Supplementary Information

A novel evolution strategy to fabricate 3D hierachical interconnected core-shell Ni/MnO_2 hybrid for Li-ion batteries

Jian Jiang, Jianhui Zhu, Yamin Feng, Jinping Liu* and Xintang Huang*

Institute of Nanoscience and Nanotechnology, Department of Physics, Central China Normal University, Wuhan 430079, Hubei (P.R. China)

E-mail:liujp@phy.ccnu.edu.cn(J. Liu), xthuang@phy.ccnu.edu.cn(X. Huang).
Fax: +86-027-67861185.

I. Experimental Details:

***Sample synthesis*.**

For Step I*. *Hydrothermal synthesis of nullaginite NFs precursors

Nullaginite NFs were prepared using a facile hydrothermal method according to the previous literature[7] and employed as the precursor materials. A stainless steel foil (35×20×0.2 mm^3) was immersed into a Teflon-lined stainless steel autoclave wherein there was a 50 mL homogeneous solution containing 1.24 g of $C_4H_6NiO_4\cdot 4H_2O$, 1.5 g of $CO(NH_2)_2$ and 0.37 g of NH_4F. Then, the autoclave was sealed and left still in an electric oven at the temperature of 130 ^oC for 5 h. Until the oven cooled down to room temperature, the sample was taken out and washed by distilled water several times.

For Step II*. *Hydrothermal synthesis of the core-shell nullaginite/MnO_2 NFs

The 3D hybrid of MnO_2/nullaginite NFs was fabricated via a secondary hydrothermal treatment toward the precursors. In details, a piece of substrate (35×10×0.2 mm^3) covered with nullaginite NFs was put into a 100 ml Teflon-lined stainless steel autoclave containing a 50 mL of 0.008 M $KMnO_4$ solution, which was subsequently maintained at 150 ° C for 5 h. Afterwards, the sample was fetched, washed with distilled water and dried at 60 °C.

For Step III*. *In-situ transformation of the core-shell Ni/MnO_2 NFs

The synthesis of MnO_2/Ni NFs was carried out in a horizontal, quartz tube-furnace system. A substrate with MnO_2/nullaginite NFs covered was put in the centre of a quartz tube. 1 mL of ethylene glycol loaded in an alumina boat was placed at the upstream zone of the quartz tube (the distance from the alumina boat to the quartz-tube center: 14 cm). Before heating, the quartz-tube reactor was sealed and flushed by Ar gas (200 sccm) for 20 min. The furnace was then heated to 740 K at a heating rate of 10 K min^{-1} under a constant Ar flow of 80 sccm, held for 15 min and allowed to cool down to room temperature naturally. Finally, the sample was taken out and kept at room temperature.

Characterizations. The microstructure and morphology of the film was characterized by powder X-ray diffraction (XRD, Bruker D-8 Avance) measurement, transmission electron microscopy (TEM) (JEM-2010FEF, 200 kV), scanning electron microscopy (SEM, JSM-6700F) and Raman spectroscopy (Witech CRM200, 532 nm). The pore size of the MnO_2 nanoflakes was determined using N_2 adsorption/desorption isotherms at 77 K with a BELSORP analyzer (JP. BELCo. Ltd.). The electrochemical measurements were carried out on a Neware battery tester at room temperature, using two-electrode cells with lithium metal as the counter electrode. The sample was cut into a disk with a surface area of 1.13 cm^2 and directly used as the working electrode. (A home-built stainless steel equipment is employed to make the disk-like electrodes: model diameter, 12 mm; area (circle), 1.13 cm^2). The electrolyte solution was 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume). The cell assembly was performed in a glovebox (Mbraun, Unilab, Germany) filled with argon and hydrogen. Before battery testing, cells were kept for 10 h. The loading weight of MnO_2 was measured by a microbalance with an accuracy of 0.01 mg. In details, we statistically determined the mean mass of nullaginite NFs disc before (M_1) and after (M_2) the growth of MnO_2 (the number of measured samples > 20). Thus, the MnO_2 loading weight M can be obtained ($M = M_2 - M_1$). Within the experimental error, the weight of MnO_2 loaded on per disc is calculated to be ~0.91 mg on average. Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI 760D, CH Instruments Inc., Shanghai) by applying an AC voltage with 5 mV amplitude in a frequency range from 0.05 Hz to 100 kHz.

II. Figures

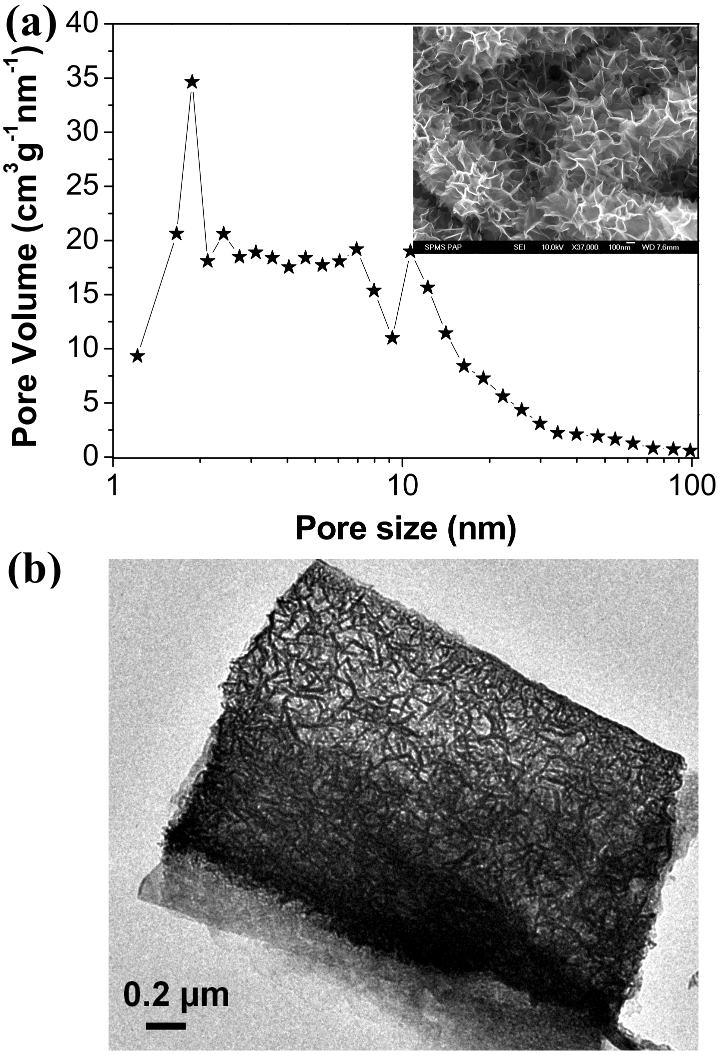

Fig. S1 (a) The pore size distribution of the MnO_2 nanoflakes. The inset SEM image shows the MnO_2 nanoflakes are interconnected with each other. (b) TEM image of the Ni/MnO_2 hybrid.

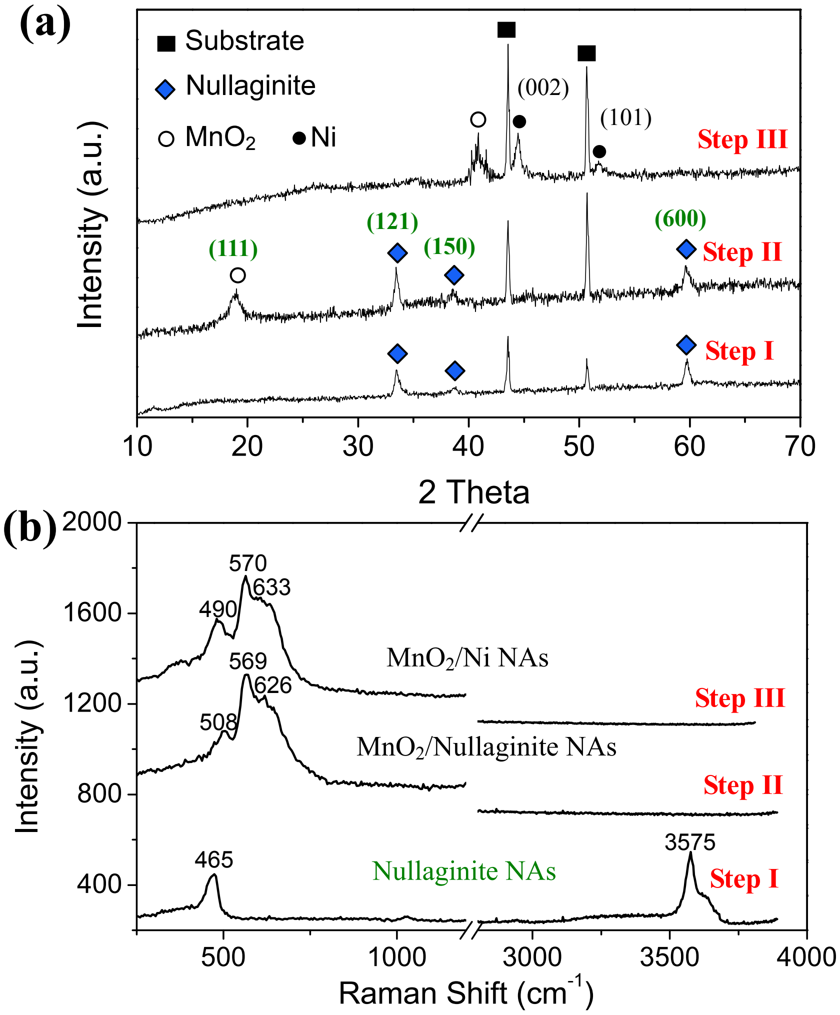

Fig. S2 (a) XRD patterns and (b) Raman spectra of the products obtained in the evolution stages.

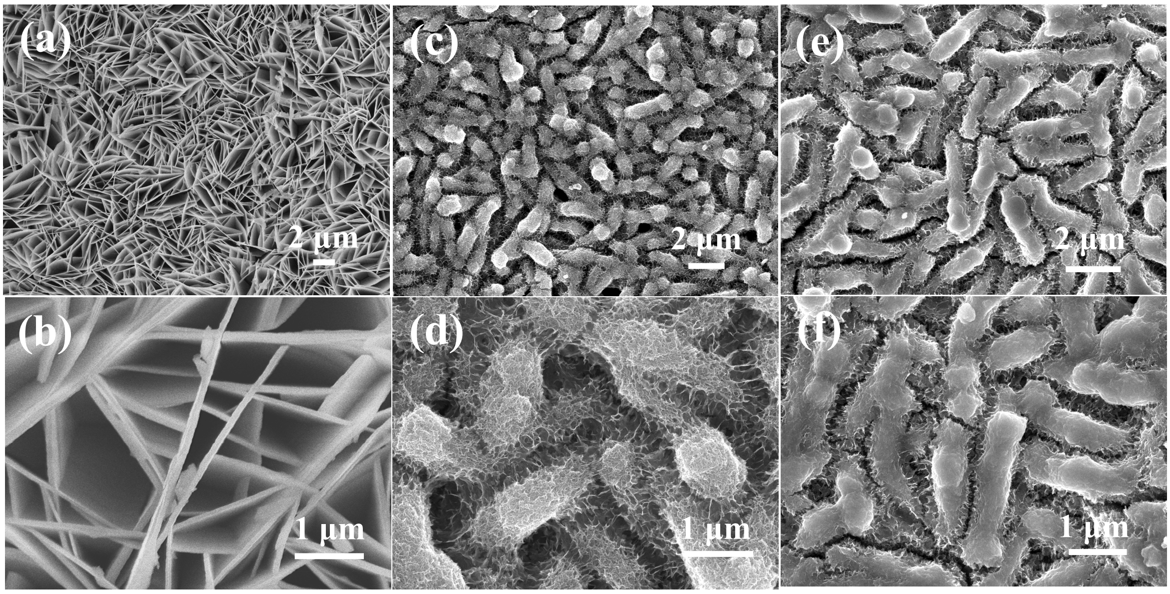

Fig. S3 SEM observations of the evolution of the Ni NFs/MnO$_2$ hybrid electrode: (a-b) nullaginite NAs; (c-d) MnO$_2$/nullaginite NAs; (e-f) MnO$_2$/Ni NAs.

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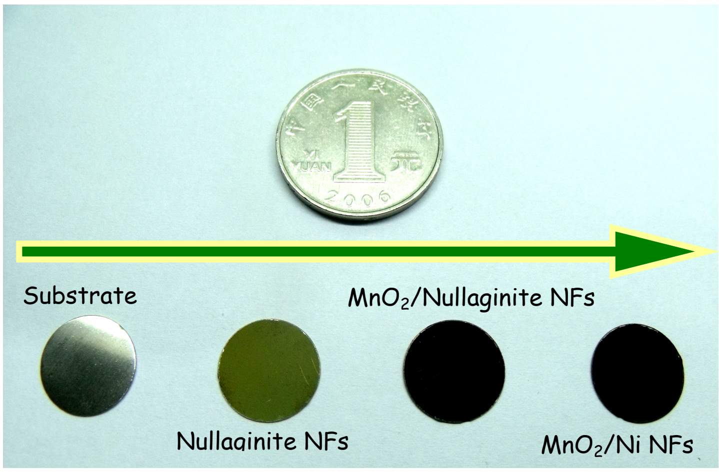

Fig. S4 Optical image illustrating the evolution process of the Ni NFs/MnO$_2$ hybrid electrode.

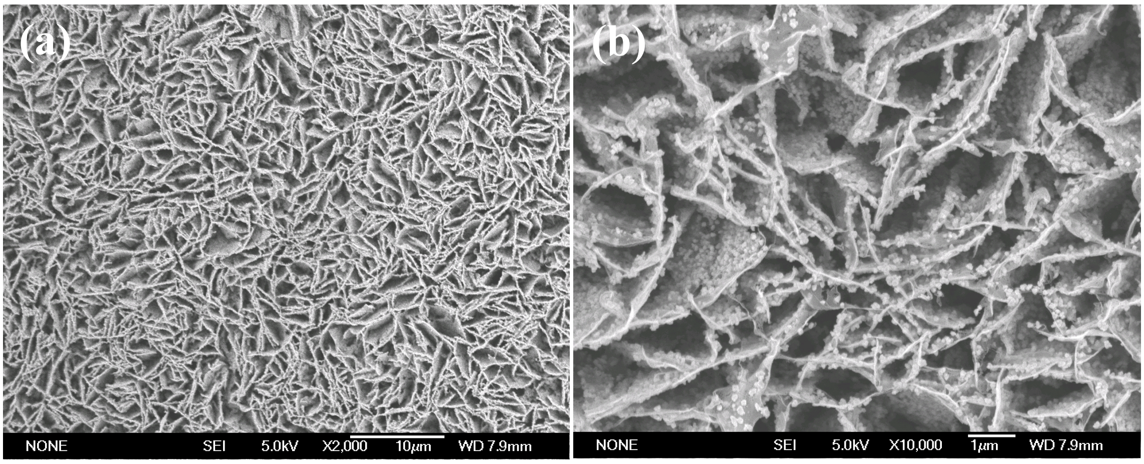

Fig. S5 SEM images of pure Ni NFs on the current collector substrate.

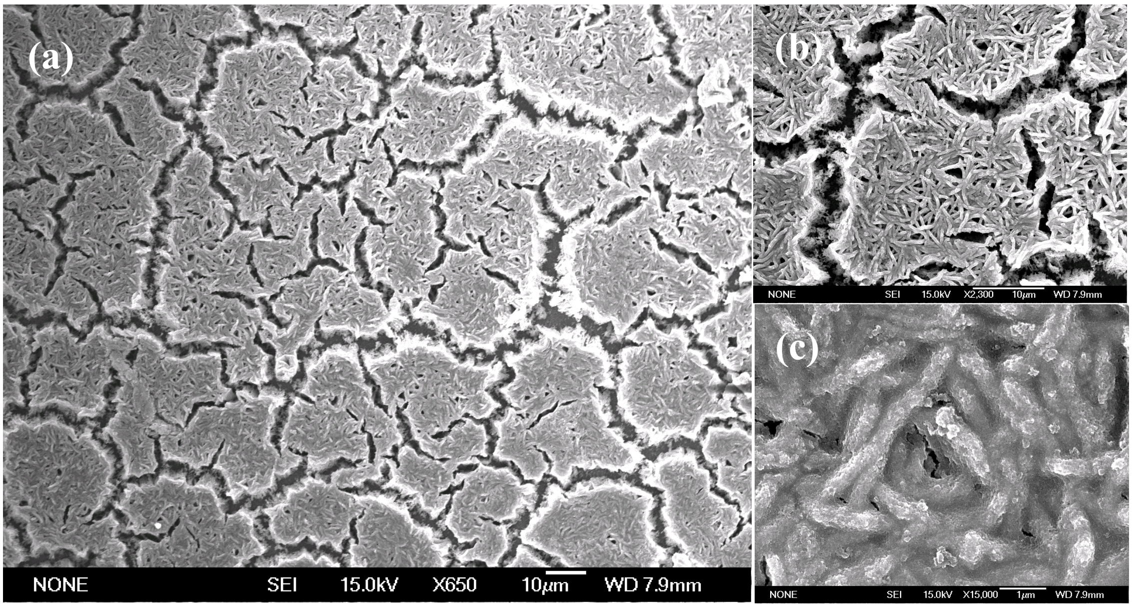

Fig. S6 SEM observations towards the Ni NFs/MnO_2 hybrid electrode after 120 programmed discharge-charge cycles.

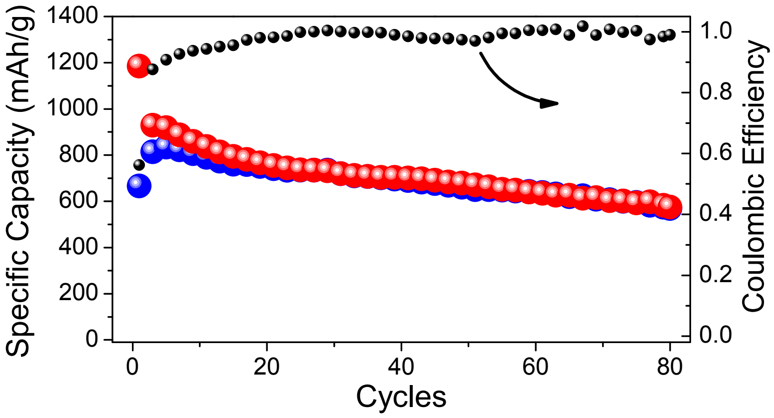

Fig. S7 Cycling performance for the Ni NFs/MnO_2 hybrid electrode at a current density of 369 mA/g.

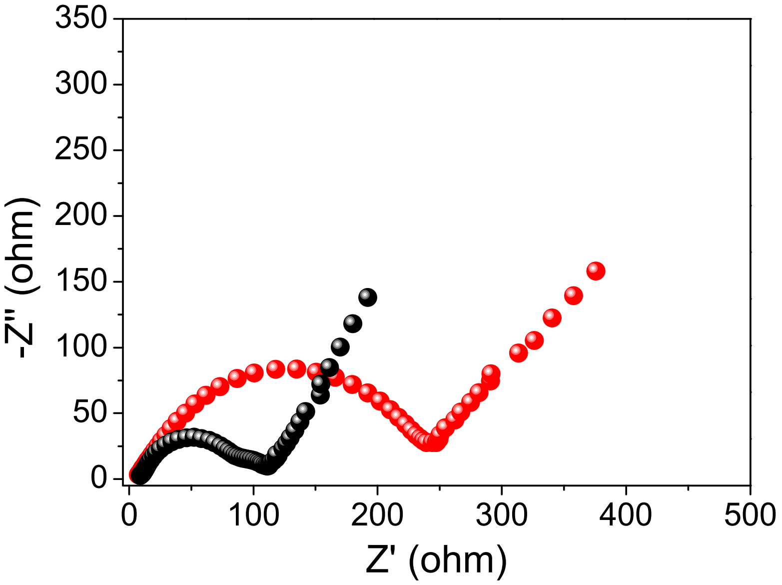

Fig. S8 Electrochemical impedance spectra of the Ni NFs/MnO_2 electrode (black) and the hybrid electrode (red) made by calcining the precursors under the Ar flow without adding the reducing agent.