Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

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Electronic Supplementary Information

Synthesis and thermodynamic investigation of MnO nanoparticles anchored N-doped porous carbon as anodes for Li-ion and Na-ion batteries

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Experimental

Chemicals

Pyrrole (99 wt%), hydrochloric acid (37 wt%), potassium permanganate ($KMnO_4$, 98 wt%), sodium sulfate (Na_2SO_4, 98 wt%), ammonium persulfate (98 wt%), and manganese monoxide (MnO) are analytical pure and were purchased from Beijing Chemical Reagents, Co. (China). Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG, Pluronic® P-123, Ma = 5800), poly(vinylidene difluoride) (PVdF), and carbon black were obtained from Sigma-Aldrich Trading Co. Ltd. (China). *N*-Methyl-2-pyrrolidone (NMP, 99.9 %) was bought from Xilong Scientific Co. Ltd. (China). Ultrapure water (18 $M\Omega$ cm) was provided by a Millipore-ELIX water purification system. No further purification was employed before the chemicals were used. Nitrogen (99.999 % purity) was purchased from Beijing Haike Yuanchang Gas Co. Ltd. (China).

Materials Preparation

The precursor polypyrrole-based hydrogel (PPH) was prepared according to our previous work.[1] In a typical procedure, P123 and pyrrole were finely mixed in aqueous hydrochloric acid solution, and the ammonium persulfate was then added in the above clear solution. After a hydrothermal process, the PPH was obtained. Manganese dioxide (MnO_2) particles were deposited on the surface of PPH through a facile redox reaction. In this procedure, $KMnO_4$ (0.025 mol) and Na_2SO_4 (0.025 mol) were dissolved in ultrapure water (250 mL). PPH was then immersed into $KMnO_4$/Na_2SO_4 solution. The above mixture was stirred at room temperature to improve the diffusion of $KMnO_4$/Na_2SO_4 solution into PPH and promote the reaction between carbon in PPH and $KMnO_4$. The hybrid hydrogel was then dialyzed with ultrapure water until the water became clear. After a freeze-drying process, MnO_2 doped polypyrrole-based aerogel (PPA–MnO_2) was obtained. Polypyrrole-based aerogel was named as PPA. MNPC was finally obtained after PPA–MnO_2 was calcined at 600 °C for 60 min in a tubular furnace with a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Different immersion time of 120, 180, and 240 min were employed to tune the MnO loading in MNPC. The corresponding samples were denoted as MNPC-*t* (*t*=120, 180, and 240 min). NPC and MnO were also used for comparison. NPC was prepared through a heat treatment of PPA at 600 °C for 60 min (nitrogen atmosphere). MnO was purchased from Beijing Chemical Reagents without any further treatment.

Instrumental Characterization

X-ray diffraction (XRD) patterns were obtained through a D/MAX-TTRIII(CBO) X-ray diffraction instrument (Rigaku Co., Japan) using Cu Kα radiation under range of 10–80°. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were taken with an S-4800 field emission scanning electron microscope (Hitachi Ltd., Japan) and a Tecnai G2 20 S-TWIN microscope (FEI, U.S.A.), respectively. High-resolution transmission electron microscopy (HRTEM) image was obtained on a Tecnai G2 F20 U-TWIN microscope (FEI, U.S.A.). Raman spectrum was measured on an inVia Raman spectrometer (Renishaw plc, U.K.) with a laser of a wavelength of 514 nm.

The laser power was about 1 mW. Thermalgravimetric analysis (TGA) was carried out through a Pyris Diamond thermogravimetric/differential thermal analyzer (PerkinElmer, U.S.A.) in air atmosphere at a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS) was taken on an ESCALab220i-XL electron spectrometer (VG Scientific Ltd., U.K.) using Al Kα radiation at 300 W. Flash EA 1112 analyzer (Thermo Electron SPA, U.S.A.) was used to measure the content of nitrogen, hydrogen, and carbon in the as-synthesized materials. The nitrogen adsorption–desorption isotherms and pore parameters were measured at 77 K by a 3-Flex surface area and porosity analyzer (Micromeritics Instrument Corp., U.S.A.). All the porous materials were degassed at 120 °C for 12 h under vacuum before measurement.

Electrochemical Measurement

The coin-type half cells with lithium (CR2025) and sodium (CR2032) counter electrodes were used to measure the electrochemical performance of the electrodes on LAND CT2001A (Wuhan Jinnuo Electronics Co. Ltd. China) and BCS system (Bio-Logic Science Instruments) at room temperature, respectively. For the electrode preparation in lithium-ion batteries (LIBs), carbon black and the binder poly(vinylidene difluoride) (PVDF) were mixed homogenously with the active materials with the weight ratio of 10:10:80 in *N*-Methyl-2-pyrrolidone (NMP) solvent, and the slurry was uniformly coated on the copper foil. For sodium-ion batteries (SIBs), carbon black and PVDF were mixed with the active materials with weight ratio of 5:10:85 in *N*-Methyl-2-pyrrolidone (NMP) solvent, and the slurry was also coated on carbon-coated copper foil.

Afterwards, the prepared electrodes were dried at 80 °C for overnight under vacuum with a loading about 0.5-2.5 mg cm^{-2}. The sodium ion batteries were tested at 0.005-2.5 V (*vs.* Na/Na$^+$). For LIBs, $LiPF_6$ (1 M) was dissolved in a 1:1 (v:v) mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) as the electrolyte. For SIBs, $NaClO_4$ (1 M) was dissolved in a 1:1 (v:v) mixture of EC and DMC as the electrolyte. Galvanostatic charge–discharge measurements were measured during the voltage range of 0.001 to 2.5 V (*vs.* Li/Li$^+$). The specific capacity of MNPC was calculated using the electrode weight. Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) in LIBs were carried out on an EG&G Princeton Applied Research VMP3 workstation (Bio-Logic Science Instruments, France). The EIS tests were taken with the amplitude of 5 mV and the frequency range was from 0.01 Hz to 100 kHz. The CV curves were scanned at a rate of 0.1 mV s^{-1} and the potential window was 0.01–2.5 V (*vs.* Li/Li$^+$). The data of the thermodynamic properties for the electrode reaction at 25 °C was obtained from the HSC Chemistry 8 software.

References

1 Y.-N. Sun, Z.-Y. Sui, X. Li, P.-W. Xiao, Z.-X. Wei, B.-H. Han, Nitrogen-doped porous carbons derived from polypyrrole-based aerogels for gas uptake and supercapacitors. ACS Appl. Nano Mater., 2018, **1**, 609.

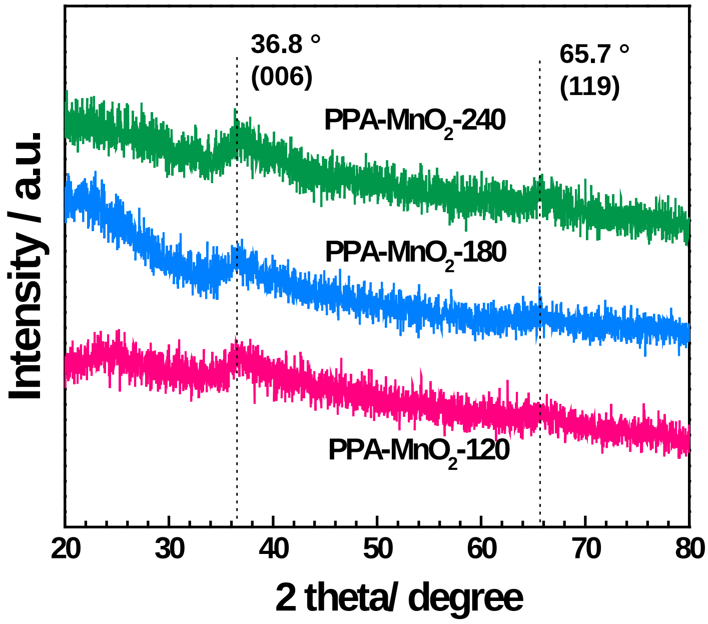

Fig. S1. XRD patterns of PPA–MnO_2-120, PPA–MnO_2-180, and PPA–MnO_2-240.

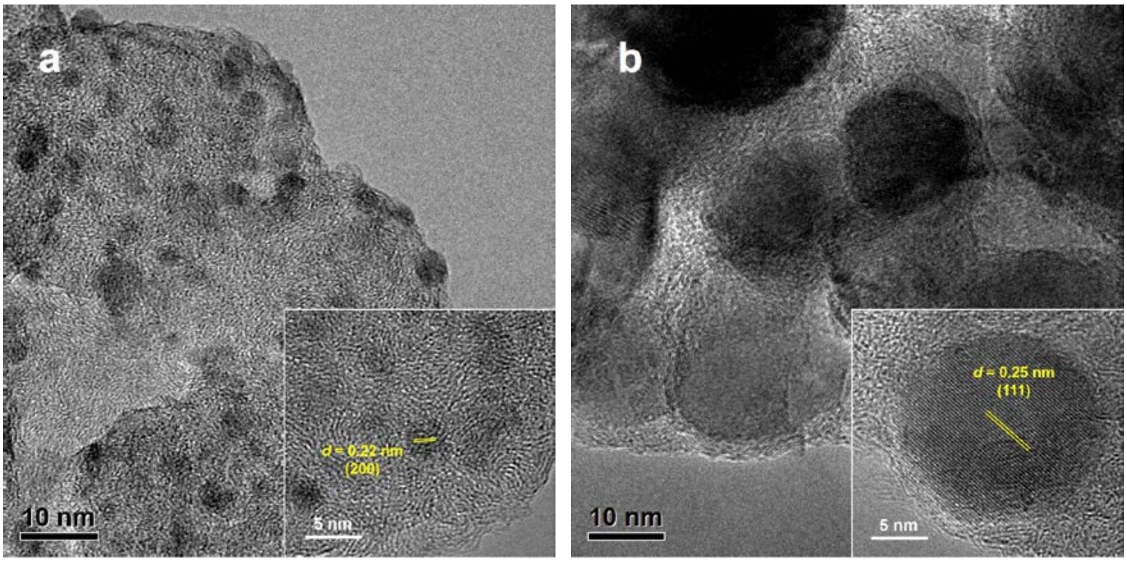

Fig. S2. HRTEM images of MNPC-120 and MNPC-240.

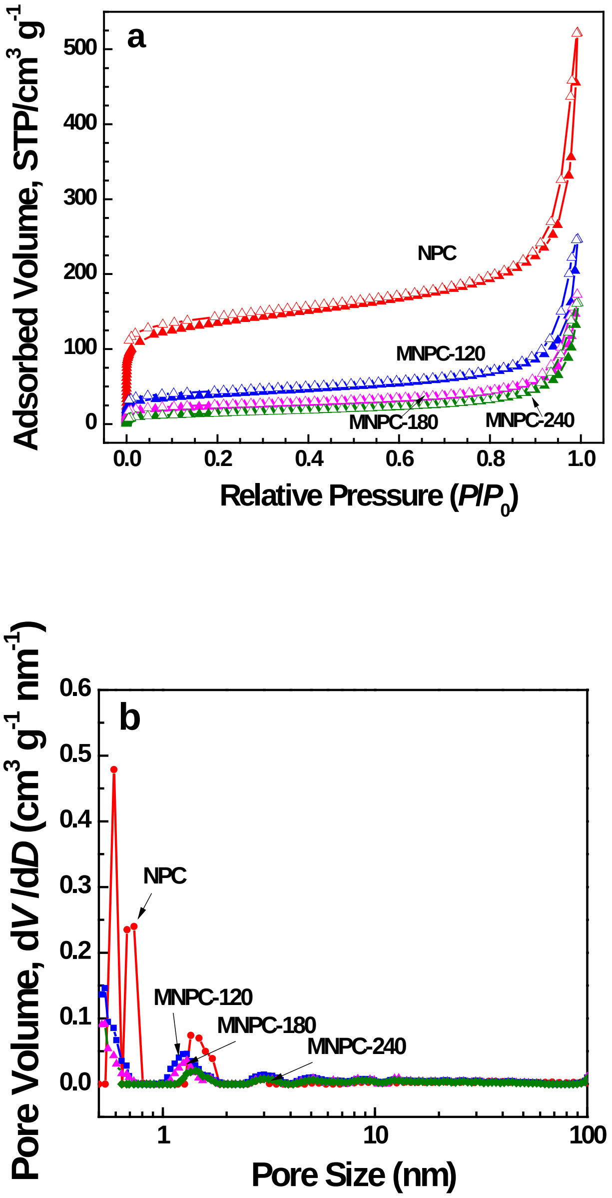

Fig. S3. (a) Typical nitrogen adsorption–desorption isotherms and (b) nonlocal density functional theory (NLDFT) pore size distribution profiles of NPC and MNPC materials (MNPC-120, MNPC-180, and MNPC-240). Solid symbols are for adsorption and open symbols for desorption.

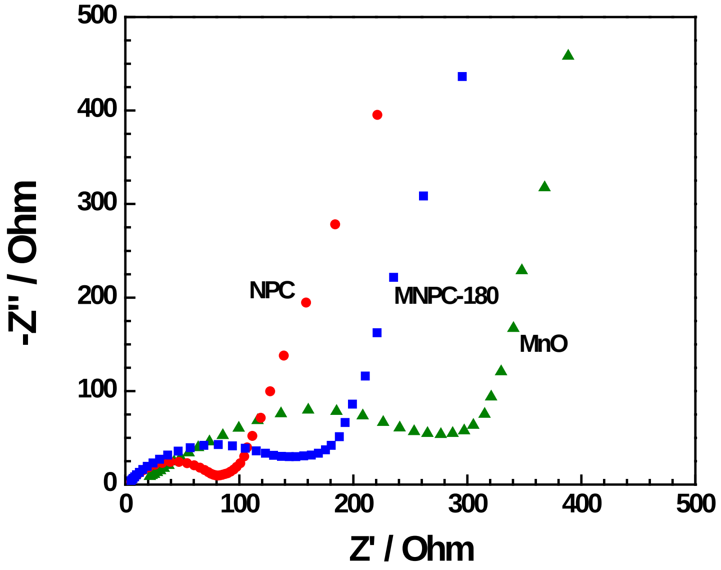

Fig. S4. Nyquist plots of MnO, NPC, and MNPC-180 electrodes before cycling in LIBs.

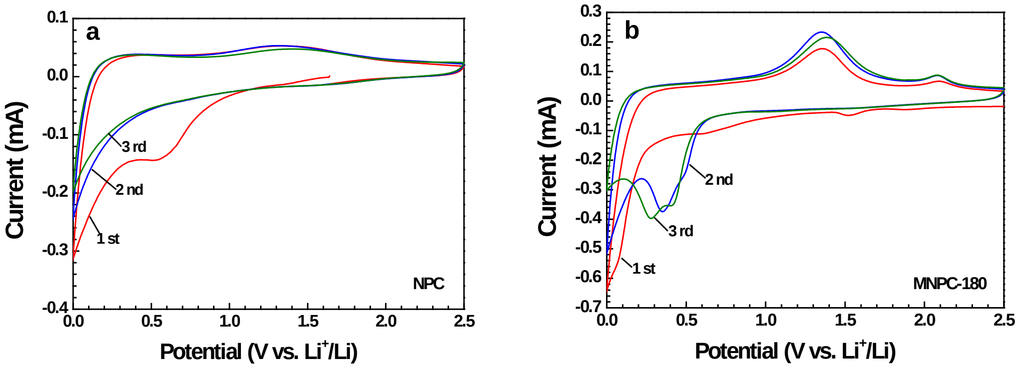

Fig. S5. Cyclic voltammetry (CV) curves of NPC (a) and MNPC-180 (b) in LIBs with scan rate of 0.1 mV S^{-1} within 0.001-2.5 V (*vs.* Li/Li$^+$).

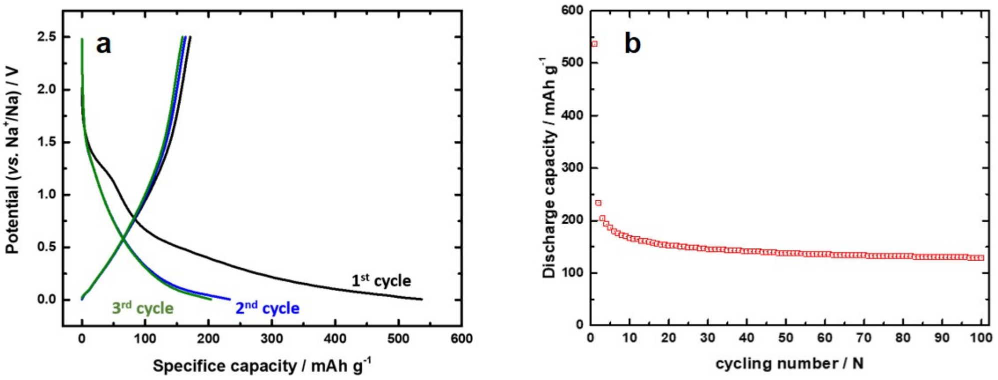

Fig. S6. Galvanostatic charge/discharge curves (a) and cycling performance (b) of NPC at 50 mA g^{-1} with a voltage window of 0.005–2.5 V for 100 cycles in SIBs.

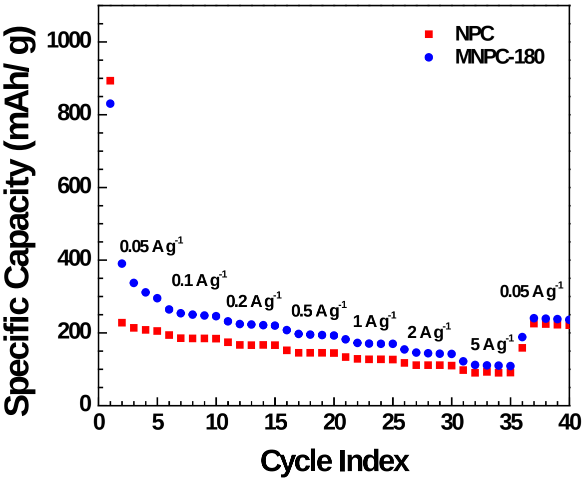

Fig. S7. Rate capacities of NPC and MNPC-180 at various current densities (0.05, 0.1, 0.2, 0.5, 1, 2, and 5 A g^{-1}) in range of 0.001–2.5 V in SIBs.

Table S1. Porous Properties of NPC and MNPCs.

Sample	S_{BET} (m^2 g^{-1}) [a]	S_{Langmuir} (m^2 g^{-1}) [b]	V_{total} (cm^3 g^{-1}) [c]
NPC	440	627	0.51
MNPC-120	133	181	0.23
MNPC-180	81	116	0.17
MNPC-240	51	77	0.14

[a] Specific surface area calculated from the nitrogen adsorption isotherm using the BET method at relative pressure range (P/P_0) during 0.05−0.30.

[b] Specific surface area calculated from the nitrogen adsorption isotherm by means of the Langmuir equation.

[c] Total pore volume at $P/P_0 = 0.97$.