An Eco-Friendly Citric Acid-Activated High-Performance Coal-Derived Hard Carbon Anode for Sodium-Ion Batteries

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Preparation of Hard Carbon Materials

Bituminous coal was crushed to 200 mesh and sequentially washed with HCl and HF solutions at 80°C to remove mineral impurities; the resulting sample is denoted BC. Then, 2 g of BC powder was ball-milled for 4 hours with citric acid at mass fractions of 10 %, 30 %, and 50 % (relative to BC mass). Subsequently, the mixed samples were placed in a tube furnace and carbonized under an argon atmosphere by heating to 1300°C at a ramp rate of 3 °C min^{-1}, followed by holding for 2 h. The resulting carbonized samples are labeled NHC-x (x=1, 3, 5, corresponding to the citric acid addition ratio). For comparison, the de-ashed bituminous coal powder (BC) was directly carbonized under identical conditions to obtain sample NHC-0.

Material Characterization

The morphology of prepared samples was characterized with scanning electron microscopy (SEM, Phenom Pro, Netherlands). X-ray diffraction (XRD, Rigaku D/Max 2500 with Cu Kα radiation) and Raman spectroscopy (Renishaw MKI-2000 with 532 nm laser) were equipped to observe the structural characterization. X-ray photoelectron spectroscopy (XPS, PHI-1600ESCA) analysis was carried out to obtain surface elemental information of materials. N_2 adsorption isotherms were measured on NOVA 3200e at 77 K.

Electrochemical Performance Evaluation

The electrochemical performance of the samples was evaluated in sodium-ion half-cells (CR2032-type). The working electrode was prepared by homogenizing 80 wt% active material, 10 wt% Super P carbon black, and 10 wt% sodium carboxymethyl cellulose (CMC) in deionized water. The resulting slurry was uniformly coated onto a copper current collector and dried at 80 °C under vacuum for approximately 12 h. The cells were assembled in an argon-filled glove box with sodium metal as the counter/reference electrode, a glass fiber separator, and an electrolyte consisting of 1.5 M $NaPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (EC: DEC = 1:1 by volume). Galvanostatic charge–discharge (GCD) tests were carried out on a LAND CT2001A system within a voltage range of 0.01–2.5 V.

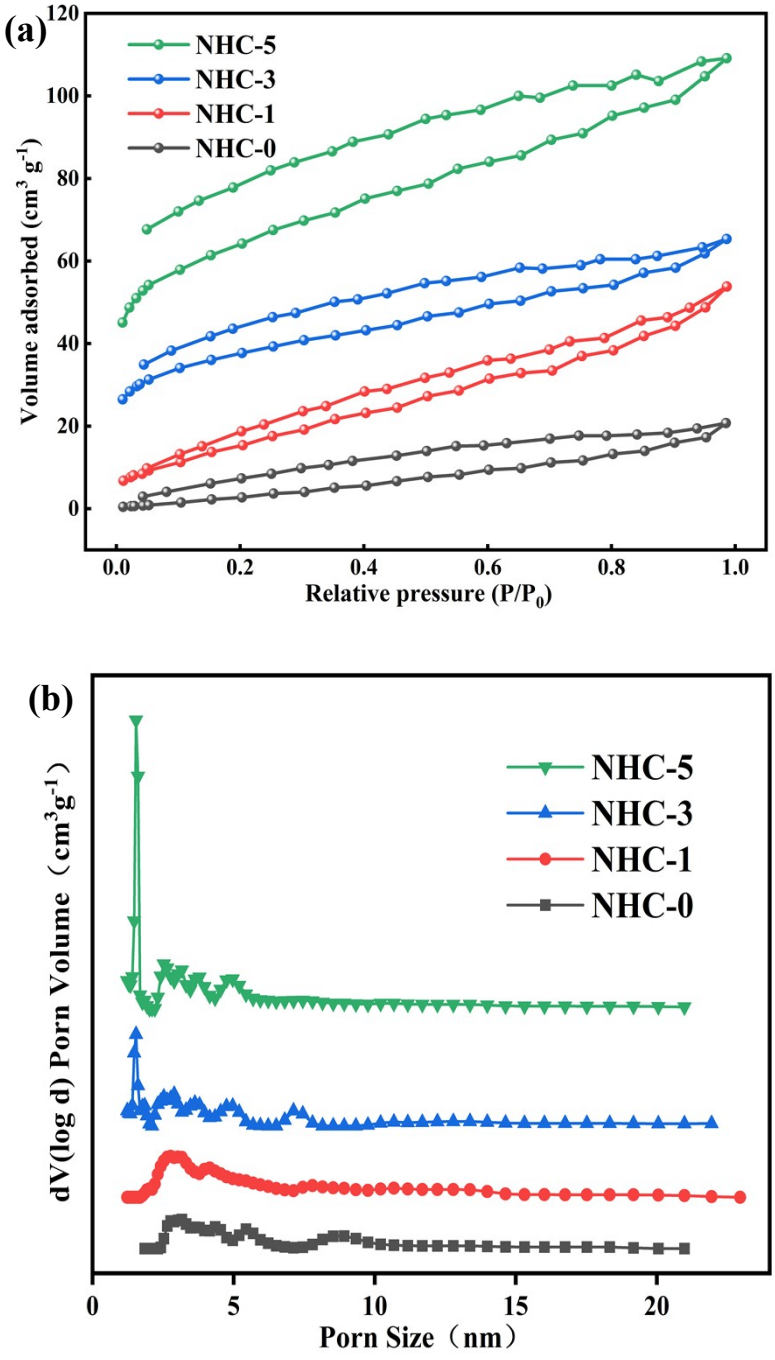

Figure S1. (a) N_2 adsorption/desorption isotherms and (b) Pore size distribution of obtain samples.

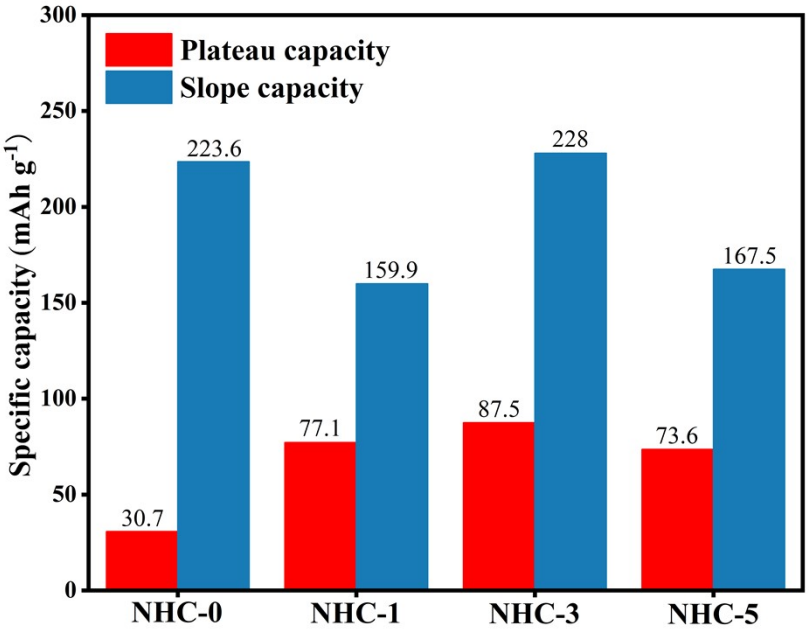

Figure S2. Comparison of plateau area capacity and slope area capacity

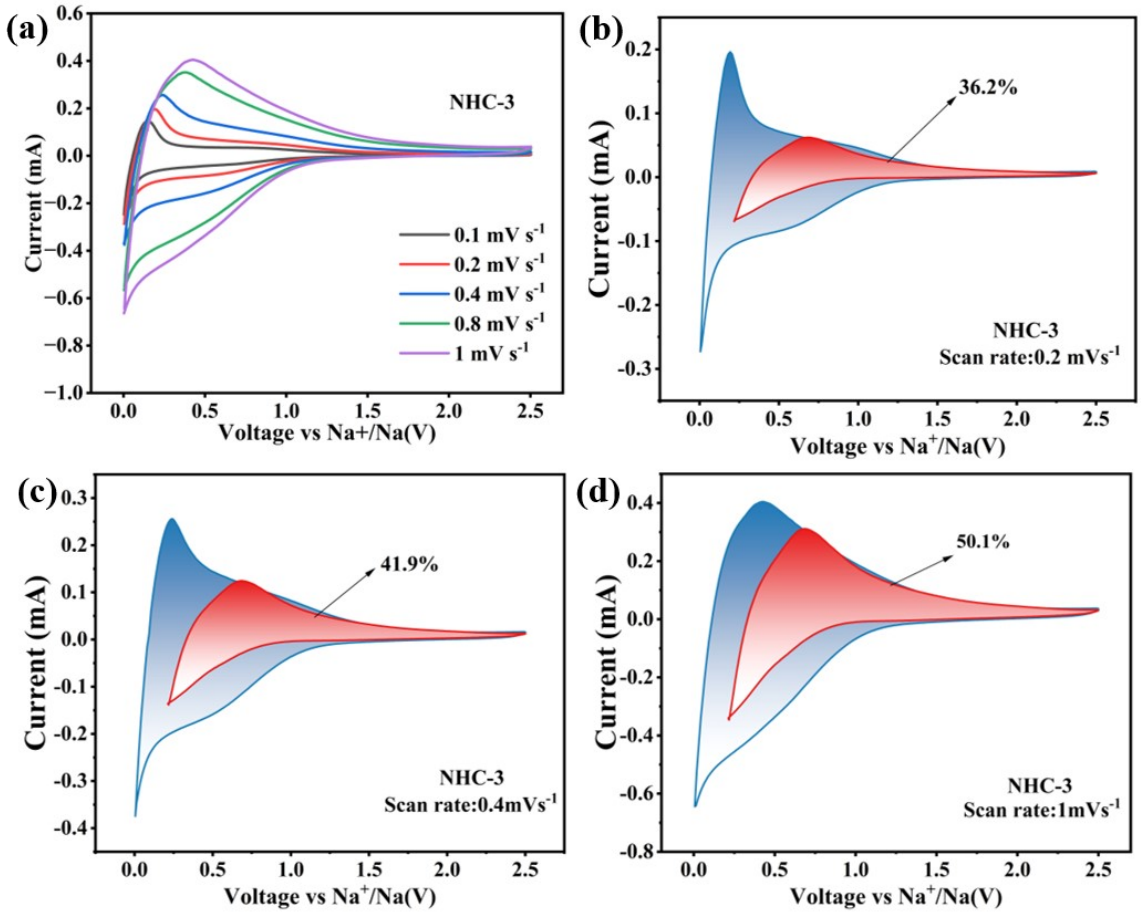

Figure S3. （a）Cyclic voltammetry (CV) curves at different scan rates；（b）Capacitive contribution ratios at different scan rates

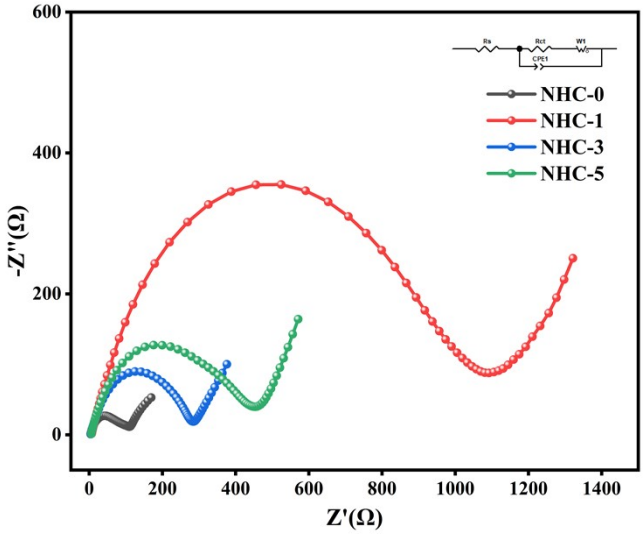

Figure S4. Nyquist plot

Table S1 BET Surface Area and Electrochemical Performance Parameters of the Prepared Samples

	SSA [m^2/g]	Pore volume [cm^3/g]	Average pore size [nm]	Charge capacity [mAh g^{-1}]	Discharge capacity [mAh g^{-1}]	ICE [%]
NHC-0	**20.8**	**0.032**	**6.157**	**254.3**	**467.1**	**54.45**
NHC-1	**63.2**	**0.082**	**3.209**	**237.0**	**346.1**	**68.49**
NHC-3	**128.0**	**0.168**	**3.079**	**315.5**	**441.6**	**71.44**
NHC-5	**219.3**	**0.101**	**3.158**	**241.4**	**344.9**	**69.99**

Table S2 The EIS fitting parameters using the equivalent circuit

	Rs (Ω)	Rct (Ω)
NHC-0	**3.535**	**79**
NHC-1	**6.403**	**1106**
NHC-3	**4.355**	**269**
NHC-5	**5.137**	**428**

Table S3 Comparison Table of Performance for Coal-Based Hard Carbon Anodes in Sodium-Ion Batteries

Precursor	Activation Method	Sodium storage capacity	ICE (%)	Rate Performance	Cycle Stability	Ref.
Bituminous coal	Citric Acid Activation (1300℃)	315.5 (0.02 A g^{-1})	71.44	86.7 mAh g^{-1} (1 A g^{-1})	87.73% (300 cycles、0.1A g^{-1})	This work
The long-flame coal	One-Step Carbonization (1500℃)	254 (0.02 A g^{-1})	79	63 mAh g^{-1} (1 A g^{-1})	72% (300 cycles、0.5A g^{-1})	26.
Subbituminous coal	H_3PO_4 Activation (1000℃)	284.4 (0.02 A g^{-1})	48.1	61.1 mAh g^{-1} (1 A g^{-1})	——	15.
Bituminous coal	KOH/H_2O_2 Activation (1300℃)	308 mAh g^{-1} (0.03 A g^{-1})	80.1	85 mAh g^{-1} (0.5 A g^{-1})	80% (200 cycles、0.05A g^{-1})	27.
Bituminous coal	O_2 Activation (1400℃)	303.1 mAh g^{-1} (0.05 A g^{-1})	64.8	225.6 mAh g^{-1} (1 A g^{-1})	73.1% (300 cycles、1A g^{-1})	28.
the high-alkali coal	Metal Salt Activation (1200℃)	322.4 mAh g^{-1} (0.02 A g^{-1})	80	237.4 mAh g^{-1} (0.2A g^{-1})	——	29.