Facile Synthesis Graphene-supported Mesoporous Mn$_3$O$_4$ Nanosheets and High-performance in Li-ion Battery

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Experimental Section


The graphene oxide (GO) nanosheets were first synthesized by a modified Hummers’ method. Mn$_3$O$_4$ NSs were then grown onto the graphene support following the illustration in Fig. 1. In a typical synthesis of Mn$_3$O$_4$/G composite, 10 ml of GO (1mg mL$^{-1}$) suspension was diluted to 300 ml solution by adding 290 ml deionized water, followed by stirring for 1 h. Then, 0.5 g Manganese(II) chloride tetrahydrate (MnCl$_2$$\cdot$4H$_2$O, Sifma-Aldrich, 99.99 %) was added into the as-prepared GO dispersion under vigorous magnetic stirring for 2 h. And then, 5 ml of Hydrazine monohydrate (NH$_2$NH$_2$$\cdot$H$_2$O, TCI, 98 wt%) was rapidly injected into the solution and the solution was stirred for another 16 h at room temperature. After the reaction, the taupe brown precipitate was collected via filtration, and washed with DI water and ethanol three times. Afterwards, the obtained powder was dried at 70 °C overnight in a vacuum oven.

Materials Characterizations.

The product morphology and structure of sample were investigated using field-emission scanning electron microscopy (SEM; Hitchi-4800), transmission electron microscopy (TEM; JEOL, JEM 1230, 80 kV) and High-resolution TEM (HRTEM; Tecnai G2 F20, 200 kV). Crystallographic information of the sample was collected using powder X-ray diffraction (XRD; Philips, PW1050, Cu Kα radiation,
Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 10 °C/min-1 from room temperature to 800 °C.

**Electrochemical Measurements.**

The working electrodes were prepared by mixing 80 wt% active material (Mn$_3$O$_4$/G nanocomposite), 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride (PVDF, 5 wt%) binder dissolved in N-methyl-2-pyrrolidinone. After coating the above slurries on Cu foils, the electrodes were dried at 120 °C for 12 h in vacuum to remove the solvent before pressing. Then the electrode were cut into disks (12 mm in diameter) and dried at 100 °C for 12 h in vacuum. Electrochemical measurements were carried out via CR2032 (3V) coin-type cell with lithium metal as the counter/reference electrode, Celgard 2400 membrane separator, and 1 M LiPF$_6$ electrolyte solution dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 v/v). The cells were assembled in an argon-filled glovebox. Charge-discharge cycles were tested by LAND CT2001A battery test system at various current densities of 0.4 Ag$^{-1}$ – 24 Ag$^{-1}$ between 3 and 0.1 V vs Li$^+$/Li at room temperature.
Fig. S1 X-ray diffraction (XRD) patterns of the sample.

Fig. S2 Thermogravimetric analysis (TGA) of the Mn₃O₄/G composite. The weight loss of ~1% below 100 °C is probably due to the evaporation of the absorbed moisture contents, which is common for nanomaterials.
Fig. S3. The discharge/charge profiles of the first ten cycles at the current density of 0.4 Ag⁻¹.

Fig. S4 Cycling performance of bare Mn₃O₄ nanosheets anode at the current rate of 80 mAg⁻¹.