Supporting Information

Direct Synthesis of 3D Hierarchically Porous Carbon/Sn Composites via In-situ Generated NaCl Crystals as Templates for Potassium-ion Batteries Anode

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2.Experimental

2.1 One-step Synthesis of 3D-HPCS

As shown in **Scheme 1**, Stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$, Aladdin, 5g) was dissolved in the distilled water (140 mL) followed by ultrasonic stirring for 30 min. Then Polyacrylate Sodium (Aladdin, 14g) which acted as carbon sources was added into the above mentioned solution and another 30 min ultrasonic stirring was conducted. After that, the white precursor solution undergo freeze-drying process. Subsequently, the white precursor was treated at 450℃, 650℃ and 850℃ for 5h in Ar atmosphere (remarked as HPCS-450, HPCS-650 and HPCS-850) with a heating rate of 3℃ min^{-1}, respectively. Then, the black precursor was washed with distilled water along with magnetic stirring for three times. Finally, the wet powder was vacuum freeze-dried for 24 h.

2.2 Structural characterization

The structure of the composites were characterized by scanning electron microscopy (SEM, Hitachi SU8220) and transmission electron microscopy (TEM, Zeiss Libra 200FE). The X-ray powder diffraction (XRD) analysis was performed with a Bruker D8 advanced X-ray diffractometer equipped with Cu Ka radiation (λ=1.5418 Å). The element content was analysed by X-Ray Photoelectron Spectrometer ESCALAB 250Xi with Al Ka as the excitation source and ICP (NWR 213-7900). The Roman spectroscopy were obtained using a Renishaw1000B Raman spectrometer (with 633 nm laser excitation). TGA were performed with a DTG-60 instrument up to 700℃ at

a heating rate of 10 ℃/min in nitrogen. The specific surface area and the pore diameter distribution were measured by Micromeritics ASAP 2460.

2.3 Electrochemical measurements

The electrochemical performance of 3D-HPCS were evaluated using 2032 coin-type half-cells. The working electrode used in electrochemical performance measurements was obtained of the active material, conductivity agent, and polyvinylidene fluoride (PVDF) binder in a 7:2:1 weight ratio. The slurry was smeared on copper foil and dried under vacuum at 60℃ overnight. The electrolyte was a 0.8 M solution of $KClO_4$ in ethylene carbon (EC) -dimethyl carbonate (DEC) (1:1, v/v) and potassium metal was applied as anode. Glass fibre (Whatman GF/D) were used as separators. Galvanostatic and rate charge–discharge tests were performed using a multichannel battery testing system (LAND-CT2001A) at room temperature (25℃). Cyclic voltammetry (CV) measurements were carried out in the 3.0–0.01 V (vs K/K^+) voltage range at a scan rate of 0.1 mV s^{-1} by electrochemical workstation.

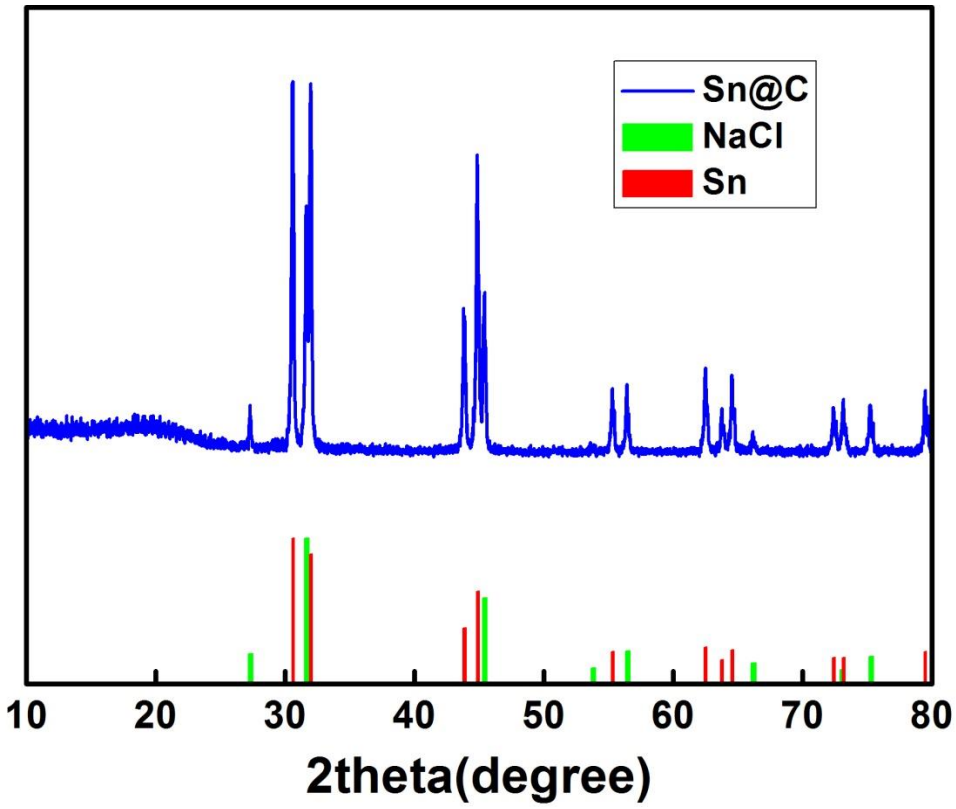

Figure S1. XRD patterns of 3D-HPCS-NaCl

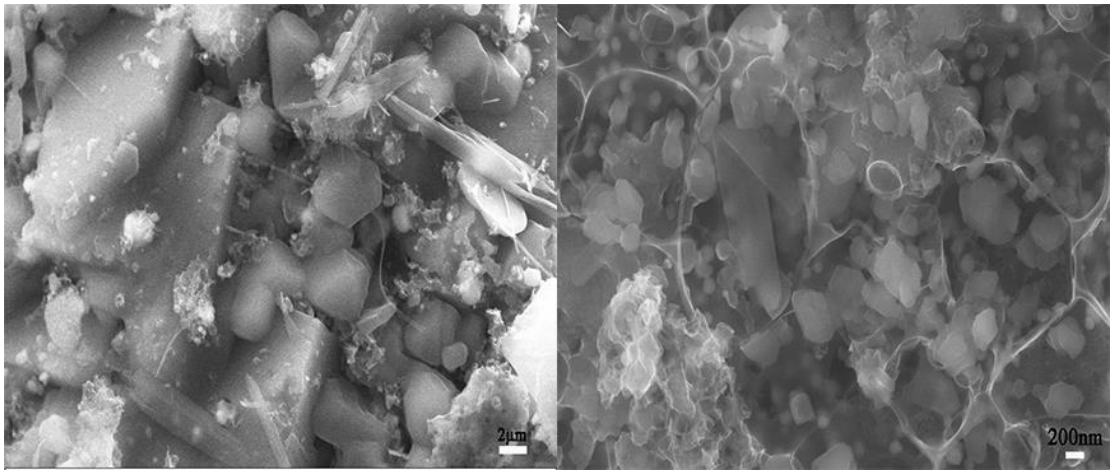

Figure S2. SEM images of the3D-HPCS-NaCl

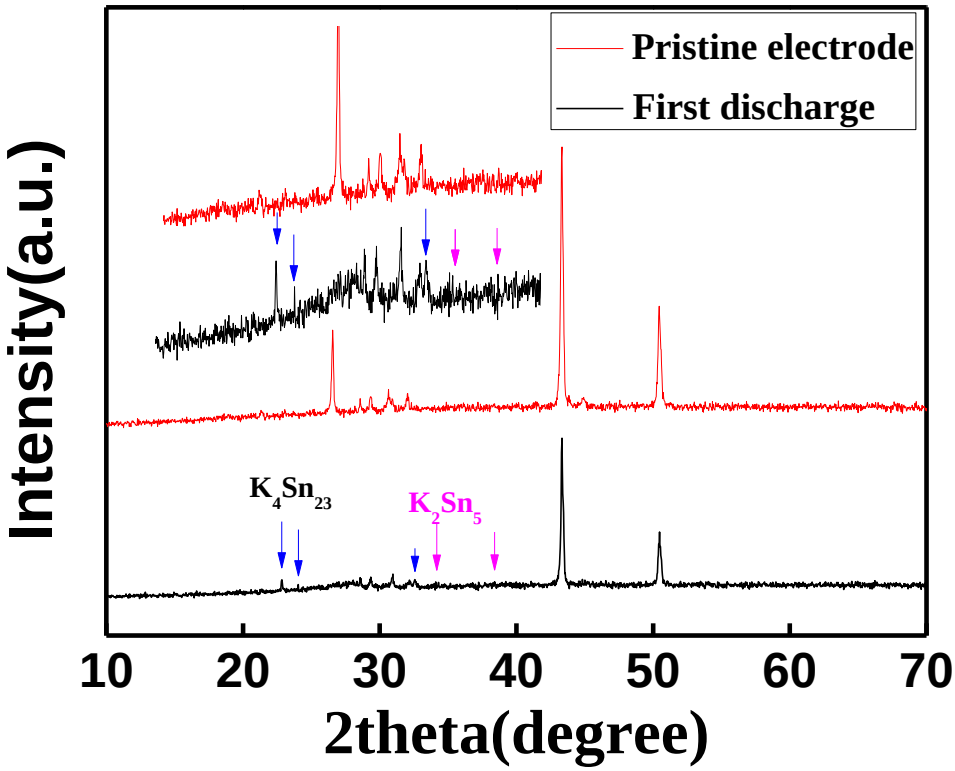

Figure S3. XRD patterns of 3D-HPCS electrode before (black line) and after CV cycles (red line)

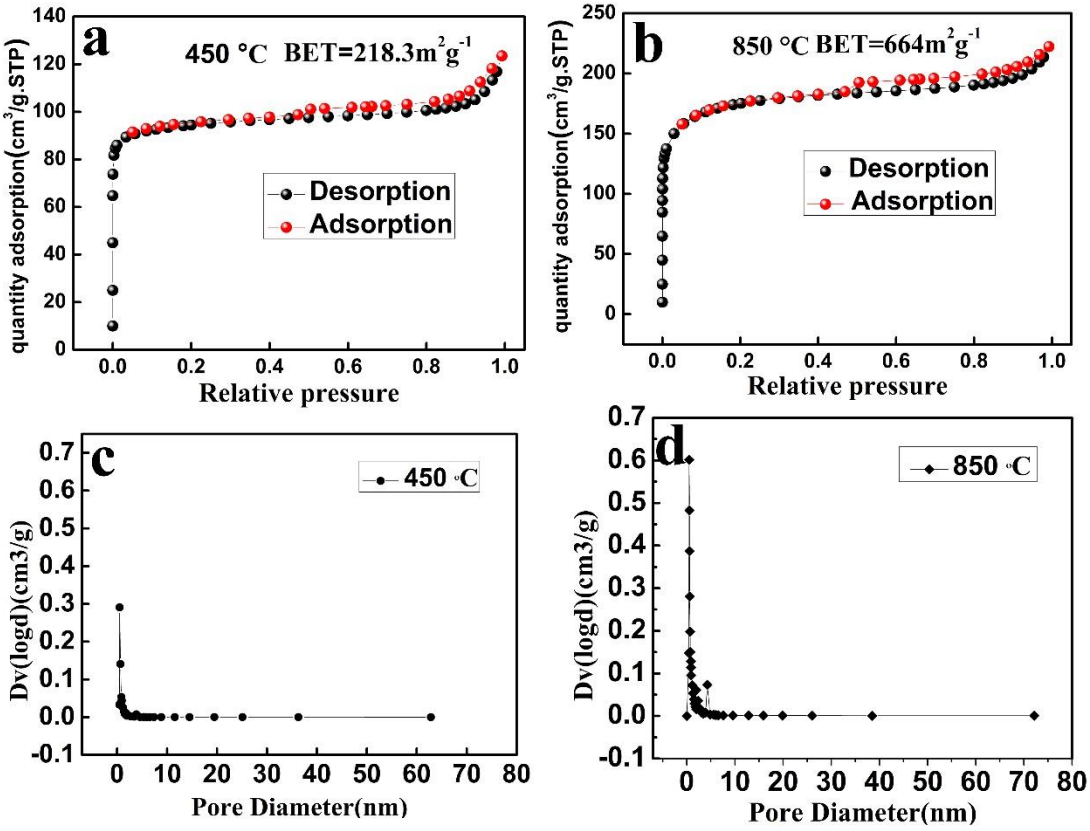

Figure S4. The N_2 adsorption/desorption isotherm, specific surface area and corresponding pore size distribution for HPCS-450, HPCS-850.

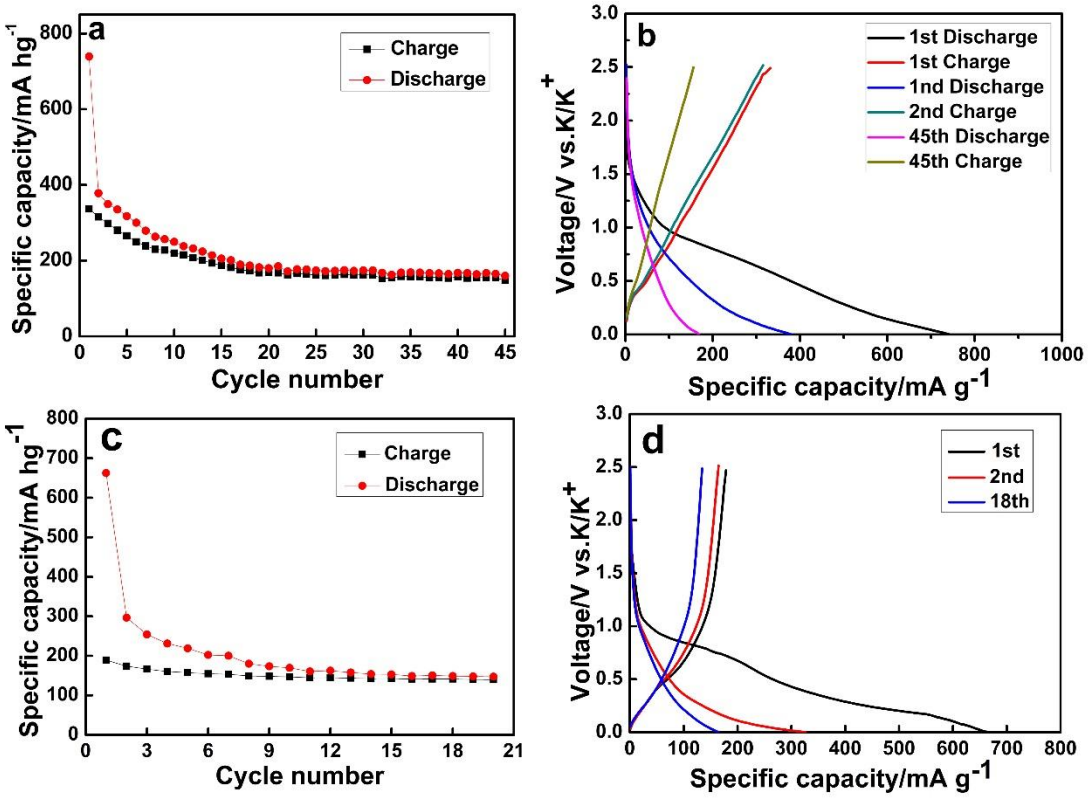

Figure S5. Electrochemical performance for porous carbon material (a, b) and conductive carbon black (c, d).

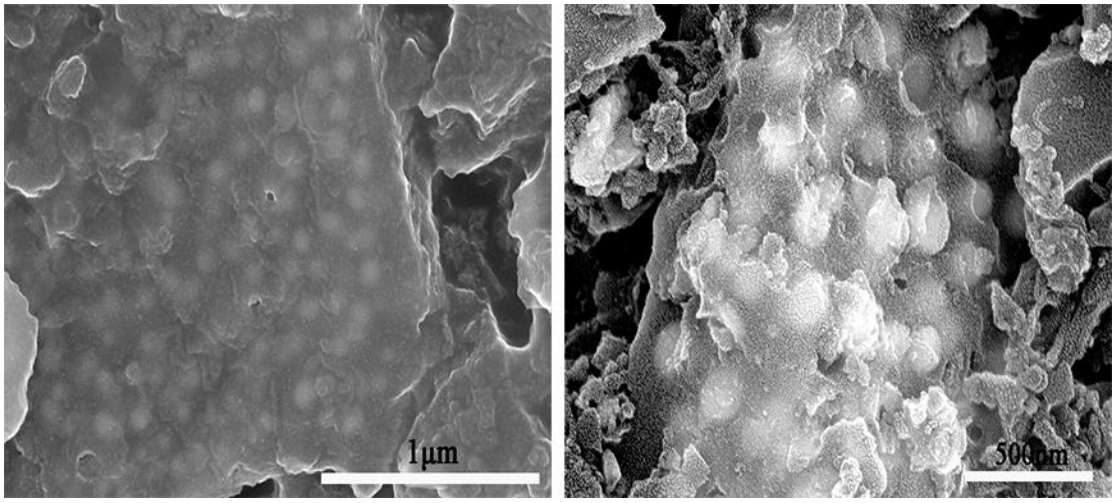

Figure S6. SEM images of 3D-HPCS electrode after 50 charge/discharge cycles.