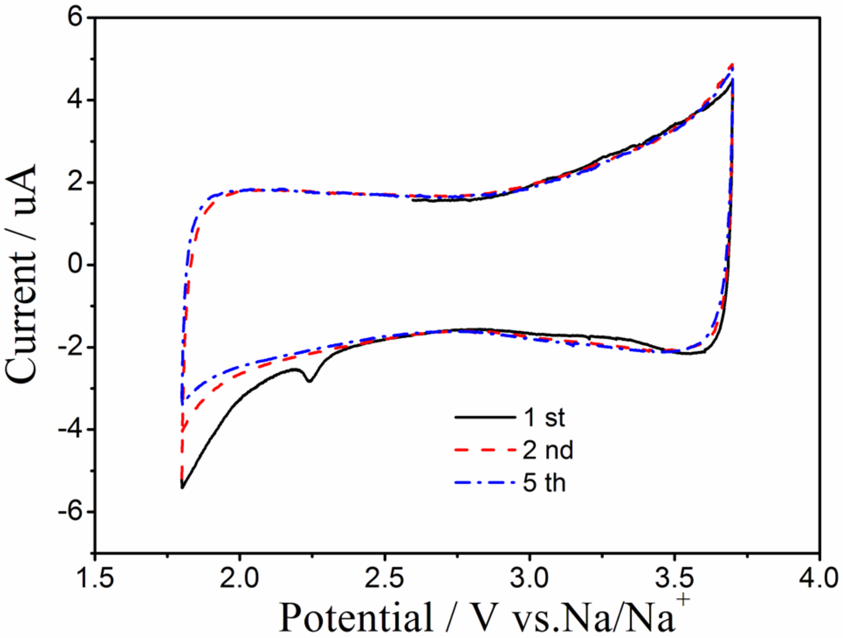

Figure S5. CV curves of the carbon addictive (KB) measured in 1.0 mol L^{-1} $NaPF_6$ + EC-DEC(V:V=1:1) electrolyte in a voltage range of 1.8 to 3.7 V. Scan rate: 0.2 mV s^{-1}

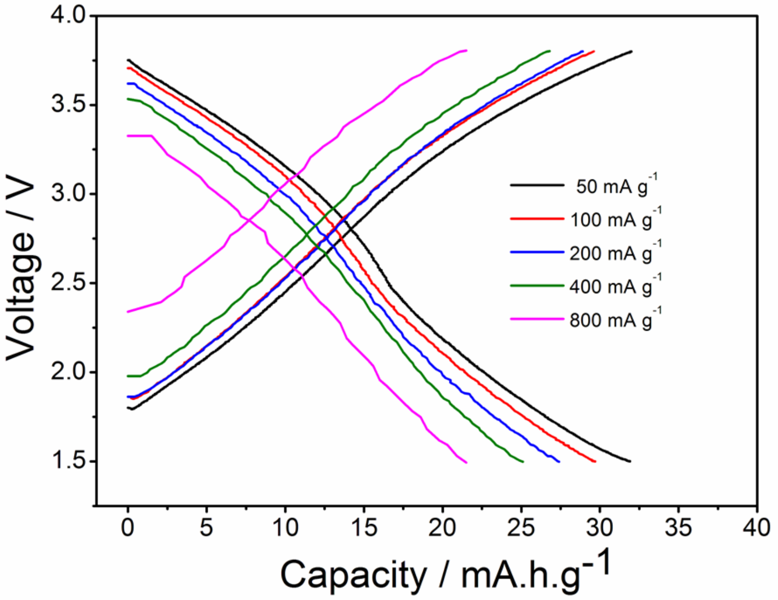

Figure S6. The charge-discharge profiles of KB electrode in 1.0 mol L^{-1} NaPF$_6$ +EC-DEC (v/v=1/1) electrolyte at various current densities in a voltage range of 1.5 to 3.8 V.

As shown in Figure S6, the carbon addictive KB can deliver 32, 29, 27, 25, 21 mAh g^{-1} at the current densities of 50, 100, 200, 400, 800 mA g^{-1} in the voltage range of 1.5 to 3.8 V. As the weight ratio of PANS/KB = 3:1, the capacity contribution of the carbon addictive is calculated to be 10.6, 9.6, 9, 8.3, 7 mAh g^{-1} at 50, 100, 200, 400, 800 mA g^{-1}.

7. The ratios of Na and polymer in the PANS electrode cycled at different depths of charge and discharge

Table S2. The ratios of Na and polymer in the PANS electrode cycled at different depths of charge and discharge

Number	States	Na (mg)/ PANS (g)	n（Na）/n($C_{12}H_8N_2SO_3Na$)
a	As-prepared	84.17	1.04
b	Charged to 3.8 V	5.69	0.07
c	Discharged to 3.0 V	57.4	0.706
d	Discharged to 1.5 V	86.56	1.06

To quantify insertion and de-insertion of sodium ions upon charge and discharge, the as-prepared PANS electrode (a), charged to 3.8 V (b), discharged to 3.0 V (c) and discharged to 1.5 V (d) were taken out from the disassembled cells and rinsed with pure diethyl carbonate solvent for 3 times. The thick film of PANS/C/PTFE was destroyed by heating in air at 600 °C for 10 h, the sodium oxides obtained was then dissolved in HNO_3 for the atomic emission analysis using IRIS Intrepid Ⅲ XSP spectrometer.