Supporting Information for

A novel anode material derived from organic-coated ZIF-8 nanocomposites with high performance in lithium ion battery

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Experimental section

ZIF-8 nanocrystals were synthesized through a simple mechanochemical synthetic protocol. Reactions were carried out in a ball mill (QM-3B, Nanjing University Instrument Factory, China) using a 80 mL stainless steel grinding jar with five 10 mm steel balls. A solid mixture of zinc oxide (ZnO, 0.407 g, 5.02 mmol) and 2methylimidazolate (2-MeIM, 0.8211 g, 8.54 mmol) was placed into the jar and ground at high speed for 15 mins. After that 500 µL methanol was added into the jar and ground for another 30 mins to give the white products of ZIF-8 nanocrystals. The products were washed with methanol (30 mL) for three times and dried at 85 °C. ZIF-8@chitosan was synthesized by mixing as-prepared ZIF-8 nanocrystals (0.5 g) and chitosan (0.2 g) and the mixture was put into a stainless steel grinding jar, 500 μ L methanol was added and milled at high speed for 30 mins. The product was dried at 85 °C. Similarly, β-cyclodextrin- and pyrrole-coated ZIF-8 were synthesized with the weight (0.2 g) and volume (400 μ L), respectively. The glucose-coated ZIF-8 was synthesized by adding ZIF-8 into 0.25 M glucose solution and stirred for 12 h, the product was centrifuged and dried at 85 °C. The citrate-coated ZIF-8 was synthesized by adding ZIF-8 into 0.1 M citric acid solution and stirred for 2 h, the product was centrifuged and dried at 85 °C. All the products were characterized by PXRD and FT-

The as-prepared organic-coated ZIF-8 nanocrystals were transferred to a tube furnace and were heat-treated at target temperatures (700 °C, 800 °C, 900 °C) under nitrogen with a heating rate of 5 °C min⁻¹ to pyrolyze the ZIF-8 nanocrystals. After reaching the target temperature, the materials were cooled down to room temperature naturally.

Characterization

Powder X-ray diffraction (PXRD) pattern was analyzed with monochromatized Cu-K α (λ = 1.54178 Å) incident radiation by a D8 Advance Bruker powder diffractometer operating at 40 kV voltage and 50 mA current. Nitrogen sorption isotherm was measured at 77 K on a Quantachrome Instrument Autosorb-IQ7 after pretreatment by heating the samples under vacuum at 150 °C for 6 h before the measurement, thermal gravimetric analysis (TGA) was carried out on a Q600 SDT thermoanalyzer (Thermal Analysis Corporation, USA) in N_2 with a heating rate of 10 °C/min. ICP (Inductive Coupled Plasma Emission Spectrometer) was tested by Varian 725 inductively coupled plasma emission spectrometer. Scanning electron microscopy (SEM and EDX; JSM7000 instrument, JEOL). X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromated Al Ka radiation. The 500 µm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about 3×10^{-10} mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. Fourier transform infrared (FT-IR) spectra were recorded on an IRPrestige-21 spectrophotometer.

To prepare the anodes, 80 wt% active material, 10 wt% Super P carbon black and 10 wt% poly(vinylidene fluoride) (PVDF) binder were mixed in N-methyl pyrrolidinone (NMP) solution to form a slurry. The slurry was cast onto copper foil and dried under a vacuum at 120 °C for 12 h. Coin cells of CR2032 type were constructed inside an argon-filled glove box using a lithium metal foil as the negative electrode and the composite positive electrode separated by polypropylene microporous separator (Celgard). The electrolyte used was 1 M LiPF_6 in ethyl carbonate (EC) and diethyl carbonate (DMC) (1:1 v/v). Assembled coin cells were allowed to soak overnight and then were charged and discharged galvanostatically between 0.02 V and 3.0 V with a LAND CT2001A instrument (Wuhan, China) at ambient temperature. The cyclic voltammetry of active materials were recorded with an electrochemical workstation (CHI 760E: CH Instrumental Inc.). The range of voltage was between 20 mV and 3.0 V with a scan rate of 0.1 mV s⁻¹. The electrochemical impedance spectra were also performed using an electrochemical workstation (CHI 760E: CH Instrumental Inc.) with the frequency range of 10⁴ Hz to 10⁻¹ Hz with an applied voltage of 0.25 V after 4 cycles at 50 mA g⁻¹.All the tests were carried out at room temperature.



Fig. S1 TGA of ball-milled ZIF-8 nanocrystals (room temperature to 1000 °C)



Fig. S2 Cycle-life performances of pristine ZIF-8 pyrolyzed at different temperatures (50 mA g^{-1}).



Fig. S3 Long cycle-life performance of carbonized ZIF-8@chitosan at current density of 200 mA g^{-1} .



Fig. S4 (a) PXRD of ZIF-8@chitosan, (b) PXRD of ZIF-8 coated by different biomolecules .



Fig. S5 (a) TEM image ZIF-8@chitosan, (b) SEM image of ZIF-8-800N.



Fig. S6 FT-IR of the different samples.



Fig. S7 TEM image and the elemental mappings of ZIF-8 -800N.



Fig. S8 Zn 2p and C 1s XPS spectra of ZIF-8@chitosan-800N.



Fig. S9 Raman spectra of the obtained nanoporous carbon samples.



Fig. S10 Cyclic voltammetry measurements on ZIF-8@chitosan-800N after 4 cycles. The voltage range was 20 mV to 3.0 V at a scan rate of 0.1 mV s⁻¹. The initial point corresponded to the open-circuit voltage of the cell.



Fig. S11 Galvanostatic charge/discharge curve of ZIF-8@chitosan-800N at different current density.



Fig. S12 EDX spectrum of the ZIF-8@chitosan-800N



Fig. S13 Nitrogen adsorption isotherms at 77 K, for (a) ZIF-8@glucose, (b) ZIF-8@citric, (c) ZIF-8@glucose-800N and (d) ZIF-8@citric-800N. Insets show the pore size distribution from DFT or BJH calculation.



Fig. S14 Nitrogen adsorption isotherms at 77 K, for (a) ZIF-8@pyrrole, (b) ZIF-8@ β -cyclodextrin, (c) ZIF-8@pyrrole-800N and (d) ZIF-8@ β -cyclodextrin-800N. Insets show the pore size distribution from DFT or BJH calculation.



Fig. S15 Cycle-life performances of the carbonized organic-coated ZIF-8 composites (50 mA g^{-1}).