Self-sacrifice template formation of ultrathin single-crystalline ZnMn$_2$O$_4$ nanoplates with enhanced Li-storage behaviors for Li-ion batteries

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Experimental Section

Materials Synthesis. All the chemicals were of analytical grade, and used directly without further purification. Graphene oxide (GO) was synthesized from natural graphite by a modified Hummers method as described by us before.\textsuperscript{1,2} 30 mL of aqueous GO solution (0.1 mg mL$^{-1}$) was mixed with 0.0826 g of KMn$_2$O$_4$ under ultrasonication. The mixture was transferred to a Teflon-lined autoclave and hydrothermally treated at 160 °C just for 10 min. The as-obtained product (denoted as MnO$_2$) after filtering and washing for several times was directly dispersed into 20 mL of de-ionized (DI) water with 0.0594 g of Zn(NO$_3$)$_2$. Under vigorous stirring, 10 mL of freshly-prepared NaBH$_4$ solution (NaBH$_4$ dissolved in NaOH solution, pH = 12) was added dropwise to the above mixture, and then stirred for 6 h. The resulting precipitate was filtered, washed repeatedly with DI water to
remove residual ions, and further vacuum-dried. Finally, the ZnMn$_2$O$_4$ product was fabricated.

**Materials Characterization.** The samples were examined by powder X-ray diffraction (XRD) (Max 18 XCE, Japan) using a Cu Ka source ($\lambda = 0.154056$ nm) at a scanning speed of 3° min$^{-1}$ over a 2θ range of 10 – 70 °. The morphologies and structures were observed with transmission electron microscope (TEM), and high-resolution TEM (HRTEM) (JEOL JEM 2100 system operating at 200 kV) with energy dispersive X-ray spectrometer (EDS) elemental mapping analysis. Fourier transform infrared (FT-IR) spectrum was measured on a Shimadzu FT-IR-8400S spectrometer.

**Electrochemical Measurements.** The working electrode consisted of the ZnMn$_2$O$_4$ NPs, conductive material (acetylene black, Super-P-Li), and sodium carboxymethyl cellulose (CMC, average $M_w$: ~250 000) at a weight ratio of 70 : 20 : 10 with water as a solvent upon the copper foil substrate. The resultant slurry was uniformly spread onto pure Cu foil using a doctor blade, and dried in a vacuum oven overnight at 100 °C overnight. CR2032-type coin cells were fabricated by sandwiching a porous Cellgard 2400 separator between the working electrode and Li metal foil (Cyprus Foote Mineral, 99.98%, USA) in a high-purity Ar-filled glove box with both the moisture and the oxygen content below 0.5 ppm. The typical loading of electrode materials per electrode is ~1.1 mg. The electrolyte used here was 1 M LiPF$_6$ in a mixed solvent of ethylene carbonate (EC), dimethylcarbonate (DMC) and diethyl carbonate (DEC) (1 : 1 : 1, V/V/V) as the electrolyte. Galvanostatic discharge and charge cycling of the cells were conducted by using a CT2001A tester (Wuhan, China) at several different rates as indicated between cut-off potentials of 0.01 and 3.00 V (vs. Li/Li$^+$). Cyclic voltammogram (CV) was performed by an IVIUM electrochemical workstation (the Netherlands).

Fig. S1 Typical crystallographic structure of the spinel ZnMn$_2$O$_4$
Fig. S2 XRD pattern of the as-obtained GO product
Fig. S3 FT-IR spectrum data of the resultant ZMO NPs sample
**Fig. S4** EDS data of the resultant ZMO NPs sample