Supporting Information

Carbon Coated MnO@Mn_3N_2 Core-Shell Composites for High Per-formance Lithium Ion Battery Anodes

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Experimental

Preparation of MnO_2 nanowires: In a typical process, 120 mL 0.1 M $KMnO_4$ aqueous solution and 82.8 mL 0.1 M $Mn(NO_3)_2$ aqueous solution were stirred for 20 min, and then transferred to an autoclave (50 mL in volume) and hydrothermally treated at 150℃ for 12 h. The resultant precipitate was washed with copious distilled water and then was dried at 60 ℃ overnight to obtain the asprepared MnO_2 nanowires.[1]

Preparation of MnO, MnO@Mn_3N_2/C and Mn_3N_2/C composites: MnO_2 nanowires were mixed with urea by manual agitation in mass ratio of 0, 200, 1000 wt % to prepare MnO, MnO@Mn_3N_2/C and Mn_3N_2/C respectively. The mixtures were calcined in a tubular furnace at 800 °C under ammonia for 3 h with a careful controlled heating ramp (room temperature to 300 °C, 5 °C min^{-1}, held for 0.5 h; 300 to 700 °C, 2 °C min^{-1}, held for 1 h; 700 to 800°C, 1 °C min^{-1}) and then cooled to room temperature.

Preparation of MnO/C: Typically, MnO_2 nanowires with 20 wt % sucrose at 800 °C under NH_3 for 3 h with a careful controlled heating ramp (room temperature to 300 °C, 5 °C min^{-1}, held for 0.5 h; 300 to 550 °C, 2 °C min^{-1}, held for 1 h; 550 to 800°C, 1 °C min^{-1}) and then cooled to room temperature.

Materials Characterization: The samples for the morphology and microstructure measurements were dispersed by ultrasonication for 0.5 h before characterized by scan electron microscopy (SEM) (JSM 7401F, 3 kV), high-resolution transmission electron microscopy (HRTEM) (JEM 2010, 120 kV), energy dispersive X-ray (EDX) measurements. X-ray diffraction (XRD) data were collected on a Bruker D8-Advance using Cu-Kα radiation (λ=1.5418 Å).

Electrochemical Measurements: The electrochemical test was measured in a CR2023-type coin cell. Metallic lithium disk was used as the reference electrode with diameter of 1 cm. The working electrode was fabricated by compressing a mixture of the active materials, conductive material (acetylene black), and binder (polytetrafluoroethylene) in a weight ratio of 8:1:1 onto an copper (Cu) foil with the same diameter of lithium disk at 10 Mpa. The electrode was dried at 70 °C for 10 h before assemble. The cell assembly was operated in a glovebox filled with pure argon. The electrolyte solution was 1 M $LiPF_6$/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethylmethyl carbonate (EMC) (1:1:1 by volume). Cyclic Voltammograms were recorded by a CHI 802B electrochemical workstation (CHI Inc., USA). Charge-discharge curves were recorded on a Roofer Battery Tester (Shenzhen, China). All electrochemical measurements were carried out at room temperature.

The calculate method of diffusion coefficient of Li ions (D_{Li+}) as followed:

The diffusion coefficient of Li ions was calculated by using the following equation:

$$D_{Li+} = R^2T^2\ (2A^2n^4F^4C^2\sigma^2)^{-1} \qquad (2)$$

In the equation, R = 8.314 MPa cm^3 mol^{-1} K^{-1}, T = 298 K, F = 96485 C mol^{-1}, as the electrode reaction was single electron reaction, namely $n = 1$; for the electrolyte consisted of 1 mol cm^{-3} $LiPF_6$ and the electrode was solid with diameter of 1 cm, thus C = 1 mol cm^{-3}, $A = 3.14 \times 0.5 \times 0.5$ cm^2; σ was estimate from the gradient of a plot of $-Z''$ vs. $\omega^{-1/2}$.

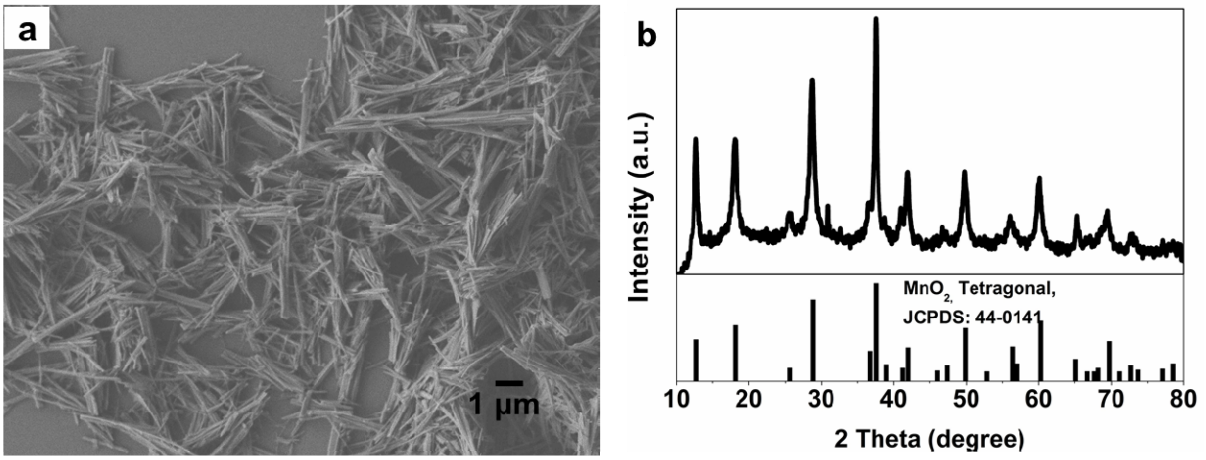

Fig. S1. SEM images (a) and XRD patterns (b) of MnO_2 nanowires.

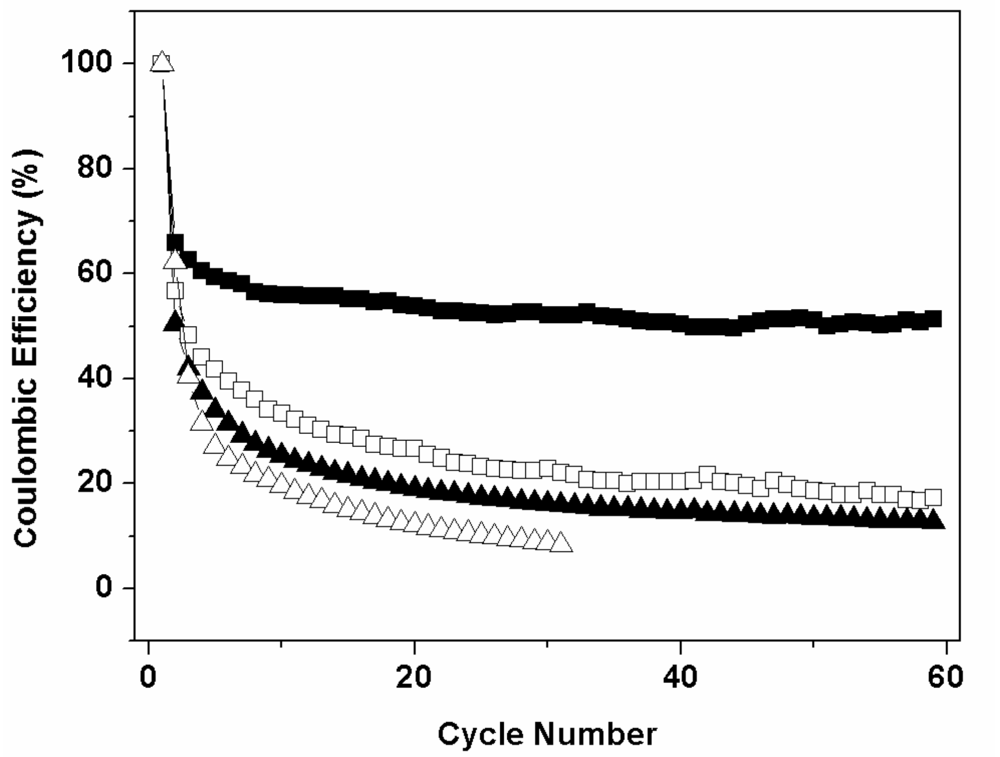

Fig. S2. Coulomb efficiency vs. cycle numbers of MnO@Mn_3N_2/C (■), Mn_3N_2/C (▲), MnO/C (□) and MnO (△), under different rates of 100 mA g-1, 200 mA g^{-1}, 500 mA g^{-1}, 1 A g^{-1} and 2 A g^{-1} between voltage limits of 3.00 and 0.05 V.

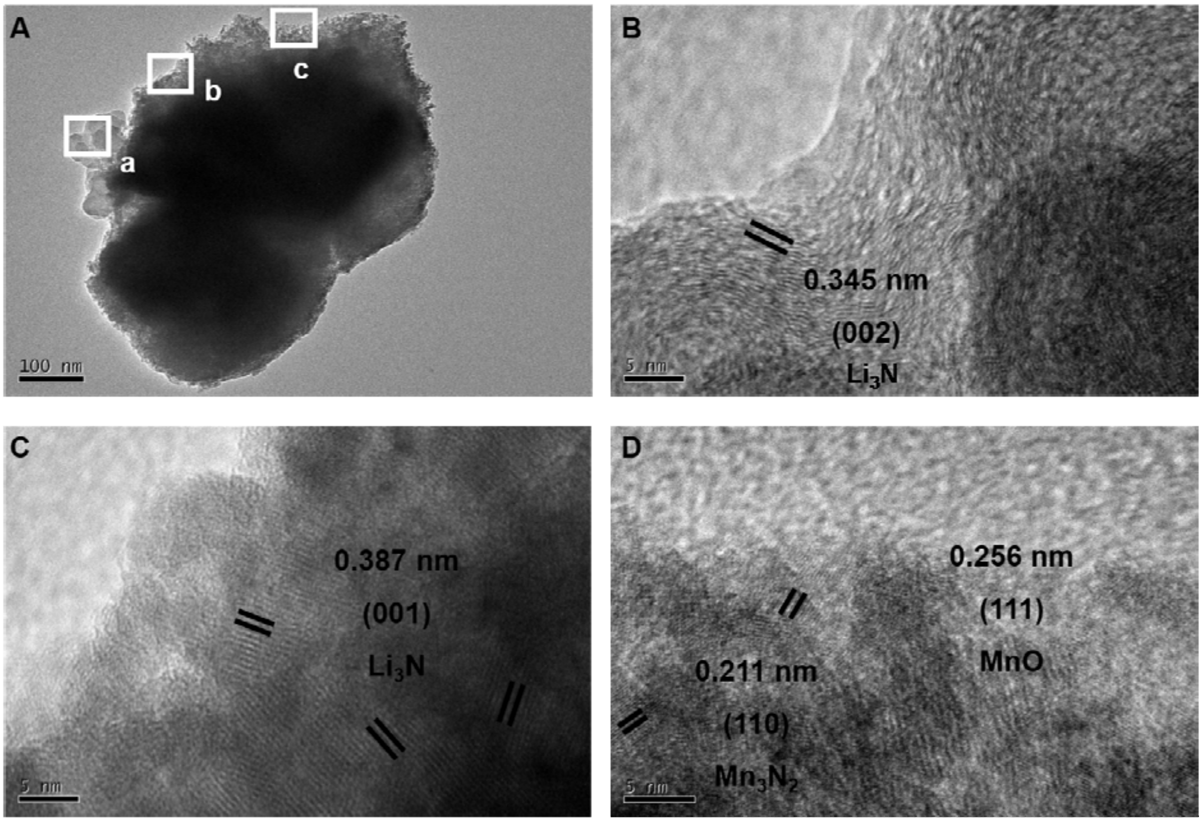

Fig. S3. HRTEM images of MnO@Mn_3N_2/C electrode after 60 Li-ion insertion/extraction cycles

Reference

1 J. Wang, E. Khoo, J. Ma, P. Lee, *Chem. Commun.,* 2010, **46**, 2468.

2 A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York, American, **1980.**