

Supporting information

Experimental Section

Materials:

Natural flake graphite was purchased from Sigma-Aldrich. Iron chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), poly(vinyl alcohol) (PVA) were purchased from Aladdin. NaNO_3 , KMnO_4 , H_2SO_4 (98 %), H_2O_2 (30 %) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ethanol and deionized (DI) water were purchased from Aladdin Reagent (Shanghai). All chemicals were of analytical grade and used as received without further purification.

Synthesis of FeOOH/GO nanosheets:

Graphene oxide (GO) was synthesized from natural graphite flakes by a modified Hummers method. For the preparation of FeOOH/GO, the suspension of GO (100 mL, 1 mg mL^{-1}) was first ultrasonicated for 0.5 h, and iron chloride (FeCl_3 and FeCl_2 with a mole ratio of 2:1) dissolved in water (100 mL) was added slowly. The mixture was then ultrasonicated for 20 min and then kept at 80 °C under stirring for 12 h. After that, the resulting suspension was collected by centrifugation, washed repeatedly with deionized water to remove the excess salt. According to the different quantities of iron (II, III) chloride added, the obtained samples were named as FeOOH/GO-1 (210 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 82 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), FeOOH/GO-2 (420 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 164 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and FeOOH/GO-3 (840 mg $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 328 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), respectively.

Synthesis of the C-Fe₃O₄/G hybrids:

PVA (1ml, 100 mg ml⁻¹) was added to the aqueous suspension of FeOOH/GO-X (10 mg mL⁻¹, X = 1, 2 or 3). Subsequently, the mixture was moved in 1 mL syringes, which was then immersed in liquid nitrogen for 5 h. The frozen cryogels were freeze-dried for 48 h and taken out from the syringe as intact monoliths. Finally, the as-prepared samples were thermally treated at 500 °C for 2 h in N₂ atmosphere to give the C-Fe₃O₄/G hybrids. According to the different quantities of iron (II, III) chloride added in the first step, the final samples are noted as C-Fe₃O₄/G-1, C-Fe₃O₄/G-2 and C-Fe₃O₄/G-3, respectively.

Synthesis of Fe₃O₄/G:

In controlled experiment, the aqueous suspension of FeOOH/GO-2 (10 mg mL⁻¹) was directly placed in 1 mL syringes, which was then immersed in liquid nitrogen for 5 h. The frozen cryogels were freeze-dried for 48 h and taken out from the syringe as intact monoliths. Finally, the as-prepared samples were thermally treated at 500 °C for 2 h in N₂ atmosphere to generate Fe₃O₄/G as the product.

Material Characterizations

Scanning electron microscopy (SEM) measurements were performed on an FEI Sirion-200 field emission scanning electron microscope. Transition electron microscopy (TEM) studies were conducted on a JEOL-2100 electron microscope at an operating voltage of 200 kV. The samples were dissolved in ethanol and the suspension was dropped onto a copper grid covered with carbon film. Atomic force microscopy (AFM) images of the materials on a freshly cleaved mica surface were

taken with a Nanoscope III in tapping mode using a NSC14/no Al probe (MikroMash, Wilsonville, Oregon). For TGA measurements, a TA Instrument Q-5000 IR model was used with a heating rate of 10 °C min⁻¹ in air. The X-ray diffraction (XRD) analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 50 mA with a scanning speed of 6°/min from 5 to 80°.

Electrochemical Measurements

Electrochemical experiments of the anode electrodes in lithium ion batteries were carried out in coin-type cells. The electrodes were prepared by mixing the hybrids, carbon black (Super-P), and poly(vinyl difluoride) (PVDF) with a weight ratio of 80:10:10 and pasting the mixture on pure copper foil (99.6%) with a thickness of 100 μm . The electrode was dried at 60 °C for 12 h in a vacuum oven and cut into sheets ($\Phi 11 \text{ mm}$). The loading mass of active material (C-Fe₃O₄/G or Fe₃O₄/G) in each cell is $\sim 0.40 \text{ mg cm}^{-2}$. Pure lithium foil was used as the counter-electrode. The electrolyte consisting of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) was obtained from Ube Industries Ltd. The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen below 1 ppm. The electrochemical performance was tested at various rates in the voltage range of 0.01-3.00 V. The capacity was calculated based on the total mass of the active materials.

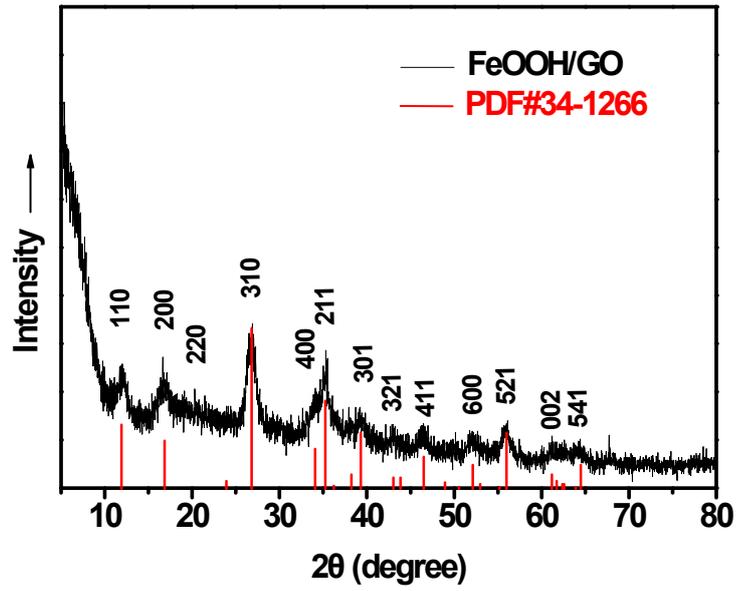


Figure S1 The XRD patterns of FeOOH/GO, which can be well indexed to JCPDS 34-1266.

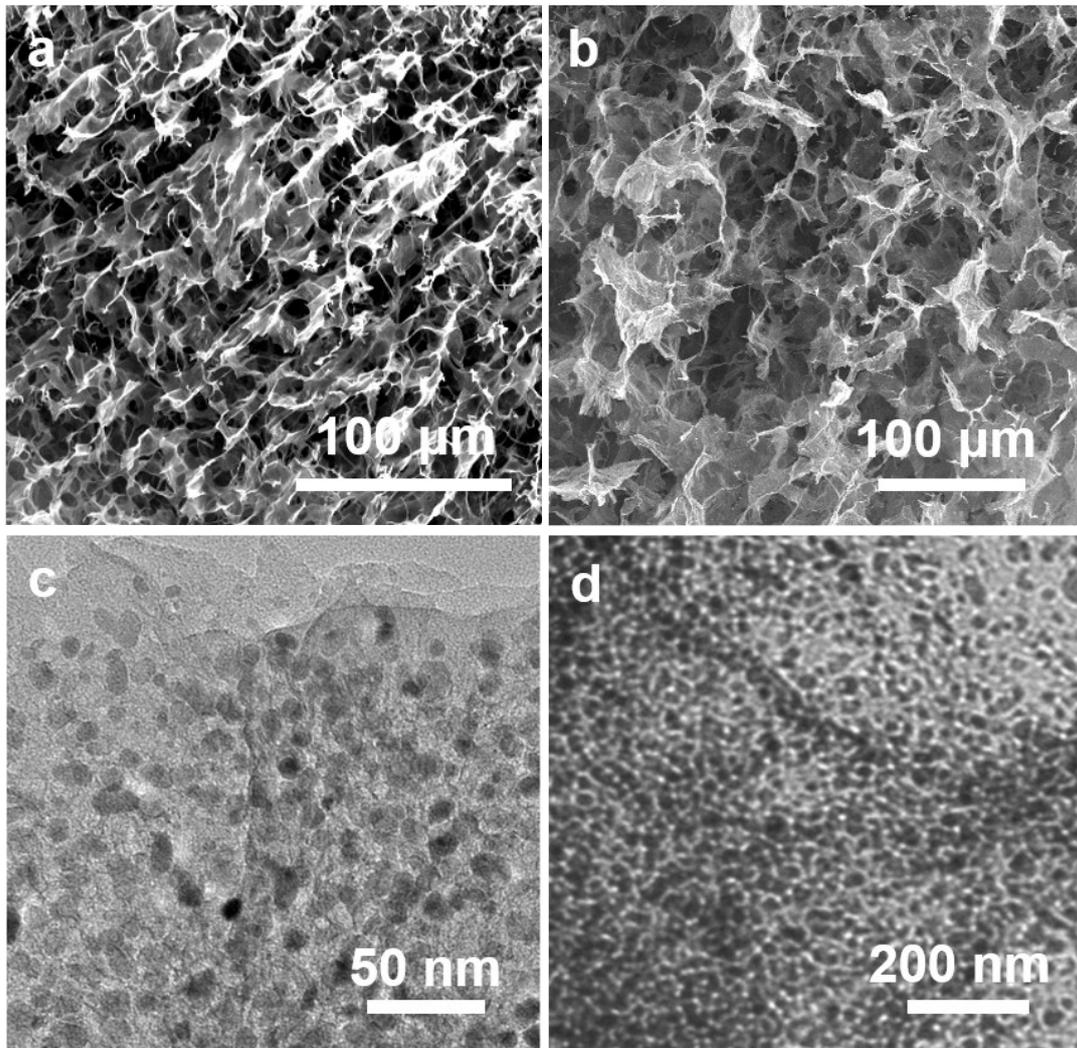


Figure S2 (a) SEM image of C-Fe₃O₄/G-2 with the ordered macroporous structures; (b) SEM image of Fe₃O₄/G with the disordered macroporous structures; (c) TEM image of C-Fe₃O₄/G-2; (d) TEM image of Fe₃O₄/G.

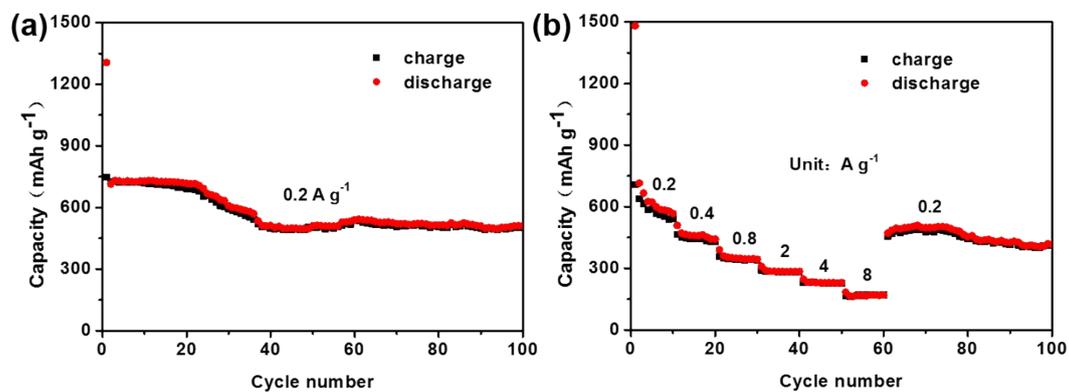


Figure S3 (a) Cycling performance of Fe₃O₄/G at a current density of 0.2 A g⁻¹; (b) The rate performance of Fe₃O₄/G at current densities of 0.2 - 8 A g⁻¹.

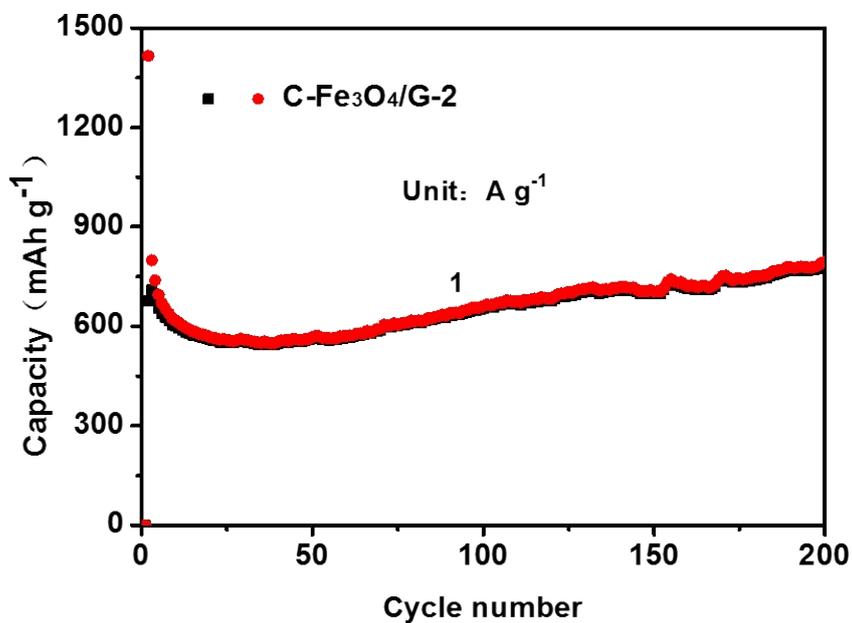


Figure S4 Cycling performance of C-Fe₃O₄/G-2 at a current density of 1 A g⁻¹.

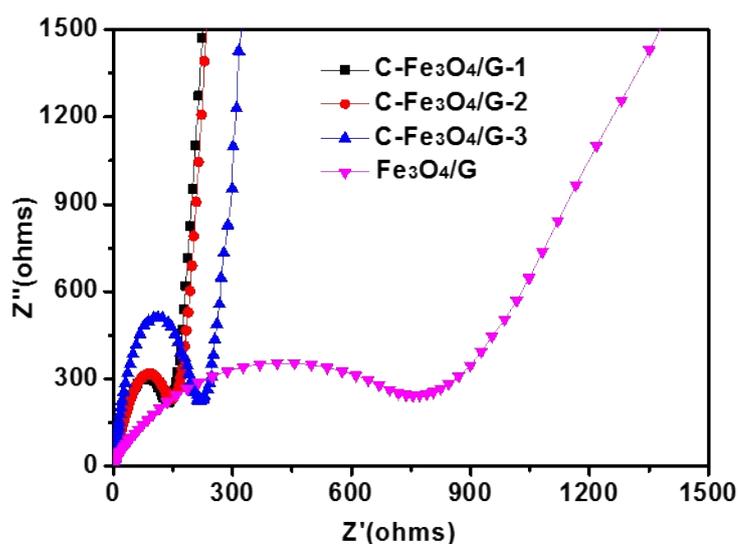


Figure S5 Nyquist plots of the C-Fe₃O₄/G hybrids and Fe₃O₄/G after 100 cycles.

Table S1 The electrochemical performance of C-Fe₃O₄/G-2 and the recently reported electrode materials based on Fe₃O₄.

Materials	Charge/discharge rates 院	Cycling number	Capacities (mA h g ⁻¹)	Ref.
C-Fe ₃ O ₄ /G-2	0.2 A g ⁻¹	200	1065	Present work
Fe ₃ O ₄ /C microrod	0.2 A g ⁻¹	100	650	[S1]
Fe ₃ O ₄ /SWNT	5C	60	790	[S2]
GF@Fe ₃ O ₄	1C	500	870	[S3]
G-Fe ₃ O ₄ -GNRs	0.4 A g ⁻¹	300	708	[S4]
G@Fe ₃ O ₄ @C	0.2 A g ⁻¹	100	920	[S5]
Fe ₃ O ₄ /C micro-rods	0.5 A g ⁻¹	200	837	[S6]
Fe ₃ O ₄ @GS/GF	0.093 A g ⁻¹	150	1059	[S7]
Fe ₃ O ₄ @C-PMCMs	0.2	50	1100	[S8]

Reference:

- [S1] Y. Wang, L. Zhang, X. Gao, L. Mao, Y. Hu, X.W. Lou, *Small*, 2014, 10, 2815.
- [S2] C. Ban, Z. Wu, D.T. Gillaspie, L. Chen, Y. Yan, J.L. Blackburn, A.C. Dillon, *Adv. Mater.*, 2010, 22, E145.
- [S3] J. Luo, J. Liu, Z. Zeng, C.F. Ng, L. Ma, H. Zhang, J. Lin, Z. Shen, H.J. Fan, *Nano. Lett.*, 2013, 13, 6136.
- [S4] L. Li, A. Kovalchuk, H. Fei, Z. Peng, Y. Li, N. D. Kim, C. Xiang, Y. Yang, G. Ruan, J. M. Tour, *Adv. Energy Mater.*, 2015, 1500171.
- [S5] Y. Su, S. Li, D. Wu, F. Zhang, H. Liang, P. Gao, C. Cheng, X. Feng, *ACS nano*, 2012, 6, 8349.
- [S6] Ma, F. X.; Wu, H. B.; Xu, C. Y.; Zhen, L.; Lou, X. W., *Nanoscale*, 2015, 7 , 4411.
- [S7] F.X. Ma, H.B. Wu, C.Y. Xu, L. Zhen, X.W. Lou. *Adv. Mater.*, 2013, 25 , 2909.
- [S8] Y. Wang, L. Zhang, Y. Wu, Y. Zhong, Y. Hu, X.W. Lou, *Chem. Commun.*, 2015, 51, 6921.