

Electronic Supplementary Information (ESI) for

Enhanced Anode Performances of Fe₃O₄-Carbon-rGO Three Dimensional Composite in Lithium Ion Batteries

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Experimental Section

Preparation of GCF: Graphene oxide (GO) was prepared from purified natural graphite according to Hummers method reported in Ref. [S1, 2]. Graphene oxide (100 mg) and water (200 mL) was ultrasonicated for 2 h to give aqueous solution of graphene oxide (GO). An aqueous solution (50 mL) of Fe(NO₃)₃·6H₂O (9045 mg) and Polyvinylpyrrolidone (PVP, MW40000, 150 mg) were added to the aqueous solution. The mixture was stirred for 4 h to complete ion exchange. Aqueous solution (20 mL) of glucose (1500 mg) and urotropine (2365 mg, 1.0 equ.) was added into the above mixture. The mixture was kept stirring for a further 1 h and then transferred into an autoclave (500 mL) and then heated to 200 °C for 48 h. After cooled to room temperature naturally, the resulted solid was washed with water and dried at 140 °C. After heated to 500 °C with a temperature ramp of 10 °C/min in Ar flow, Fe₄O₃@carbon-reduced graphene oxide composite (GCF) was obtained.

Characterization: Fourier transform infrared (FT-IR) spectra measurements were carried out on a NICOLET 560 Fourier transform infrared spectrophotometer. Raman spectrum was recorded on a Renishaw RM-1000 with excitation from the 514 nm line of an Ar-ion laser with a power of about 5 mW. The phase structure of as-prepared products were characterized with X-ray diffraction (XRD, Bruker D8 advance) with Cu Kα λ=1.5418 Å. X-ray photoelectron spectrum (XPS) were recorded on a PHI quantera SXM spectrometer with an Al Kα = 280.00 eV excitation source, where binding energies were calibrated by referencing the C1s peak (284.8 eV) to reduce the sample charge effect. The morphology of as-prepared products was studied by using transmission electron microscope (TEM, JEOL JEM-2100, operating at 100 kV), high resolution TEM (HRTEM, JEOL JEM-2010F electron microscope, operating at 200 kV), and scanning electron microscope (SEM, QUANTA 200 FEG, operating at 25 kV). For atom force microscopy (AFM) measurement, the samples were coated on Si surface and AFM studies were performed using a Digital Instruments Dimension 3100 microscope in the tapping mode. N₂ adsorption-desorption was tested on TriStar II 3020 (Micromeritics Instrument Corporation, USA).

Lithium ion battery performance was determined using CR 2032 type coin cells assembled in an argon-filled glove box (MBRAUN). The working electrodes prepared by mixing the GCF and Carboxymethyl Cellulose Sodium (CMC, 3 wt.%) at a weight ratio of 90:10 were pasted on pure Cu foil (15 μm). Celgard 2400 was used as a

separator. Lithium foil was used as the counter electrode. The electrolyte consisted of a solution of LiPF_6 (1 M) containing vinylene carbonate (2 wt.%) in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1, volume ratio). A galvanostatic cycling test of the assembled cells was carried out on a BS-9300K system in the voltage range of 0.001–3.0 V (vs. Li^+/Li) at current density of 0.2 C (200 mA g^{-1}), 0.5 C, 1.0 C, 2.0 C, and 5.0 C, respectively. The weight of GCF in the working electrode was used to estimate the specific discharge capacity of the battery, which was expressed in mA hg^{-1} of GCF.

In order to investigate the difference between GCF and sole samples, the theoretical capacity (Q) of the hypothetical mixture of GCF is calculated shown as follows: [S3]

$$Q_{\text{theoretical}} = Q_{\text{Fe}_3\text{O}_4} \times \text{mass percentage of Fe}_3\text{O}_4 + Q_{\text{Graphite}} \times \text{mass percentage of Graphite} = 925 \times 90\% + 372 \times 10\% = 838 \text{ mA hg}^{-1}$$

References

- [S1] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339–1339.
[S2] B. J. Li and H. Q. Cao, *J. Mater. Chem.*, 2011, **21**, 3346–3349.
[S3] S. M. Paek, E. J. Yoo and I. Honma, *Nano Lett.*, 2009, **9**, 72–75.

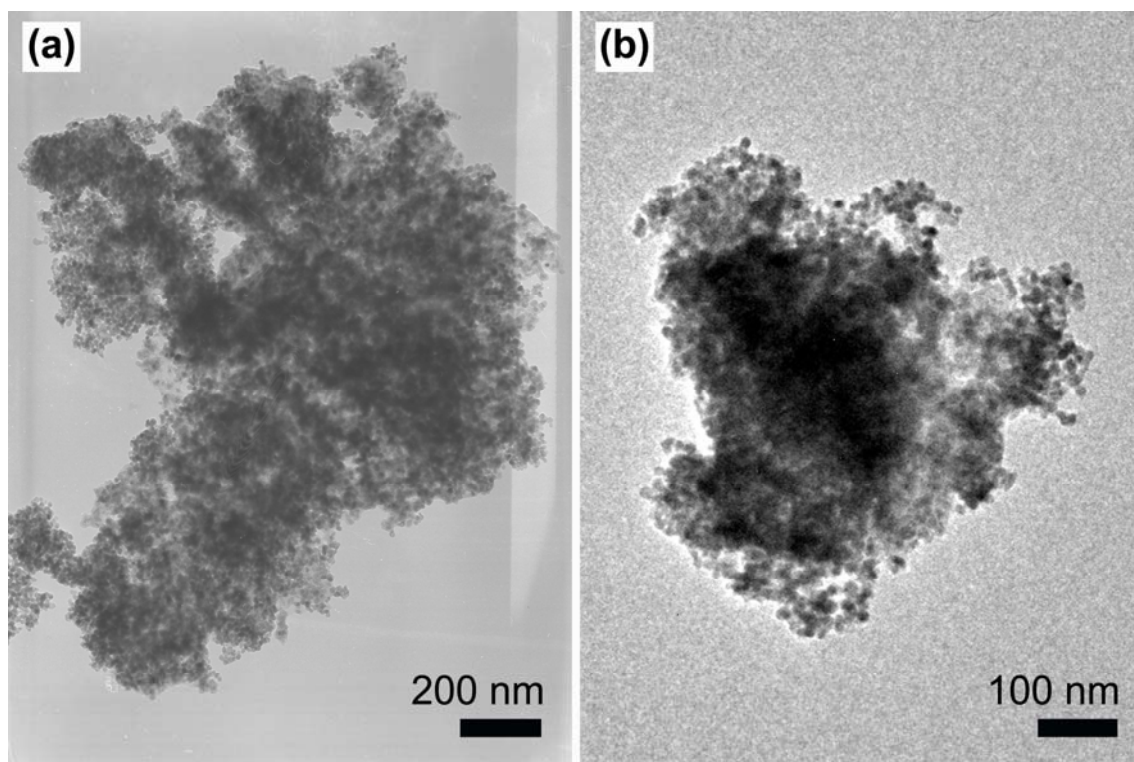


Fig. S1 (a, b) TEM images of GCF.

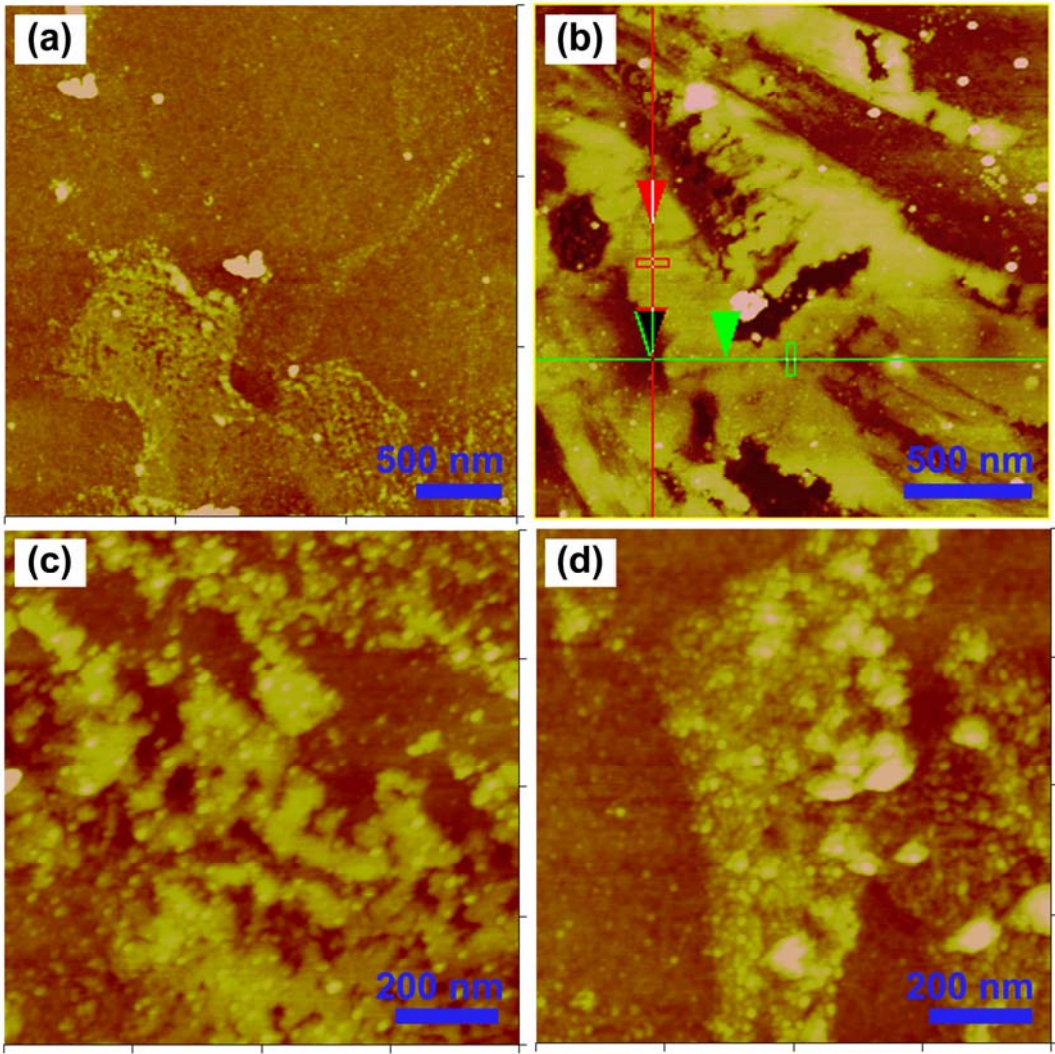


Fig. S2 (a-d) AFM images of GCF.

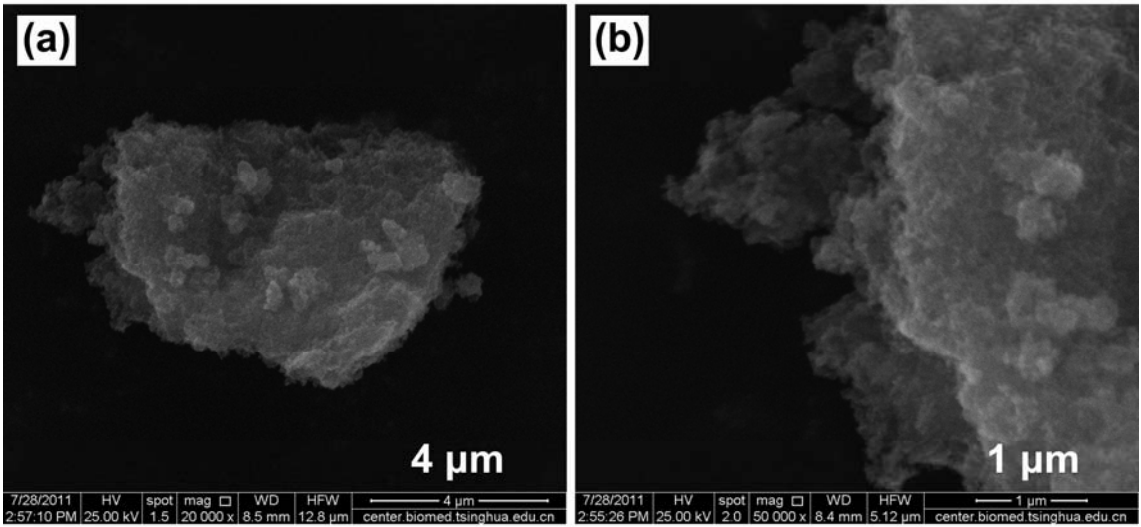


Fig. S3 (a, b) SEM images of GCF.

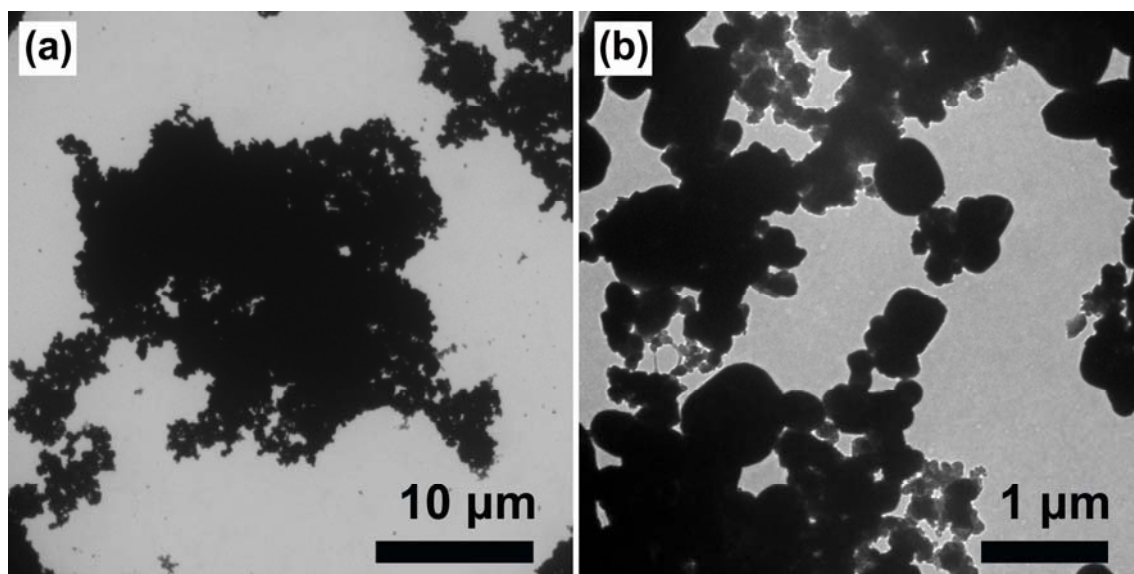


Fig. S4 (a, b) TEM images of commercial Fe_3O_4 NPs.

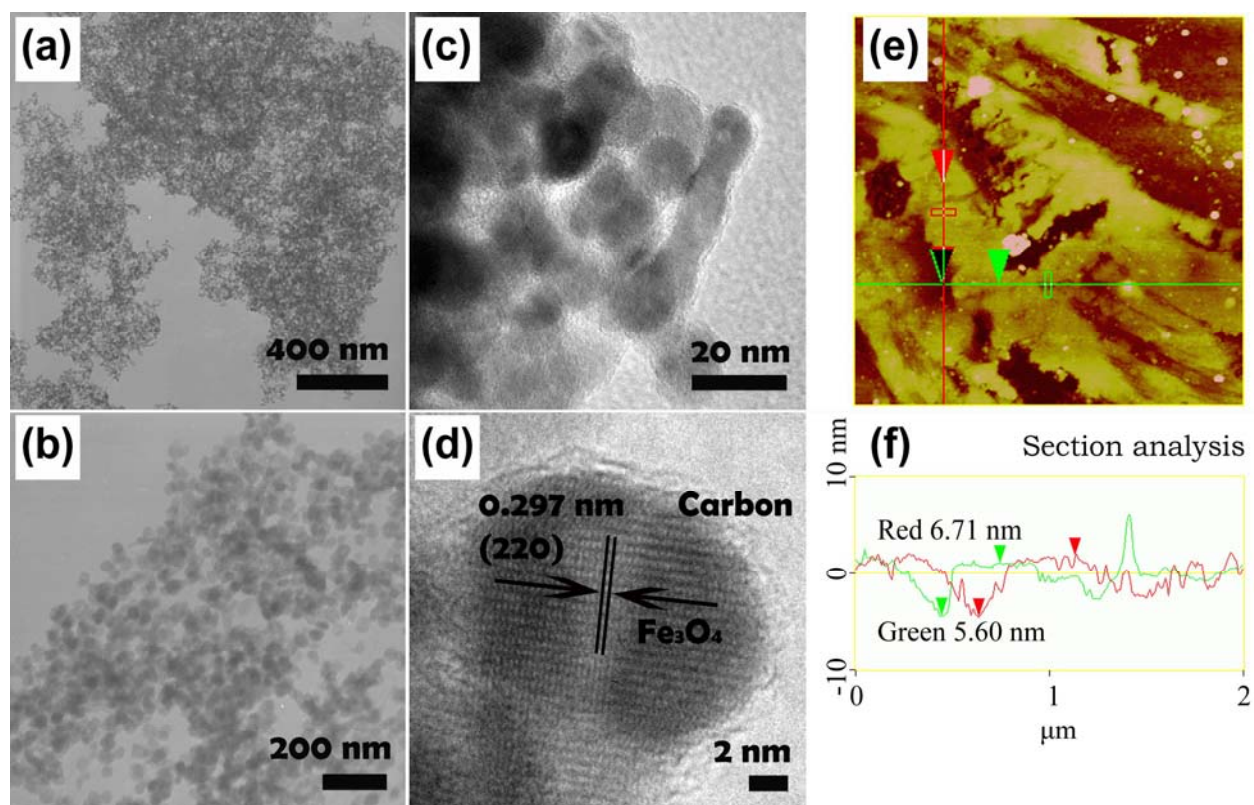


Fig. S5 The enlarged version of (a, b) TEM images, (c, d) HRTEM images, (e) AFM image of GCF, and (f) its section analysis.