

Electronic Supplementary Information (ESI)

Renewable chitin-derived hard carbon as free-standing anode for sodium-ion batteries

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Experimental

1. Materials and Methods

Chemicals: All reagents used in the experiment were of analytical purity grade and used as received without further purification. Typically, the purified chitin powders ($(C_8H_{13}NO_5)_n$, practical grade) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium hydroxide (NaOH), urea (CH_4N_2O), epichlorohydrin (ECH, C_3H_5ClO) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China). And the hydrochloric acid (HCl, 36-38%) was purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). The deionized water (DI water) was used for all of the experiments.

In the initial exploratory phase, to ascertain the optimal chitosan concentration for gelation, we prepared chitin solutions with concentrations of 1%, 2%, and 3% respectively. Subsequently, we carried out the carbonization process at a heating rate of $5^\circ\text{C}/\text{min}$ to select carbon materials with superior morphological structures.

The hard carbon materials derived from chitin were synthesized basing on a facile process of low-temperature dissolution, chemical crosslinking and high temperature carbonization. Typically, 2g of the purified chitin powders mixed with 8g of NaOH, 4g of urea, and 88g of DI water mixed aqueous suspension under stirring. Then the pension was frozen in a -50°C refrigerator for 4h and then melted at ambient temperature for 2h. After five-times repeating of this freezing-melting process, the added chitin powders were completely dissolved in the alkaline aqueous solution. Then centrifugation treatment was carried out to remove the air bubbles inside, finally forming a homogenous chitin suspension. After that, 3g of ECH was added drop by drop into 50g of the above chitin solution with continuous stirring for 1h until the solution becomes transparent. Then the solution was centrifuged for five minutes at 0°C and 7000 rpm to remove bubbles and then loaded into the mold. This solution was heated at 60°C in the oven for 1h until complete cross-linking, thus forming the cross-linked gel. This gel was soaked in pure water for 3 days until the NaOH and urea were completely removed. And the collected hydrogel was dried in a freeze dryer

at -60°C for 48 h to obtain chitin aerogel. Then, this chitin aerogel was placed in a quartz boat and was carbonized under nitrogen atmosphere at 800°C for 2 h, in which the heating rate was set as 1, 2, 5, $10^{\circ}\text{C min}^{-1}$. After cooled to room temperature, all the carbonized products were soaked with 2 mol L^{-1} of HCl for 12 h, dried for 12 h at 60°C in a vacuum drying box to obtain chitin-derived carbon products, which were labeled as CN-1, CN-2, CN-5 and CN-10 (CN-X, X refers to the heating rate), respectively.

2. Microscopic Characterization

X-ray diffraction (XRD, Bruker D8 ADVANCE) was used to characterize the crystallographic structure of the chitin-derived carbon products. Thermo Scientific Raman Imaging Microscope (DXR2xi) was used for Raman measurements (at 532 nm). And an Micromeritics ASAP-2460 analyzer was used for Brunauer-Emmett-Teller (BET) measurements. X-ray photoelectron spectroscopy (XPS, Kratos AXIS SUPRA+) was applied to determine the elemental composition, which was equipped with a Al $K\alpha$ anode for photoexcitation. The detailed microstructure and morphology of the chitin-derived carbon materials was investigated by field-emission scanning electron microscope (FE-SEM, HITACHI Regulus 8100) and transmission electron microscope (TEM, FEI Gatan F30).

3. Electrochemical measurements

For the battery test, the electrochemical sodium storage performance of these products was measured based on CR2025 coin-type cells assembled in an argon-filled glove box. The as-synthesized CN-1, CN-2, CN-5 and CN-10 products were punched to wafers with ~ 12 mm in diameters and ~ 0.2 mm in thickness, and used directly as working electrodes. A piece of Na foil was used as both the counter electrode and the reference electrode, the Celgard 2400 polypropylene microporous film was used as separator, and a solution of 1 M NaPF₆ in ethylene carbonate and dimethyl carbonate (EC:DMC=1:1, v/v) was used as electrolyte. Cyclic voltammetry (CV) curves were measured by a CORRTEST CS2350M electrochemistry system at a scan rate of 0.5 mV s^{-1} . And the galvanostatic charge-discharge measurements were performed on a

LAND CT3002A battery-testing instrument. All these electrochemical tests were conducted in the potential range of 0.005-3V (vs. Na^+/Na).

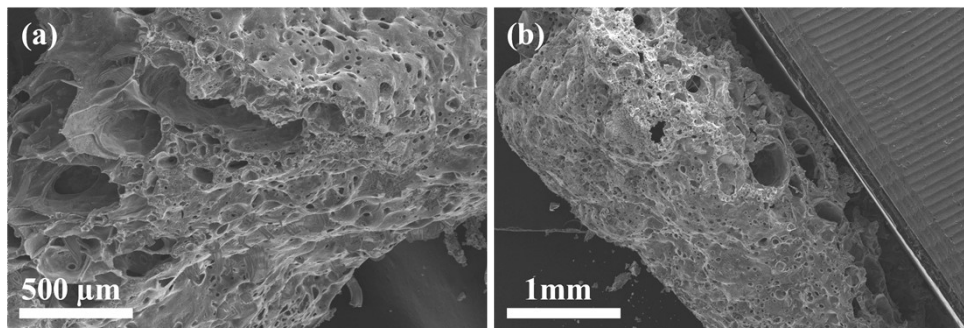


Fig. S1 the SEM images of chitin with a concentration of (a) 1%, (b) 3%.

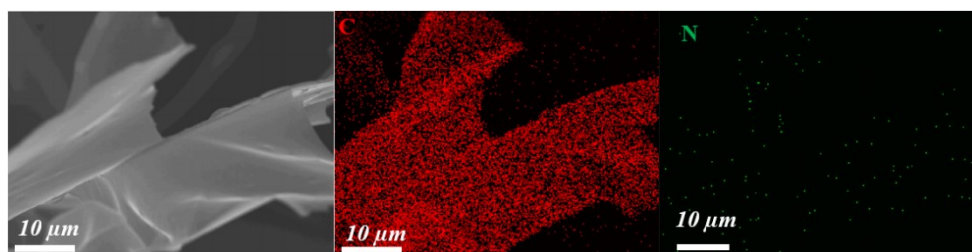


Fig. S2 Elemental mapping of the CN-2 samples with C and N elements.

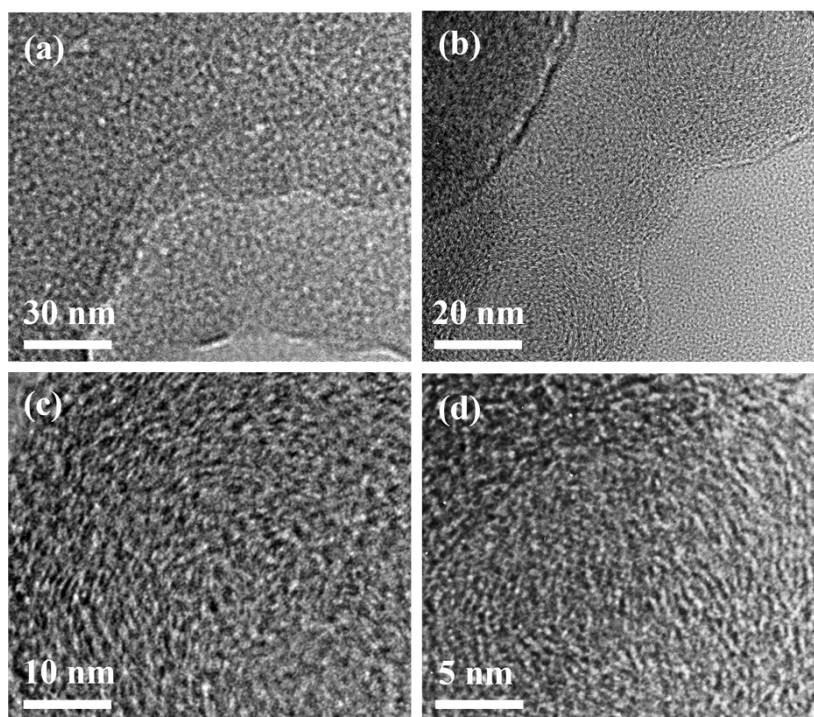


Fig. S3 (a-b) typical TEM and (c-d) HRTEM of CN-2.

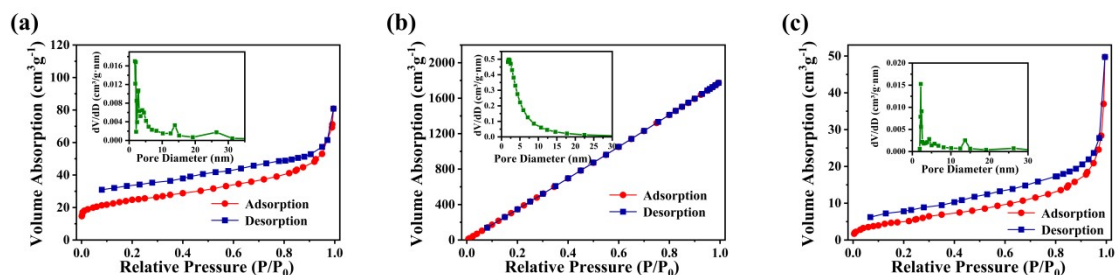


Fig. S4 N₂ adsorption/desorption isotherm and the corresponding pore size distribution of (a) CN-1, (b) CN-5 and (c) CN-10.

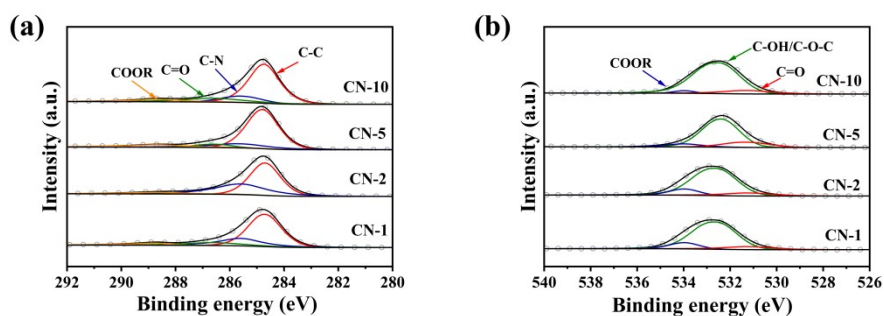


Fig. S5 High-resolution XPS spectrum of (a) C 1s and (b) O 1s in CN-1, CN-2, CN-5 and CN-10.

Table S1 The N content of different chitin-derived carbon samples

Sample	N species (at %)				Total N (at %)
	Pyrolic-N	Pyridinic-N	Graphitic-N	Oxidized-N	
CN-1	32	34	26	8	3.27
CN-2	26	43	25	6	3.82
CN-5	25	42	22	11	3.46
CN-10	27	35	20	8	3.43

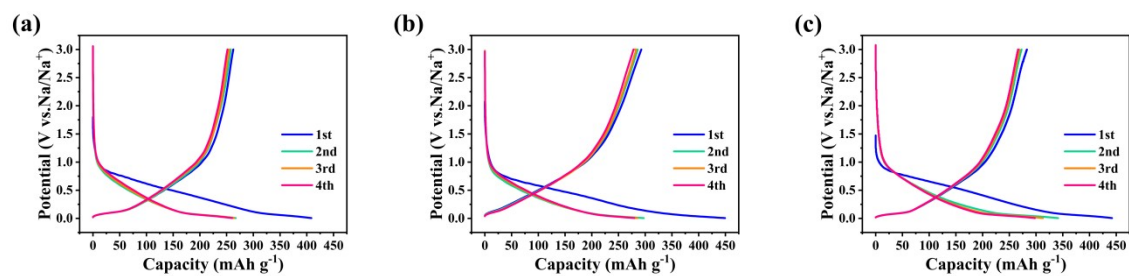


Fig. S6 Galvanostatic charge-discharge voltage profiles of the (a) CN-1, (b) CN-5 and (c) CN-10 electrodes at the current density of 40 mA g⁻¹