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Supporting Information for

Synthesis of Open Helmet-Like Carbon Skeletons for Application in Lithium-Ion Batteries

Chun Cheng Yang,‡ Wen Tao Jing,‡ Chao Li, Qing Jiang*

Key Laboratory of Automobile Materials (Jilin University), Ministry of Education, and School of Materials Science and Engineering, Jilin University, Changchun 130022, China.

* *Corresponding author. Tel.: +86-431-85095371; Fax: +86-431-85095876; E-mail: jiangq@jlu.edu.cn (Q. Jiang).*

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‡ These authors contributed equally to this work.

Materials and methods

Preparation of SiO_2 spheres: The SiO_2 spheres were synthesized by a modified Stöber method [Refs.[23-25] of the text]. In a typical synthesis, 0.6 mL tetraethylorthosilicate (TEOS) was added into a mixture of 64 mL isopropanol, 22 mL ultrapure water and 14.0 mL ammonium aqueous solution (28 wt%). The solution was stirred at room temperature for 1 h. Then, 5 mL TEOS was added into the solution, followed by vigorous stir at 35 °C for 2 h. After that, the SiO_2 spheres were centrifugally separated and rinsed with ethanol and ultrapure water several times before drying in a vacuum oven at 70 °C for 10 h.

Preparation of RF/SiO_2 spheres: 1 g as-prepared SiO_2 spheres were dispersed in a solution of 70 mL ultrapure water and 28 mL ethanol, followed by ultrasonication for 30 min. Then 2.3 g hexadecyltrimethyl ammonium bromide (CTAB), 0.35 g resorcinol, and 0.11 mL ammonia were added into the solution. After stirring for 30 min at room temperature, 0.5 mL formaldehyde solution was added into the dispersion. The dispersion was heated to 35 °C with continuous stirring for 8 h. Finally, the RF/SiO_2 spheres were collected by centrifugation, rinsed with ethanol and ultrapure water, and dried in a vacuum oven at 70 °C for 10 h.

Preparation of NiO/CNHs: 1.45 g Nickel(II) nitrate hexahydrate and 1.4 g hxamethylenetetramine were dissolved into a mixture of 25 mL ultrapure water and 10 mL ethanol. Then 1 g RF/SiO_2 spheres were dispersed in the solution. After stirring for 10 min, the dispersion was transferred into a 40 mL autoclave and maintained at 100 °C for 10 h. The products were collected by centrifugation and dried at 80 °C for 10 h. After that, the products were annealed at 600 °C for 2 h with a heating rate of 1 °C min^{-1} and cooled to 350 °C under an atmosphere of high-purity argon. Then, the products were cooled from 350 °C to room temperature in the air.

Finally, after soaking and stirring in 3 M sodium hydroxide aqueous solution at 70 °C for 48 h, the NiO/CNHs composites were collected by centrifugation, rinsed with ethanol and ultrapure water, and dried in a vacuum oven at 70 °C for 10 h.

Materials characterization: The microstructure of the specimens was characterized by field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL, 15 keV) and transmission electron microscopy (TEM, JEM-2100F, JEOL, 200 keV). X-ray diffraction (XRD) was carried out on a D/max2500pc diffractometer using Cu-K_α radiation. Raman spectrum was collected using a micro-Raman spectrometer (Renishaw) with a laser of 532-nm excitation wavelength. The constituent of the sample was tested by thermogravimetric analysis (TGA) in air with a heating rate of 10 °C min^{-1} over a temperature range of 50-800 °C using an SDT Q600 instrument. The specific area and pore sizes were determined by nitrogen adsorption and desorption using a Micromeritics ASAP 2020 analyzer.

Electrochemical measurements: The electrochemical measurements for LIBs were conducted on coin-type cells (CR2016), which were assembled in an argon-filled glove box ($[O_2]<1$ ppm, $[H_2O]<1$ ppm). The metallic lithium foil was used as the both counter and reference electrode. The separator was Celgard (2500) membrane and the electrolyte was 1M $LiPF_6$ dissolved in the mixture of ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate with a volume ratio of 1:1:1. The working electrodes were fabricated by mixing active material (NiO/CNHs), conductive material (Super P) and binder polyvinylidene difluoride (PVDF) with a weight ratio of 7:2:1 with N-methyl-2-pyrrolidone (NMP) as the solvent, which were pasted on Cu foil and dried in vacuum at 100 °C for 10 h. Then the working electrodes were cut into discoidal pieces with 1 cm^2 in area and 30 μm in thickness. The working electrodes using NiO/hollow carbon spheres as the active material were also fabricated with the same method in order to compare the volumetric density of NiO/CNHs and NiO/hollow carbon spheres on a full electrode level. The galvanostatic charge/discharge cycling tests were performed by using a LAND CT2001A battery testing system in the voltage range between 0.01-3.0 V. Cyclic voltammetry (CV) measurements were performed on an IVIUM electrochemical workstation with a potential scan rate of 0.2 mV s^{-1} in the range of 0.01-3.0 V. Electrochemical impedance spectroscopy (EIS) measurements were carried out with an amplitude of 10 mV in the frequency range of 100 kHz to 10 mHz at room temperature.

Supplementary Figures

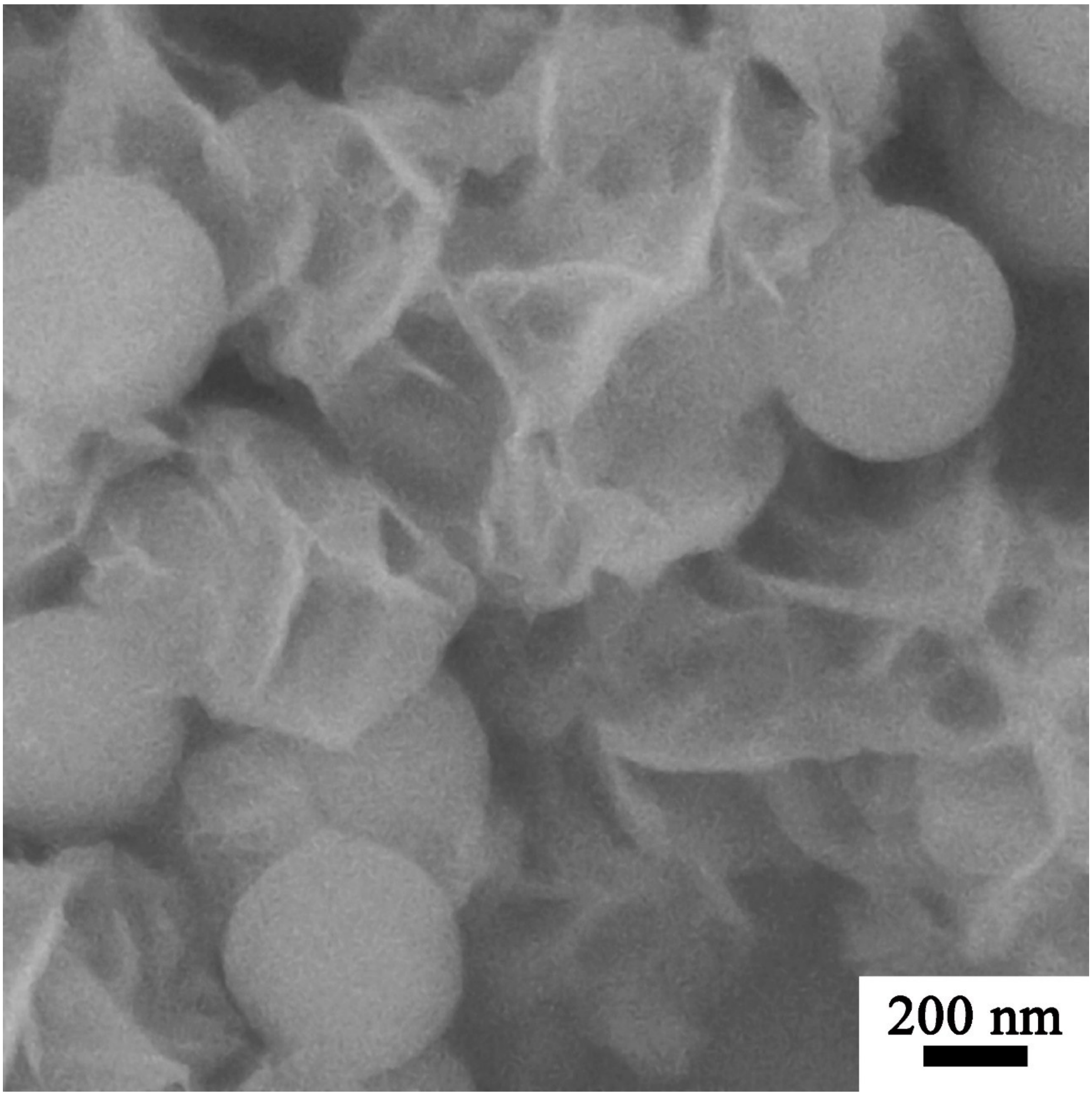

Fig. S1 SEM image of $Ni(OH)_2/RF/SiO_2$.

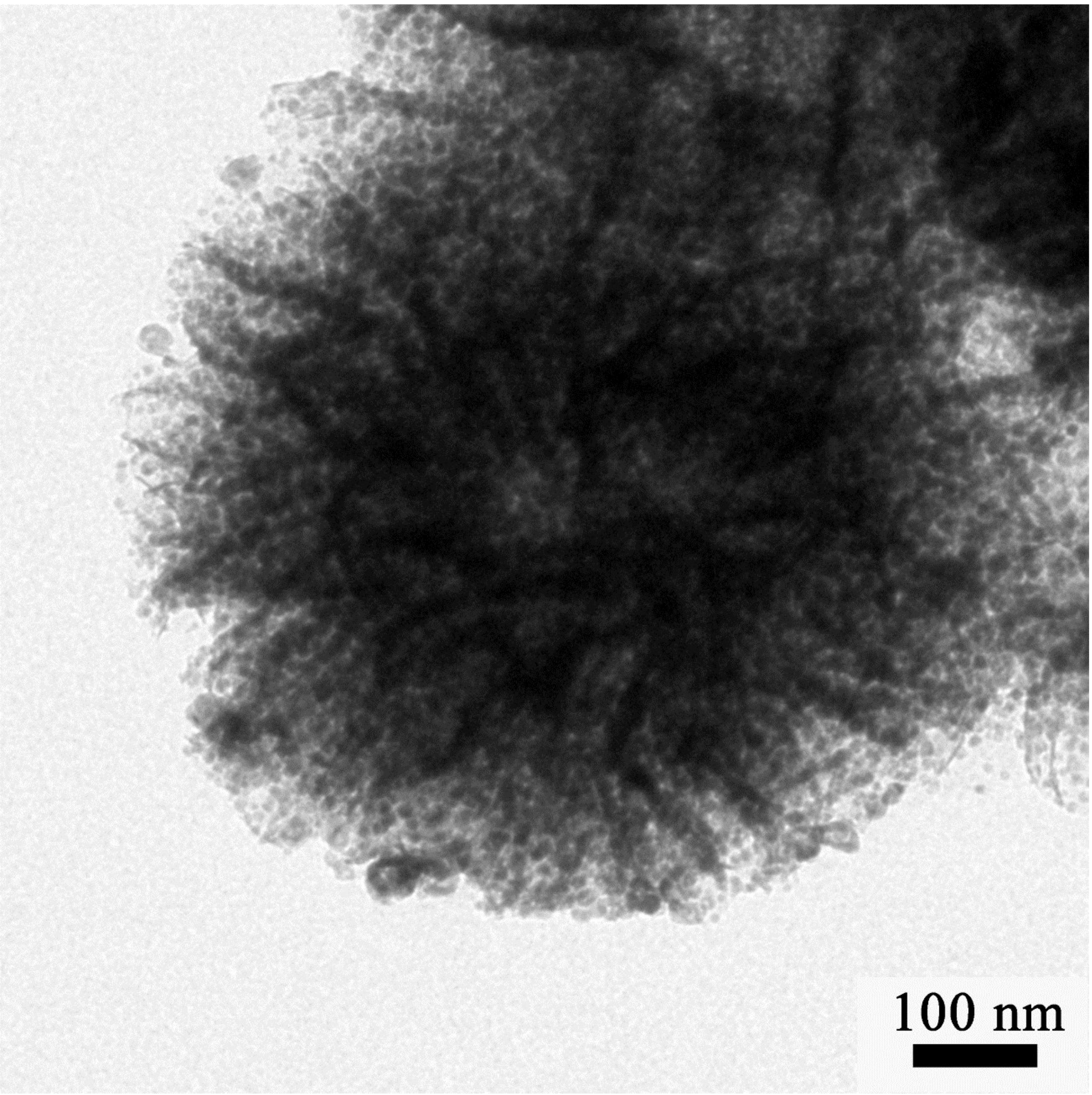

Fig. S2 TEM image of NiO/C/SiO_2.

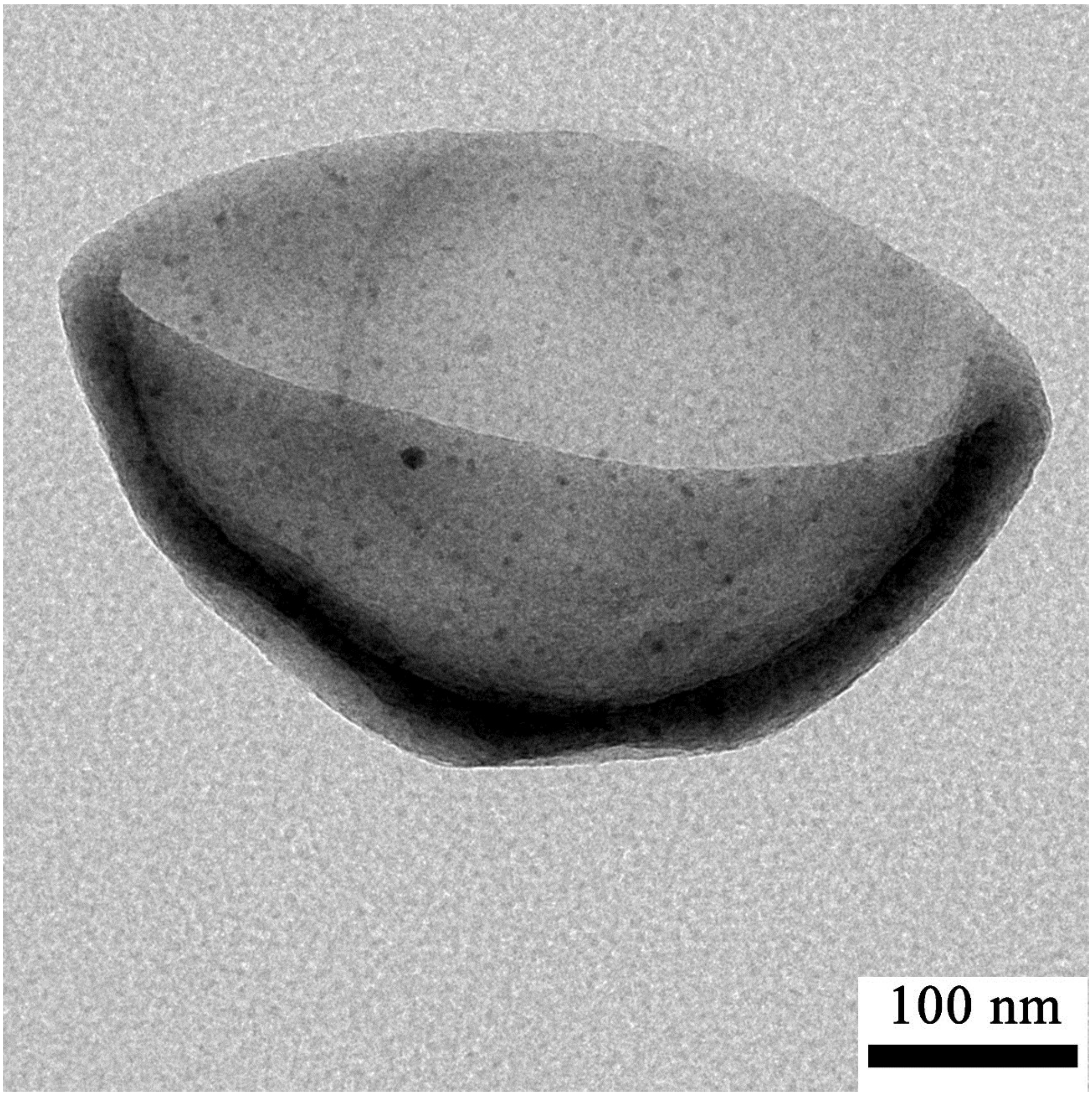

Fig. S3 TEM image of Co_3O_4/CNHs.

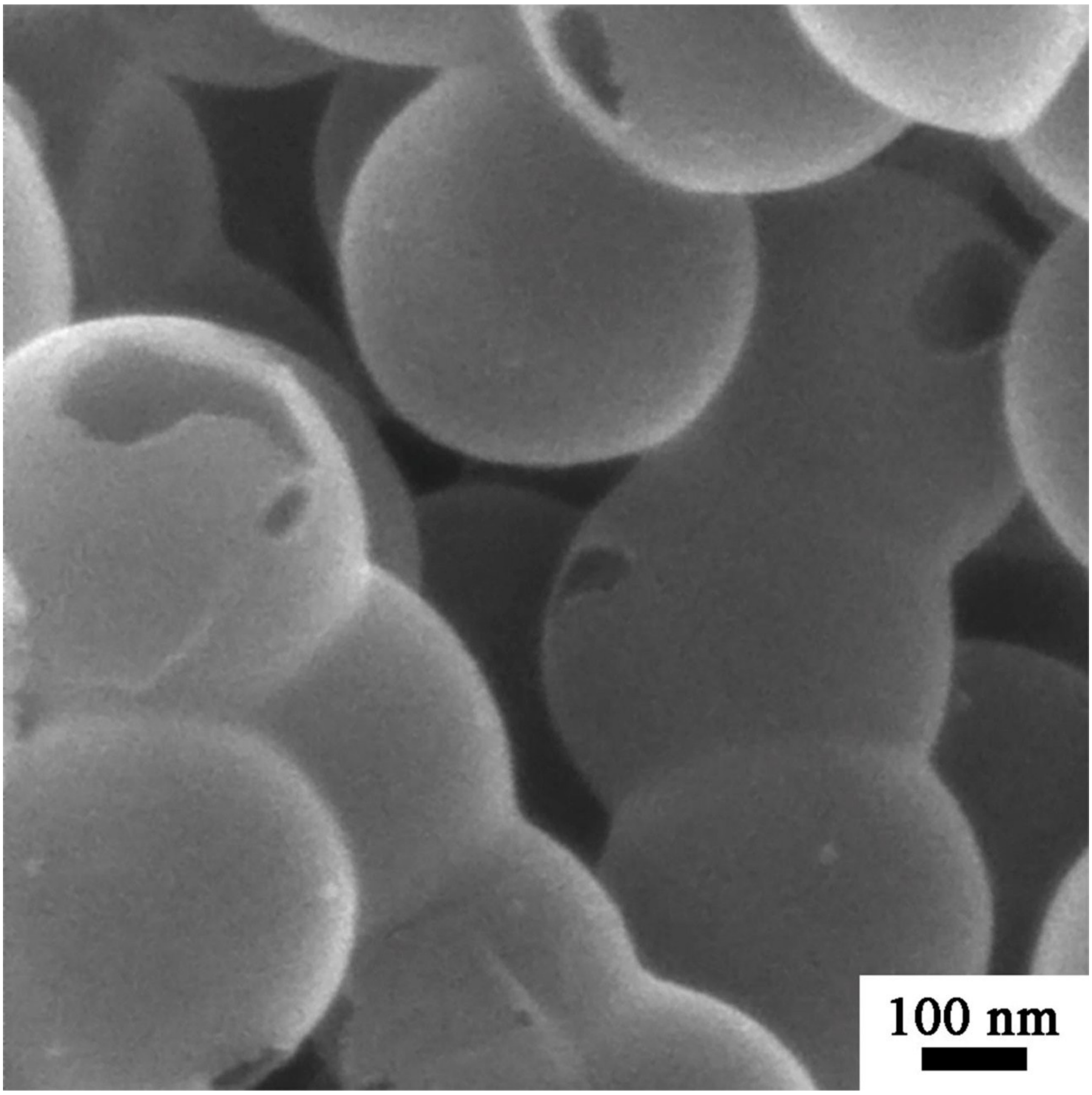

Fig. S4 SEM image of hollow carbon spheres.

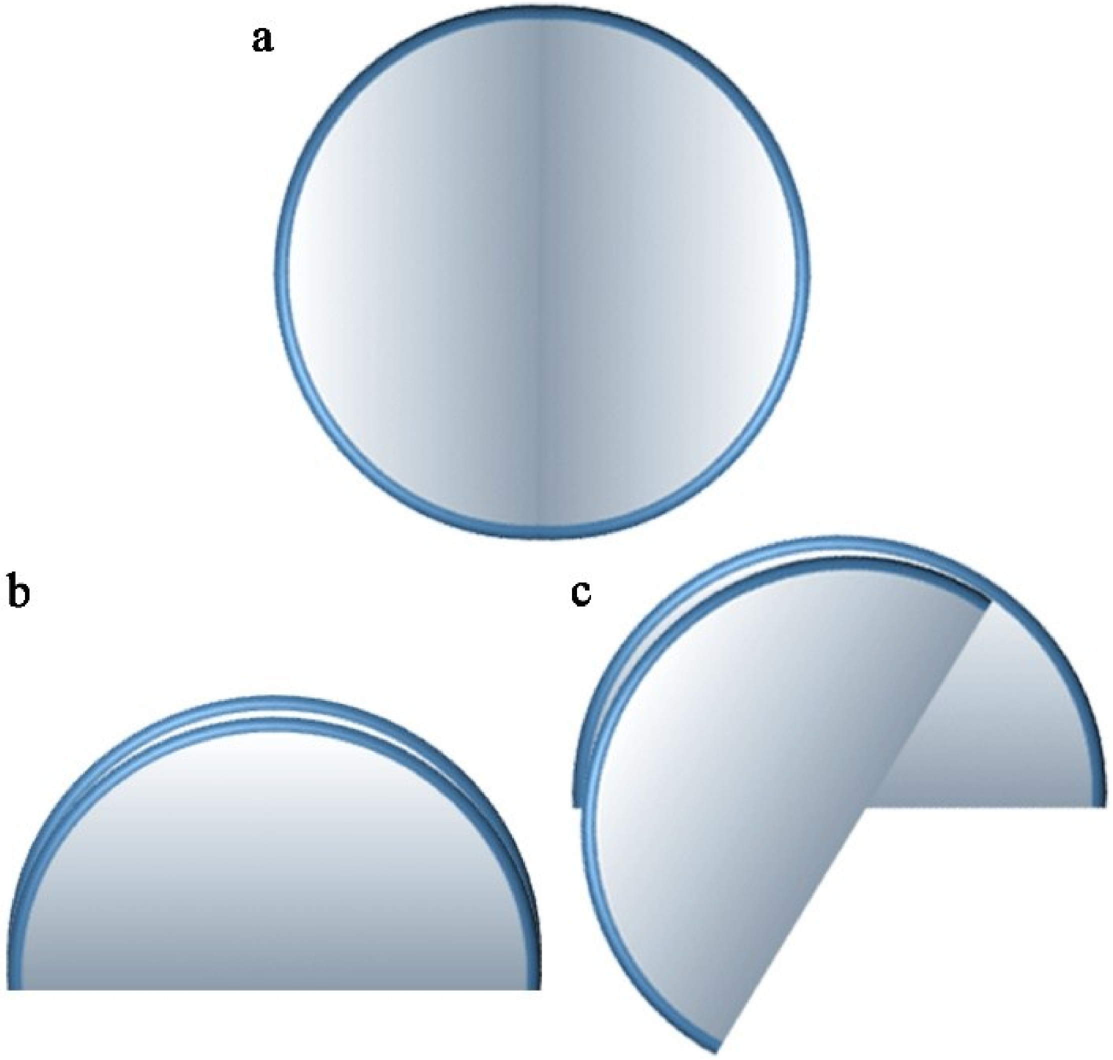

Fig. S5 Stacking schematics of a carbon sphere before (a) and after its fracture (two helmets in b and c, corresponding to perfect and imperfect stacking, respectively).

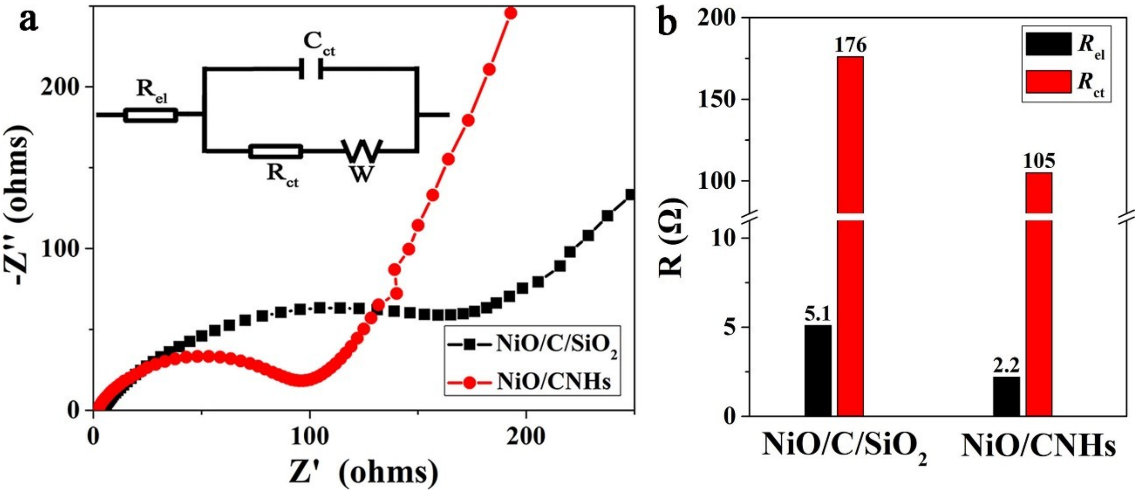

Fig. S6 (a) EIS of NiO/C/SiO_2 and NiO/CNHs electrodes in fresh LIBs, where the inset shows the equivalent circuit diagram. (b) Comparisons of intrinsic electrode/electrolyte resistances (R_{el}) and charger transfer resistances (R_{ct}) values between NiO/C/SiO_2 and NiO/CNHs, which are obtained according to the equivalent circuit diagram in (a).

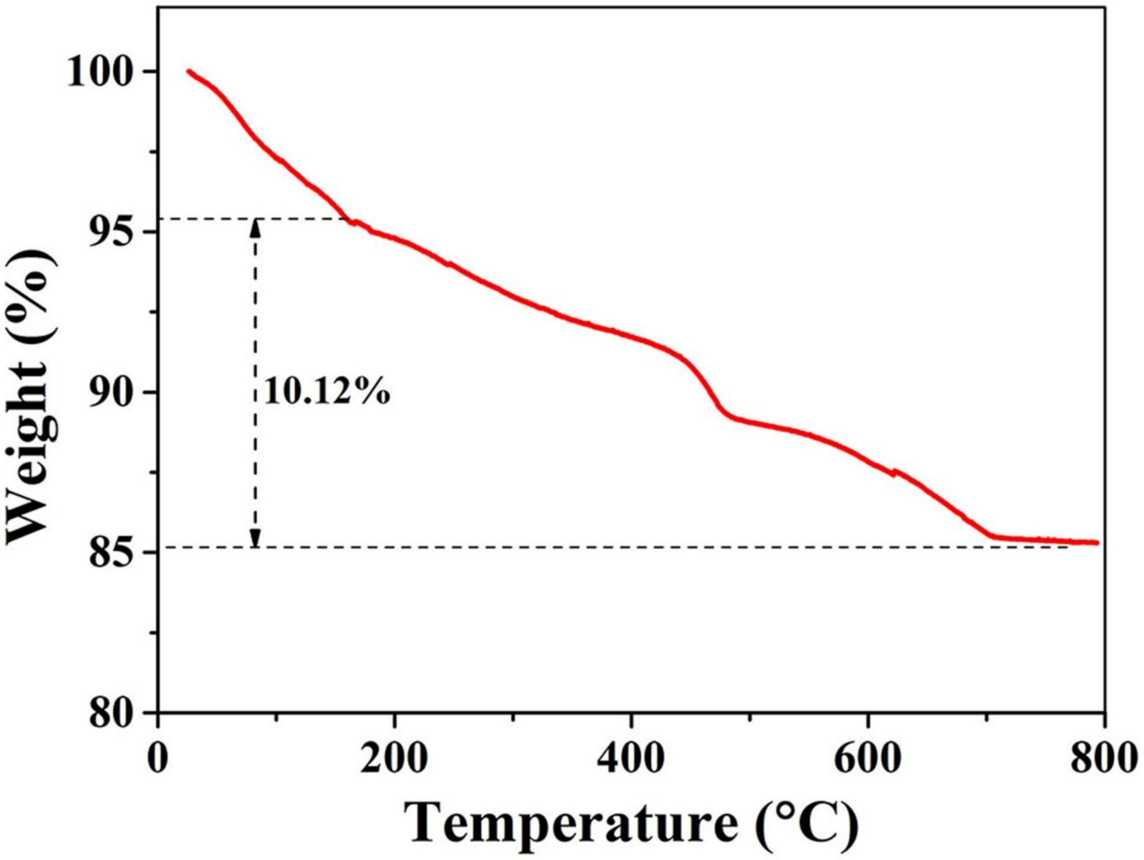

Fig. S7 TGA curve of NiO/CNHs.

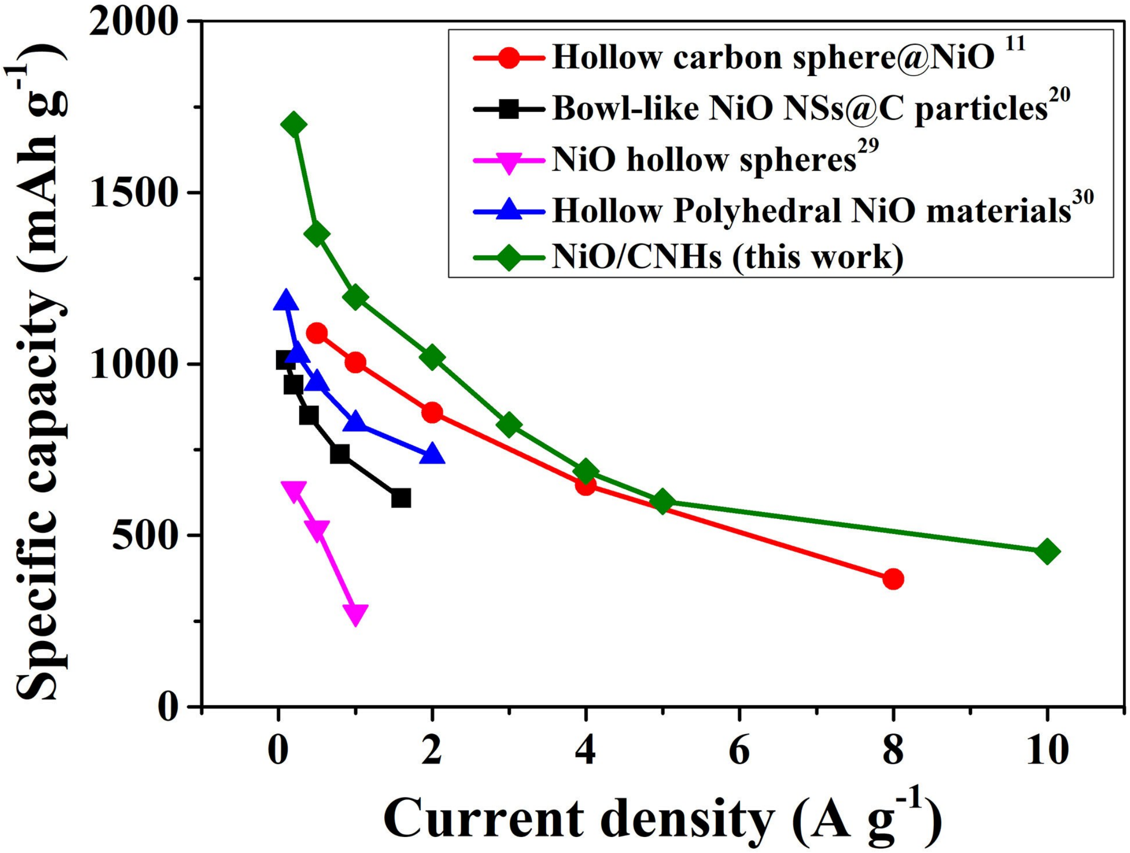

Fig. S8 Comparisons of rate performances of NiO/CNHs in LIBs and recent reported experimental data of other NiO-based hollow structures (Refs.[11,20,29,30] of the text).

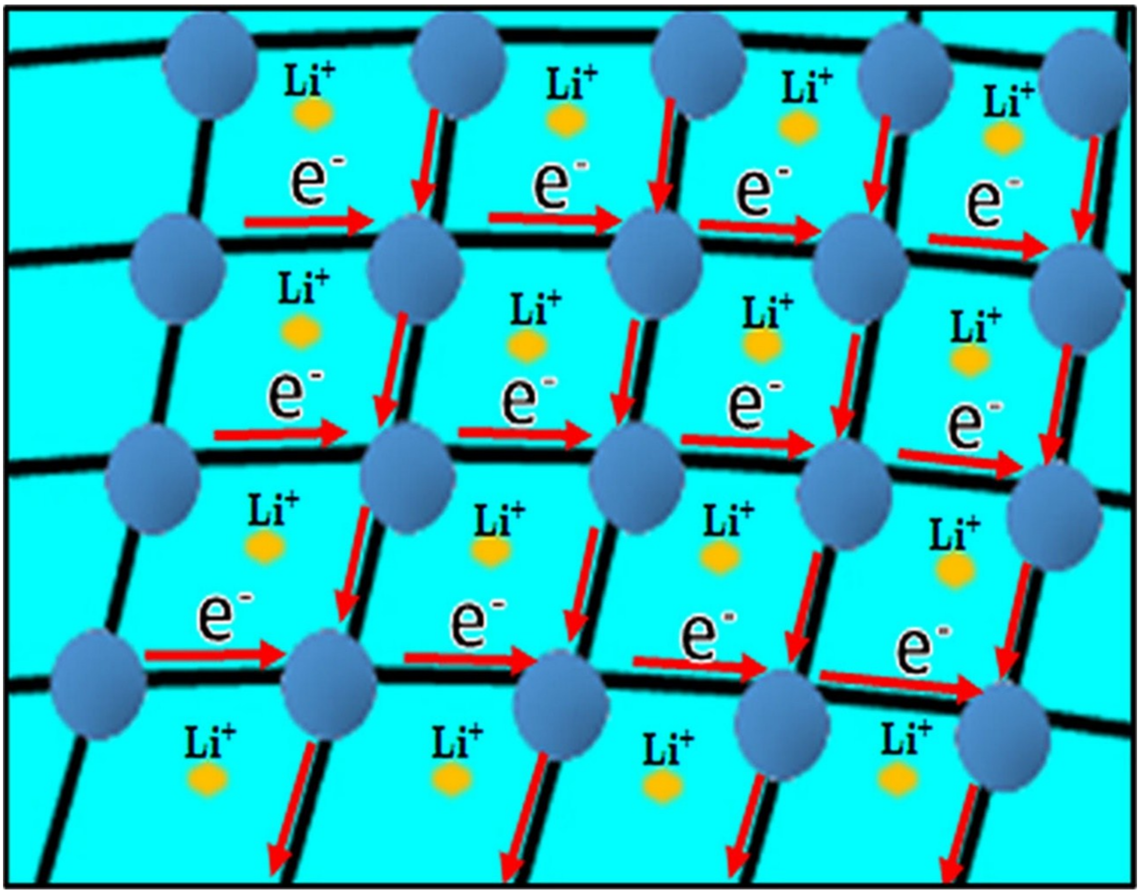

Fig. S9 Schematic illustration of the electron/Li$^+$ diffusion in NiO/CNHs.

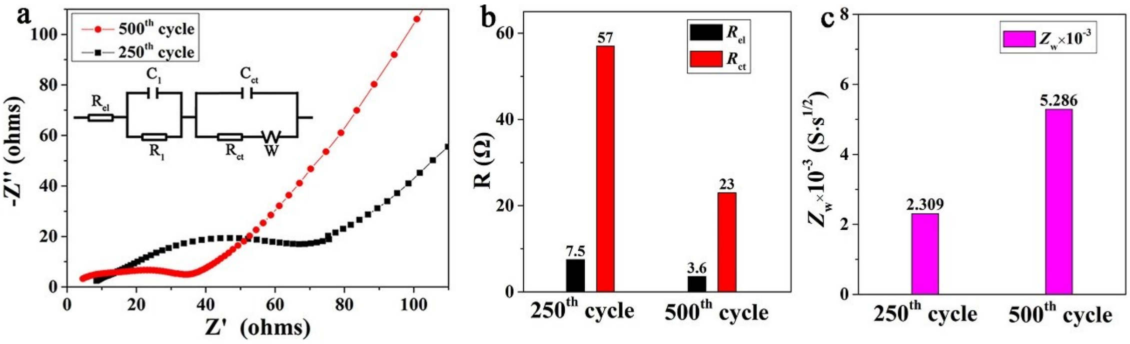

Fig. S10 (a) EIS of the NiO/CNHs electrode in LIBs at the 250th cycle and 500th cycle tested at a current density of 7.5C (5 A g^{-1}), where the inset shows the equivalent circuit diagram. (b) Comparisons of R_{el} and R_{ct} values between the 250th cycle and 500th cycle, which are obtained according to the equivalent circuit diagram in (a). (c) A comparison of Warburg resistance (Z_{W}) values between the 250th cycle and 500th cycle, which are obtained according to the equivalent circuit diagram in (a)

Supplementary Table

Table S1. The comparison of volumetric density between NiO/CNHs and NiO/hollow carbon spheres on a full electrode level. M_{Cu} denotes the average mass of Cu foil. $M_{\mathrm{electrode}}$, $V_{\mathrm{electrode}}$ and $D_{\mathrm{electrode}}$ are the average mass, volume and volumetric density of the working electrodes, respectively.

	$M_{\mathrm{Cu}}{}^{a}$ (mg)	$M_{\mathrm{electrode}}$ (mg)	$V_{\mathrm{electrode}}{}^{b}$ ($\mathrm{cm^3}$)	$D_{\mathrm{electrode}}{}^{c}$ ($\mathrm{g/cm^3}$)
NiO/CNHs	10.75	11.90	0.003	0.268
NiO/hollow carbon spheres	10.75	11.62	0.003	0.203

[a] Ten working electrodes were fabricated for each active material (NiO/CNHs and NiO/hollow carbon spheres). M_{Cu} and $M_{\mathrm{electrode}}$ are average values of measured results.

[b] $V_{\mathrm{electrode}}$ is calculated from the area (1 $\mathrm{cm^2}$) and thickness (30 μm) of discoidal working electrodes.

[c] $D_{\mathrm{electrode}} = 0.7(M_{\mathrm{electrode}}-M_{\mathrm{Cu}})/V_{\mathrm{electrode}}$.