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Supporting Information

N, O co-doped Porous Carbon Derived from Pine Needles for Zinc-Ion Hybrid Supercapacitors

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1. Experimental

1.1 Synthesis of PN and PNMNC-X Samples

All chemicals and reagents were of analytical grade and used without further purification. The pine needles (Pinus tabuliformis Carrière) were collected, washed with ethanol and deionized water to remove impurities, and dried at 60 °C for 12 h. Then the pine needles were pre-carbonized at 500 °C for 2 h under an Ar atmosphere. The yield was marked as PN. The obtained product was ball-milled by a planetary ball miller (XGB2, Nanjing Boyuntong Corp.) with a 50 mL stainless steel tank and stainless steel beads at 500 rpm for 30 mins. The product was mixed with KOH solution (according to the weight ratios of KOH: carbon were 1:1, 2:1, and 3:1, respectively) and freeze-dried, then pyrolyzed in a horizontal tube furnace under Ar atmosphere at a heating rate of 5 °C min^{-1} at 800 °C for 2 h. The product was washed thoroughly with 1 M HCl solution, then deionized water until pH≈7 to remove impurities and finally dried overnight at 60 °C. The as-obtained samples were termed PNMNC-X, where X is the KOH: carbon weight ratio. For comparison, one control sample was prepared by direct carbonization and activation without freeze-drying and designated as PNNC-2.

1.2 Physicochemical characterizations

Morphologies and structure features of the materials were characterized by scanning electron microscopy (FESEM JSM-7800F) and a transmission electron microscope (TEM, JEOL JEM-2100). The crystal structure was investigated by X-ray diffraction (XRD, Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation (λ= 1.5418 Å) at 40 kV and 30 mA and a scan rate of 7 ° min^{-1} over the 2 theta range of 10-80 °). The Brunauer-Emmette-Teller (BET) specific surface area and pore size distribution were evaluated by a Micromeritics Tristar II 3020 surface area analyzer at 77 K. The Raman spectrum was recorded on a Zolix RTS2 Confocal Laser Raman microscope at the excitation wavelength of 532 nm. Fourier transform infrared (FT-IR) spectra were obtained by a Thermo Fisher Scientific Nicolet iS50. The X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo Scientific K-Alpha instrument.

1.3 Electrochemical measurements

The ZHSCs were assembled into CR2032 coin-type cells. Zn foil was used as an anode electrode, which was pouched into electrodes with 15 mm diameter. To fabricate the cathode, a slurry was prepared by mixing the activated carbon powders, acetylene black and polyvinylidene difluoride (PVDF) with a mass ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). Then the slurry was coated on a stainless-steel foil with a mass loading of 0.9-1.2 mg cm^{-2}. The prepared electrodes were dried in an oven at 60 °C for 12 h. The glass fiber membrane was used as the separator, a Zn foil as the anode, and an aqueous solution of 2 M $ZnSO_4$ as the electrolyte. Cyclic voltammetry (CV) tests with different scanning rates of 2-50 mV s^{-1}, galvanostatic charge-discharge (GCD) curves at various current densities of 100-20000 mA g^{-1} with an open circuit potential of 0.2-1.8 V and electrochemical impedance spectroscopy (EIS) measurements in the frequency ranging from 0.01 to 10^5 Hz were conducted on an electrochemical workstation (CHI660C, China). A CT2001A instrument (Wuhan LAND Electronics Co., Ltd) was used to obtain the cycle and rate performances of the ZHSCs. The specific capacitance (C_s, F g^{-1}) of ZHSCs was calculated according to the following equation:

$$C_s = (I \times \Delta t) / (m \times \Delta V) \qquad \text{(S1)}$$

where I (A) represents the discharge current, m (g) is the loading mass of active materials on the electrode, Δt (s) is the discharge time, and ΔV is the potential drop during the discharge processes.

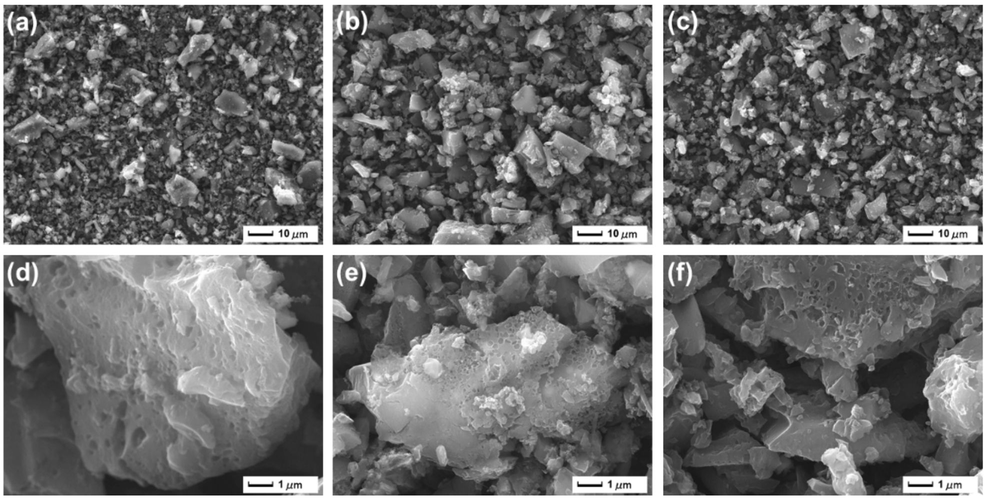

Figure S1. SEM images of (a,d) PNMNC-0, (b,e) PNMNC-1, and (c,f) PNMNC-3.

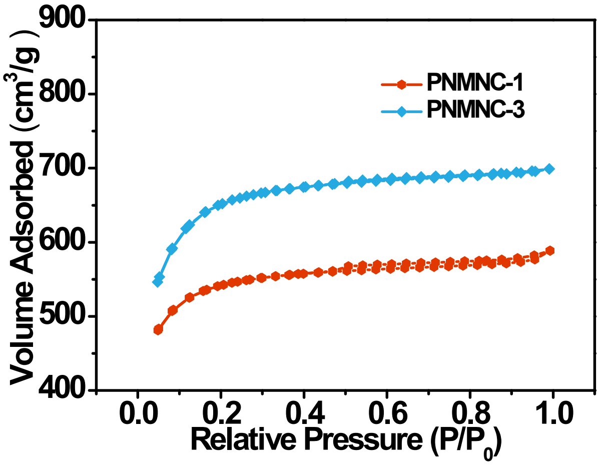

Figure S2. N_2 adsorption-desorption isotherms of PNMNC-1 and PNMNC-3.

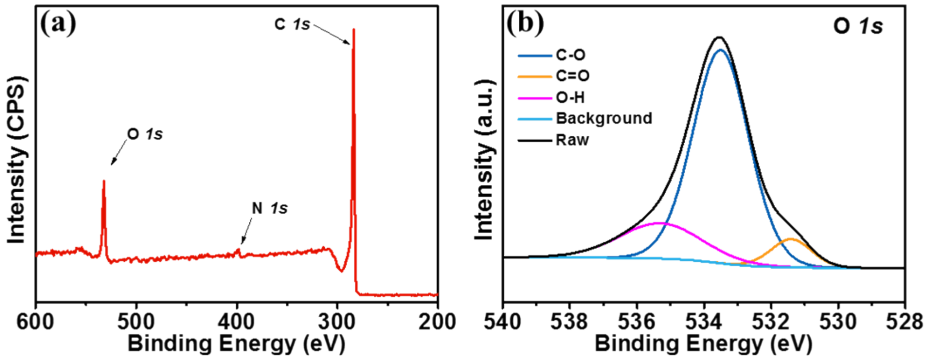

Figure S3. XPS spectra of PNMNC-2. (b) the high-resolution O 1s of PNMNC-2

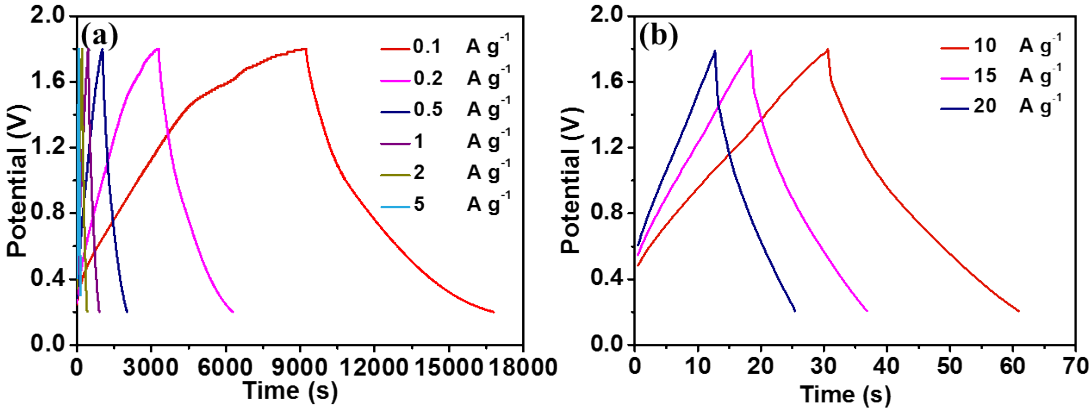

Figure S4. Galvanostatic charge-discharge curves of (a), (b)PNMNC-2 at different current density.

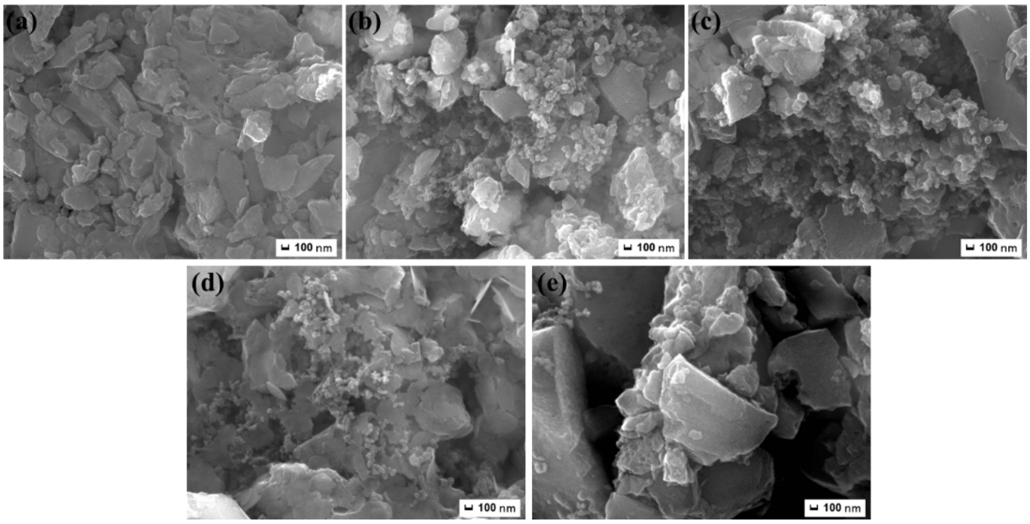

Figure S5. SEM images PNMNC-2 cathodes (a) state A, (b) state B, (c) state C, (d) state D, (e) state E.

Table S1. Specific surface area, and pore structure characterization parameters of PNMNC samples.

Sample	**Specific surface area (m^2 g^{-1})**	**Total pore volume (cm^3 g^{-1})**	**Average pore diameter (nm)**
PNMNC-0	75.42	0.0277	3.41
PNMNC-1	1671.88	0.6211	2.22
PNMNC-2	2493.45	0.4975	2.12
PNNC-2	1507.27	0.2789	2.45
PNMNC-3	2036.28	0.6366	2.11

Table S2. XPS surface elemental composition of PNMNC samples (Atomic **%**).

Sample	**Carbon at. %**	**Oxygen at. %**	**Nitrogen at. %**
PNMNC-0	90.62	7.25	2.12
PNMNC-1	90.57	6.75	2.67
PNMNC-2	85.74	11.79	2.47
PNMNC-3	78.12	19.53	2.35