

Supporting Information

Nitrogen and Atomic Ni Co-Doped Carbon Material for Sodium Ion Storage

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1. Experimental Section

Chemical and Reagents

Pyrrole (99%), propionic acid (99.9%), *N,N*-dimethylformamide (DMF, 99.9%), tetrahydrofuran (99.9%), triethylamine (99.9%), isopropyl alcohol (99.9%), dichloromethane (99.9%), hexane (99.5%), and methanol (MeOH, 99.9%), 2,2'-azobisisobutyronitrile (AIBN, 99%), nickel oxide (NiO, 99.9%), nickel(II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 99%) were purchased from Aladdin. 4-vinylbenzaldehyde were purchased from Huaweiruike Chemical. Silica gel (200–300 mesh) was bought from Qingdao Haiyang Chemical Plant. Pyrrole was distilled under a N_2 atmosphere before each time using. Other chemical reagents were employed as received without further purification.

Synthesis

Tetra(4'-vinylphenyl)porphyrin, 1000 mL two-necked round-bottomed flask was charged with a solution of 4-vinylbenzaldehyde (13.2 g, 100 mmol) in 500 mL propionic acid and heated to reflux, freshly distilled pyrrole (6.7 g, 100 mmol) was added slowly, reaction for 3 h, and then cooled to room temperature. The as-obtained precipitate was filtered and washed with methanol, the crude product obtained. Further purification by silica gel column chromatography, obtain purple powder (TVPP). Second, 250 mL three-necked round-bottomed flask was charged with a solution of TVPP (0.72 g, 1.0 mmol) and nickel (II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ 1.24 g, 5.0 mmol) in 150 mL *N,N*-dimethylformamide, refluxed for 3 h, under a nitrogen atmosphere. The mixtures were evaporated to remove the DMF solvent, and the residue was purified by silica gel column chromatography, brown powder (NiTVPP) was obtained. Third, under a nitrogen atmosphere, 125 mL three-necked round-bottomed flask was charged with a solution of TVPP (1.08 g, 1.5 mmol), NiTVPP (58.17 mg, 0.075 mmol) and AIBN (98.5 mg, 0.6 mmol) in 50 mL DMF. After heated at 180 °C and reflux for 24 h, the solution was cooled to room temperature. The as-obtained precipitate was filtered and washed with MeOH, THF, and DMF to give the crude product. Further purification was carried out by Soxhlet extractions for 24 h with methanol and dichloromethane, respectively. After dried at 80 °C in vacuum for 24 h, the precursor poly-NiTVPP was obtained. At last, the precursor Ni-N-C was heated to 600 °C for 3 h at the heating rate of 5 °C min^{-1} under flowing nitrogen gas in a tube furnace, and then naturally cooled to room temperature to obtain Ni-N-C.

Characterization.

Elemental analyses (EA) was performed on Vario EL cube instrument. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was obtained by PerkinElmer OPTIMA 8000DV. Raman spectrum was measured by Renishaw inVia Laser Micro-Raman Spectrometer at 514 nm. Brunauer-Emmet-Teller (BET) surface areas were performed on a Micromeritic ASAP2020M analyzer at 77 K. The crystal structure of catalysts were collected by X-ray diffraction (XRD) patterns and obtained on a Bruker D8 Advanced diffractometer with Cu K α , at 40KV and 40 mA with the rate of 5 ° min⁻¹. X-ray photoelectron spectroscopy (XPS) measurements were collected on an ESCALab250 XPS system with Al K α source and a charge neutralizer, and used the contaminated C 1s (284.8 eV) as the referenced. Transmission electron microscopy (TEM) images and high-angle annular dark-field scanning transmission electron microscopy (STEM) images were obtained on FEI Tecnai G2 F30 operated at 300 kV. Aberration corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) images and energy dispersive X-ray spectroscopy (EDS) mapping images were obtained on a JEM-ARM200F transmission electron microscopy operated at 200 kV, which incorporated with double spherical aberration correctors and a super-X EDS system. The extended X-ray absorption fine structure spectra (EXAFS) was performed in fluorescence mode on BL14W1 beamline at the Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, China, operated at 3.5 GeV with injection currents of 140–210 mA and monochromatized with Si (111) double-crystal.

Electrocatalytic Performance Test.

Electrochemical measurements were carried out using two-electrode coin cells (LIR2032), with a sodium plate as both the counter and reference electrodes, and glass microfiber (Whatman, GF/F) as the separator. Each work electrode was composed of active materials (Ni-N-C / N-C), acetylene black and poly(vinylidene fluoride) (PVDF) binder in a weight ratio of 80:10:10. The electrolyte was 1 M NaClO₄ dissolved in ethylene carbonate (EC) and propylene carbonate (PC) (1:1 w/w). The cells were assembled in a glove box filled with pure argon. Galvanostatic charge/discharge cycles were tested by a LAND CT2001A battery test system.

2. Supplementary Figures and Tables

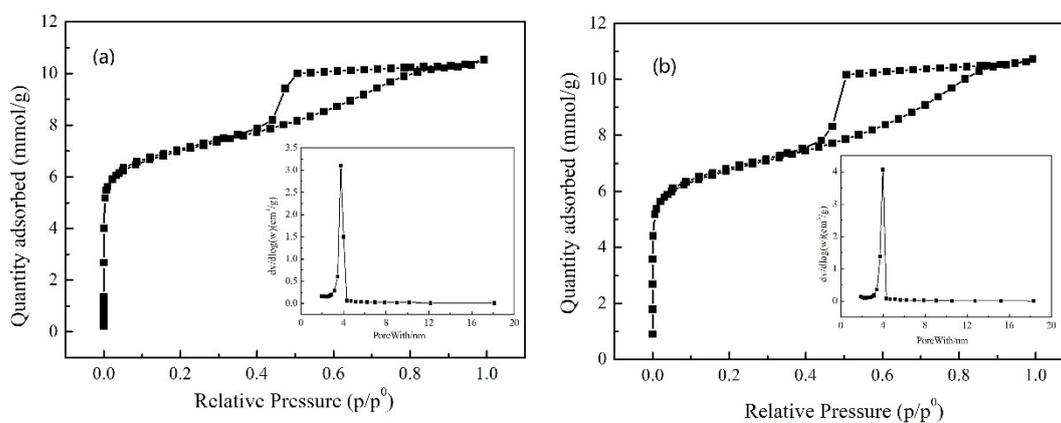


Fig. S1 N₂ adsorption - desorption isotherms of (a) N-C and (b) Ni-N-C. The insets show the pore size distribution.

Table S1. EXAFS fitting parameters at the Ni K-edge of Ni-N-C ($S_0^2 = 0.86$)

samples	Shell	C. N. ^[a]	R (Å) ^[b]	$\sigma^2 (\times 10^{-3} \text{ \AA}^2)$ ^[c]	ΔE (eV) ^[d]	R factor ^[e]
Ni-N-C	Ni-N	3.7±2.3	1.95±0.03	5.2±2.9	9.6±7.7	0.03

^aC. N.: coordination numbers; ^bR: bond distance; ^c σ^2 : Debye-Waller factors; ^d ΔE_0 : the inner potential correction. ^eR factor: goodness of fit.