Supplementary Information

Low Temperature Plasma Synthesis of Mesoporous Fe_3O_4 Nanorods Grafted on Reduced Graphene Oxide for High Performance Lithium Storage

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Experimental

Growth of β-FeOOH nanorods on GO

The growth of β-FeOOH nanorods on GO was conducted using an aqueous solution method. Prior to the synthesis, 1.48 mmol of $FeCl_3 \cdot 6H_2O$, 15.4 mmol of NaCl and 2.5 mL of PEG-200 was dissolved in 50 mL of deionized (DI) water to form a homogenous solution. This solution was added dropwise into a 50 mL suspension of GO (2 mg mL^{-1}) under stirring. After heating to 120 ^oC within 30 min, 100 mL of Na_2CO_3 aqueous solution (0.1 M) was added to above solution through a syringe pump at a rate of 2 $mL \cdot min^{-1}$. The resulting solution was aged at 120 ^oC for 1 h. The precipitate was collected by several rinse-centrifugation (7000 rpm) cycles with water before drying at 80 ^oC.

Spindle-like β-FeOOH on GO can also obtained by using $FeCl_3$ with low concentration (0.015 M), while the same procedure as the preparation of β-FeOOH nanorods on GO was used as mentioned above.

Synthesis of the rGO decorated with mesoporous Fe_3O_4 nanorods

The rGO decorated with mesoporous Fe_3O_4 nanorods was prepared by DBD plasma technique with H_2 as working gas at ambient temperature and pressure. A certain amount of β-FeOOH/GO composite was put into a vertical quartz tube (10 mm in diameter and ca. 100 mm in discharge length) with a porous plate in the middle. Prior to the discharge, the reactor was purged with H_2 to exhaust the air. The DBD plasma was then initiated at an input AC power of 50 V ×1.2 A at ambient conditions for 30 min. Fe_3O_4 nanospindles on rGO (S-Fe_3O_4/rGO) was obtained by treating the composite of spindle-like β-FeOOH grown on GO with the same procedure as mentioned above.

Materials characterization

All samples were characterized by field-emission scanning electron microscopy (SEM, QUANTA 450, 20KV), transmission electron microscopy (TEM, FEI Tecnai G20, 200 KV), X-Ray diffraction (XRD, D/Max 2400 diffractometer, Cu Kα, λ = 1.5406 Å), Raman spectroscope (JY LabRam HR800, excited by 532 nm laser) and nitrogen adsorption/desorption (Micromeritics ASAP 2020 instrument). The weight ratio of Fe_3O_4 in the composite was estimated by thermogravimetric analysis (TGA, TA-Q50) from 30 to 900 ^{o}C at a ramp rate of 10 ^{o}C min^{-1} in air. The weight increase due to the conversion of Fe_3O_4 to Fe_2O_3 was subtracted following the stoichiometry of the compound.

Electrochemical measurement

The working electrodes consist of an active material (Fe_3O_4/rGO, pure Fe_3O_4 or rGO), carbon black and polyvinylidene difluoride (PVDF) at a weight ratio of 7:2:1, respectively. The mixture was spread onto a copper foil and dried at 120 ^{o}C for 12 h under a mechanical vacuum. The electrolyte that was used is 1.0 M $LiPF_6$ in a 50:50 (wt./wt.) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The electrodes were assembled into CR2016-type coin cells with pure lithium foil as the counter and reference electrode at room temperature in a glove box. The galvanostatic charge/discharge tests were performed on a LAND CT2000 battery tester at different current densities with a cut-off voltage window of 0.01-3.00 V. The calculation of the specific capacity is based on the total mass of the composite. The cyclic voltammograms (CV) were conducted using a CHI660D electrochemistry workstation between 0.01-3.0 V at a scan rate of 0.1 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were carried out using a CHI660D workstation by applying an AC amplitude of 5 mV over the frequency range of 100 kHz to 0.01Hz.

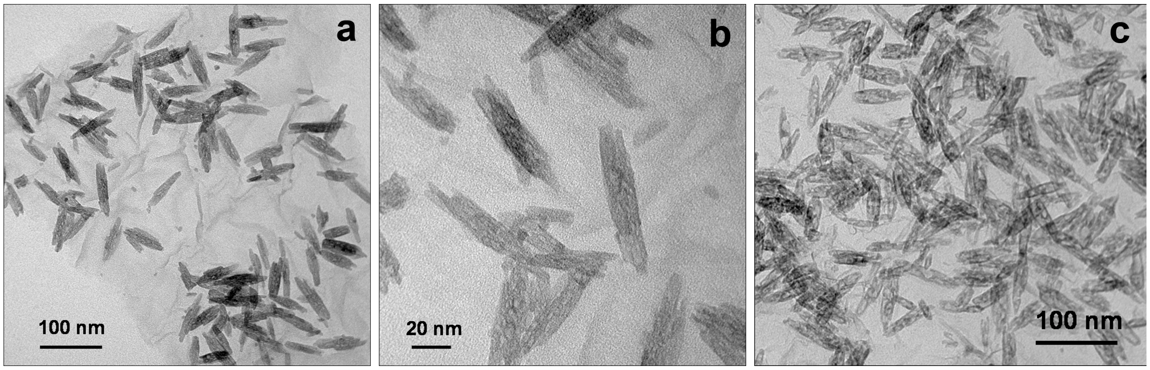

Fig. S1 TEM images of β-FeOOH/GO (a, b) and Fe_3O_4/rGO (c) composites, which were prepared at a lower concentration (0.015 M) of $FeCl_3$ solution.

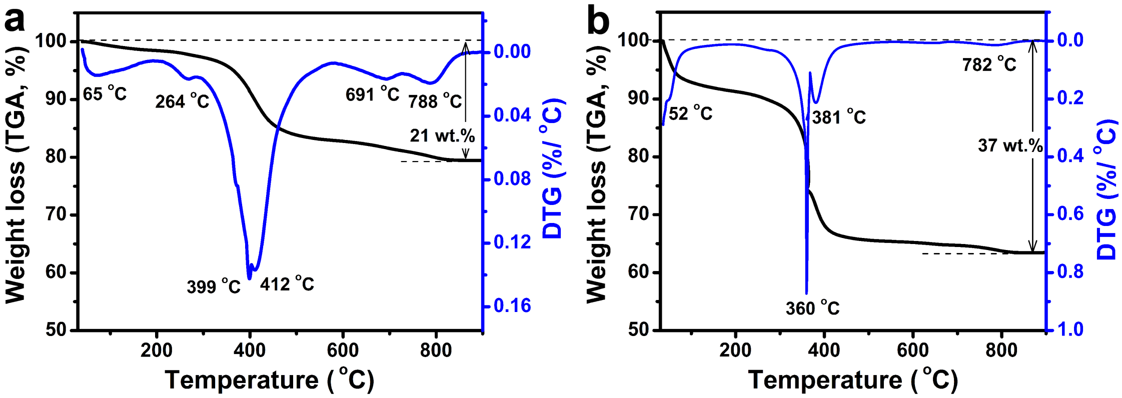

Fig. S2 TGA curves of the Fe_3O_4/rGO composites prepared at 0.1 M (a) and 0.015 M (b) concentration of $FeCl_3$ solution.

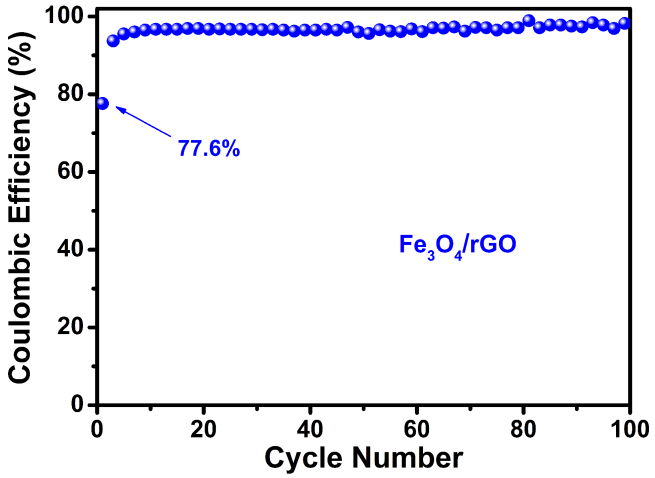

Fig. S3 Coulombic efficiency of Fe_3O_4/rGO cycled between 0.01-3V at a current density of 500 mA g^{-1}.

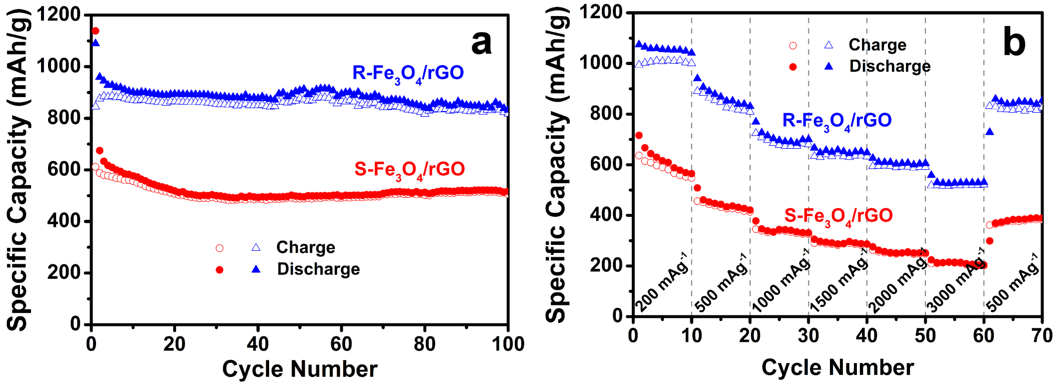

Fig. S4 (a) Cycling performance and (b) rate capability of R-Fe_3O_4/rGO and S-Fe_3O_4/rGO composites.

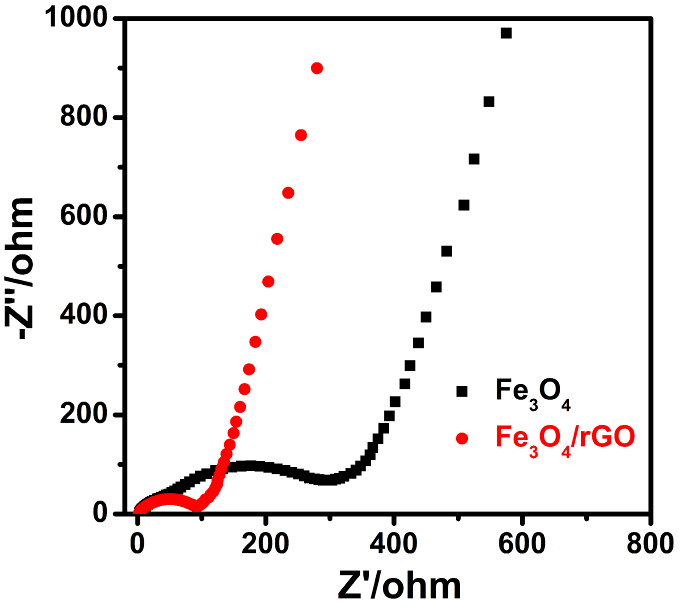

Fig. S5 Nyquist plots of the electrodes composed of pure Fe_3O_4 and Fe_3O_4/rGO composite.