Supplementary Information

Fabrication of $NiMn_2O_4$/C hollow spheres with trilaminar shell structure as anode material for sodium-ion batteries

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Experimental section

Synthesis of CHSs

70 mL of absolute ethanol was mixed with 10 mL of H_2O and 3 mL of ammonium hydroxide. The mixture was stirred for 15 min to form a homogeneous solution. Then, 3.46 mL of tetraethyl orthosilicate (TEOS) was dropwise added and stirred for another 20 min. 0.44 g of resorcinol and 0.5 mL of formaldehyde were added into the above solution and continuously stirred for 24 h. After washing with H_2O and ethanol, SiO_2@PF was obtained. SiO_2@PF was annealed at 800 ℃ for 2 h under N_2 atmosphere to prepare the SiO_2@C. Finally, CHSs were harvested by the etching of SiO_2@C with hydrofluoric acid.

Fabrication of $NiMn_2O_4$@CHS

20 mg of CHSs was added into 80 mL of H_2O and treated with ultrasonic for 10 minutes to form a uniform dispersion. Then, 1.5 mmol $KMnO_4$ and 0.75 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ were added to the mixture and continuously stirred for 5 min. The solution was transferred into a Teflon autoclave and maintained at 120 ℃ for 10 h in the oven. NiMn-LDH/CHS was obtained after washing with distilled water and anhydrous ethanol. Finally, NiMn-LDH/CHS was converted into $NiMn_2O_4$@CHS after calcination at 350 ℃ for 2 h under N_2 atmosphere. For comparison, pure $NiMn_2O_4$

without carbon spheres was prepared under the same hydrothermal conditions.

Material characterization

X-ray diffraction (XRD) patterns were collected on the Shimadzu XRD 6100 diffractometer (Cu K_α, λ = 0.15418 nm). The microstructure morphology was observed by field emission scanning electron microscope (FESEM, JSM-7500) and transmission electron microscopy (TEM, Titan G2). X-ray photoelectron spectroscopy (XPS) was collected on Thermo ESCALA 250. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) and the pore size distribution via the Barret-Joyner-Halender (BJH) method. were determined on the micromeritics nitrogen adsorption apparatus (ASAP 2020).

Electrochemical characterization

The preparation procedure of the working electrode is as follows: first, $NiMn_2O_4$@CHS, carbon black, and PVDF (polyvinylidene fluoride) (the weight ratio of 7:2:1) were mixed to form a uniform slurry. Then, the paste was coated on the copper foil and dried in a vacuum at 80 ℃ for 12h. Finally, the copper foil was cut into a disc with a diameter of 10 mm as the working electrode. The mass loading of active material was about 1.2 mg cm^{-2}. In half cell, sodium metal foil is used as counter and reference electrode. Glass fiber membrane (Whatman) and 1M $NaClO_4$ were used as separator and electrolyte, respectively. The coin cells were assembled in a glove box containing high-purity argon (H_2O and O_2 < 0.5 ppm). All the electrochemical tests of the samples were carried out in the battery test system (Neware) and electrochemical workstation (CHI 760E).

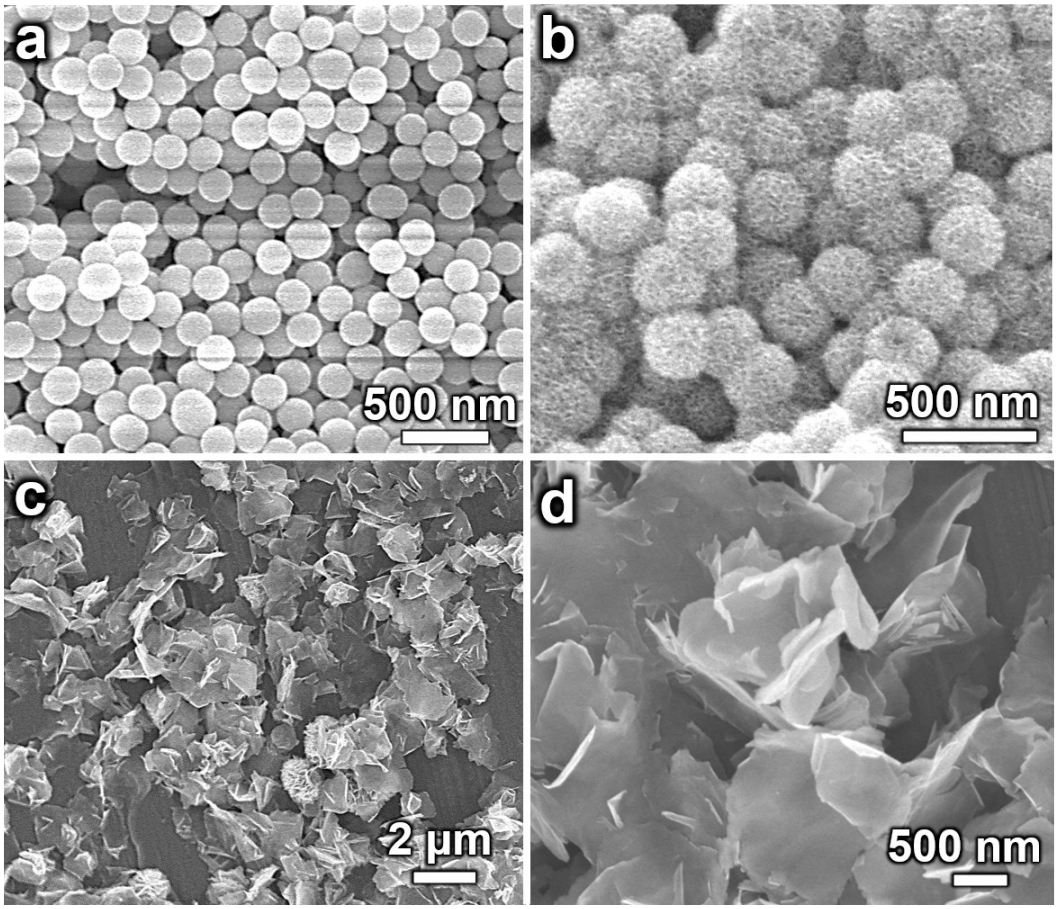

Figure S1. FESEM images of (a) CHS, (b) $NiMn_2O_4$/CHS, and (c, d) pure $NiMn_2O_4$.

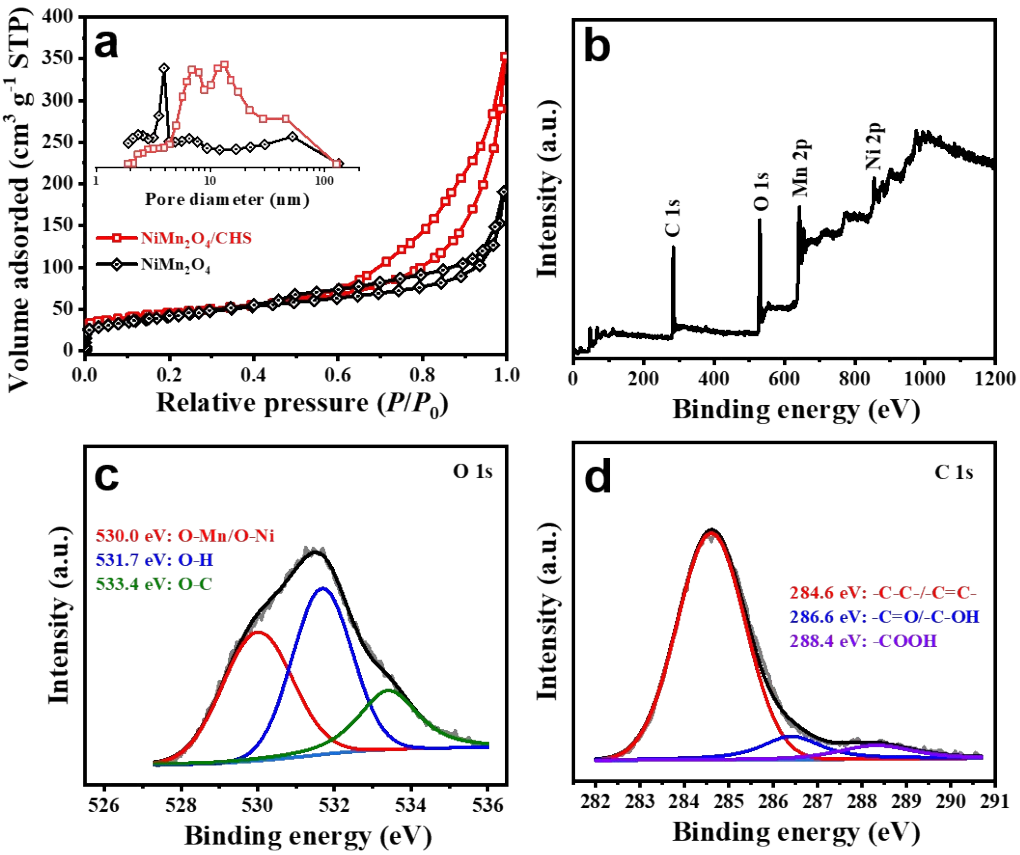

Figure S2. (a) N_2 adsorption/desorption isotherms of $NiMn_2O_4$ and $NiMn_2O_4$/CHS together with their corresponding pore size distribution. (b) XPS survey spectrum of $NiMn_2O_4$/CHS. High-resolution XPS spectra of (c) O 1s and (d) C 1s.

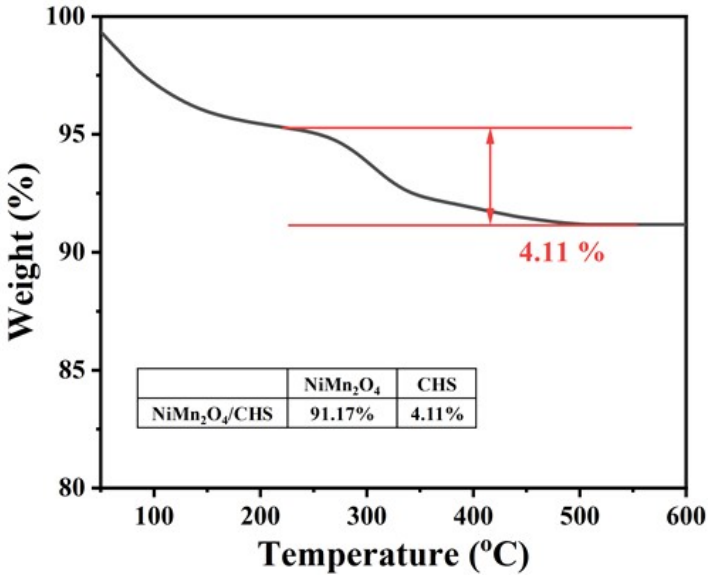

Figure S3. Thermogravimetric analysis of $NiMn_2O_4$/CHS composite.

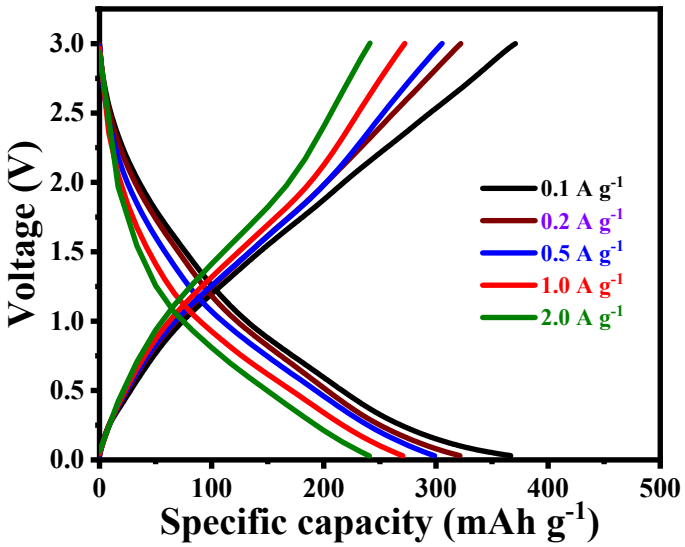

Figure S4. Voltage profiles of $NiMn_2O_4$/CHS at various current densities.

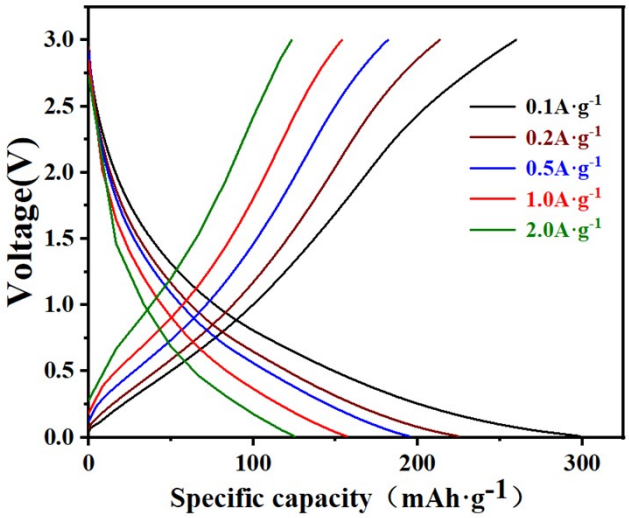

Figure S5. The constant current charge/discharge curves of CHS at different current densities.

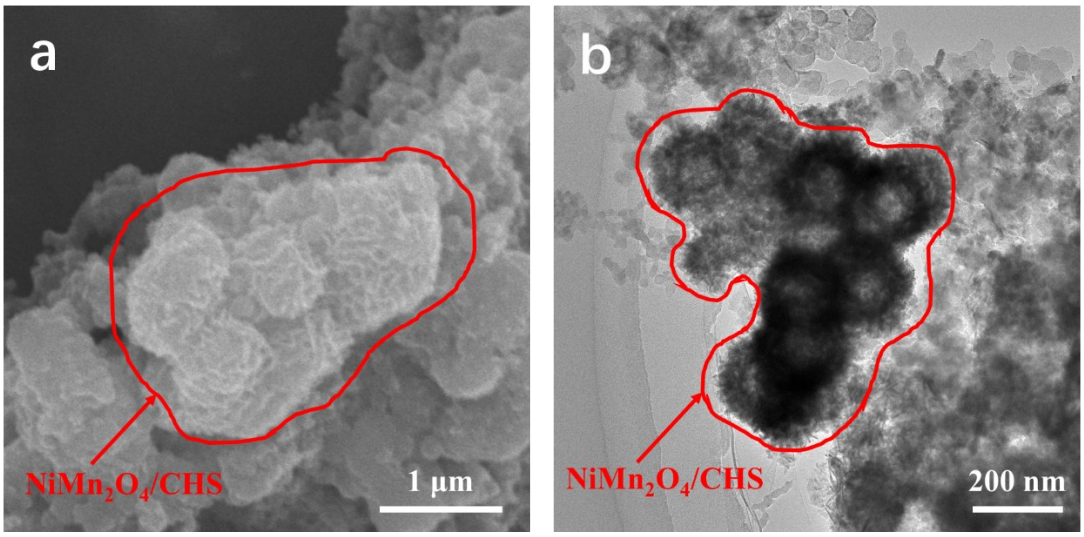

Figure S6. The (a) SEM and (b) TEM image of $NiMn_2O_4$/CHS after cycling test.