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Large-scale fabrication of graphene-wrapped FeF₃ nanocrystals as

cathode material for lithium ion batteries

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Experiment Section

Preparation of the precursor Fe₃O₄/G

Fe₃O₄/G was prepared by a one-pot solvothermal reaction referring to the literature.¹ In a typical ⁵ procedure, graphene oxide (GO, 100 mg), which was prepared by a modified Hummers' method, was ultrasonically dispersed in 50 mL ethylene glycol (EG) to get a brown suspension. Then, a certain amount of FeCl₃·6H₂O (0.2 g, 0.5 g and 0.8 g) was dissolved in the GO solution by stirring constantly for 30 min. Afterwards, 3.6 g of NaAc and 5 mL of polyethylene glycol (PEG-600) were added, followed by sonicating for 2 h. The mixture was then transferred to a stainless steel autoclave and ¹⁰ heated at 200 °C for 12 h. Subsequently, the suspension was centrifuged and washed with ethanol and distilled water several times and was dried at 60 °C in a vacuum oven. (Fe₃O₄ was prepared by the same procedure except that no GO was added) Finally, the dry powder was heat-treated at 500 °C for 2 h under 95%Ar/5%H₂ atmosphere. After being cooled to room temperature (RT), a black fluffy powder was obtained.

15 Preparation of FeF₃/G nanocomposites

0.2 g of the as-prepared Fe₃O₄/G nanocomposites was wrapped by filter paper. Then the wrapped powders were put on a Teflon cylinder, which is higher than the level of HF solution. Afterwards, the cylinder with the wrapped powders was transferred in a 90 mL Teflon-lined autoclave with 30 mL HF solution (48 wt%) and sealed by a stainless-steel shell. (Note that HF solution is highly corrosive and ²⁰ must be manipulated very carefully.) The reaction system was kept at 120 °C for 3 h (or other designed time). After naturally cooled to RT, the wrapped powders (FeF₃·3H₂O/G) were taken out and dried at 60 °C for 20 h in a vacuum oven. The final product (FeF₃/G) was obtained after heat-treating FeF₃·3H₂O/G at 200 °C for 4 h in ambient Ar atmosphere. Bare-FeF₃, MnF₂ and CoF₂ were fabricated by the same procedure from Fe₃O₄, Mn₃O₄ and Co₃O₄, respectively.

For comparison, FeF₃ was also fabricated by precipitation method in solution.² Firstly, β -FeF₃·3H₂O particles, 8.11 g of iron (III) chloride (FeCl₃, Sigma-Aldrich, \geq 98%) was dissolved in 10 mL of ethylene glycol (EG) to form a clear yellowish solution which was then poured into HF solution (48 wt%, 20 mL) under magnetic stirring at RT. A large amount of pink precipitates formed instantly after ⁵ 10 mL absolute ethanol was introduced into the mixture solution. The precipitates (powders) were washed with ethanol and deionized water for several times. After centrifugation, the powders were dried at 60 °C overnight in a vacuum oven. Then the powders were heat-treated at 200 °C for 4 h in a tube furnace under a continuous high-purity Ar gas flow.

Physical characterization

¹⁰ X-ray diffraction (XRD) patterns in the 2θ range of 10-90° were obtained by employing a Siemens D500 diffractometer with Cu Kα radiation at a scan rate of 0.02° s⁻¹. To confirm the content of graphene in the as-preapred FeF₃/G nanocomposites, thermogravimetric (TG, Q50) analysis was employed from RT to 650 °C under an air ventilation of 40 mL min⁻¹ at a heating rate of 5 °C min⁻¹. The morphology of the precursor and FeF₃/G nanocomposites was examined with a Philips XL30 FEG is field-emission scanning electron microscope (FESEM), while the morphology of CoF₂ and MnF₂ was examined by JEOL-820 SEM. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained from the equipment of JEOL JEM 2100F operated at 200 kV. EDX mapping was achieved together with STEM in a large number of crystals. The morphology of FeF₃/G after 100 discharge-charge cycles was also examined by TEM, after the experimental Li-ion cells were ²⁰ disassembled in an Ar-filled glove box, rinsed in dimethyl carbonate (DMC) and washed with ethanol

several times.

Electrochemical performance evaluation

The active material (FeF₃/G or FeF₃), carbon black and poly(vinylidene fluoride) (PVDF) binder with a mass ratio 80:10:10 were dispersed in N-methylpyrrolidone solution. The resultant slurry was then

uniformly coated on an Al foil current collector and dried overnight under vacuum at 100 °C. After dried in vacuum oven, the Al foil with active material was punched into circular discs (1.6 cm^2). The net mass of active material on each disc is about 3.68 mg. So, the active material loading was about 2.3 mg cm⁻². Coin cells (CR2032) were assembled with lithium metal foil as counter-electrode, Celgard ^s 2400 membrane as the separator and LiPF₆ (1 M) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 vol %) as the electrolyte. Both cyclic voltammogrtams (CV) and impedance measurements were performed on a Zahner IM6 electrochemical workstation. CV curves were recorded at RT between 1.5 and 4.5 V (vs. Li⁺/Li) at a scan rate of 0.2 mV s⁻¹. Galvanostatic electrochemical experiments were carried out (Arbin Instruments, College Station, TX) between 1.5 and 4.5 V vs. Li⁺/Li at RT, at ¹⁰ different current densities for rate performance and at 20.8 and 208 mA g⁻¹ for cycling performance. Electrochemical impedance spectra (EIS) were obtained after a 2 h rest by applying an ac voltage of 2.5 mV amplitude over the frequency range from 100 kHz to 10 mHz at different states, such as after the initial discharge and the 100th cycle. The EIS parameters were simulated by ZSIMPWIN software.



¹⁵ Fig. S1 XRD patterns of (a) Co_3O_4 and (b) CoF_2 , respectively; SEM images of (c) Co_3O_4 and (d) CoF_2 , respectively.



Fig. S2 XRD patterns of (a) Mn_3O_4 and (b) MnF_2 , respectively; SEM images of (c) Mn_3O_4 and (d) MnF_2 , respectively.



⁵ Fig. S3 SEM image of FeF₃ fabricated by precipation method in solution.



Fig. S4 (a) SEM image of bare FeF₃ fabricated by vapour-solid method (b) Magnified SEM image of (a).



Fig. S5 TG curves of Fe_3O_4/G with different contents of graphene (a) $87.7\%Fe_3O_4/12.3\%G$ (b) $58.9\%Fe_3O_4/41.1\%G$.



⁵ Fig. S6 SEM images of FeF₃/G fabricated by vapour-solid method: (a) 91.2%FeF₃/8.8%G, (b) 67.7%FeF₃/32.3%G; Cycling performance of FeF₃/G fabricated by vapour-solid method: (a) 91.2%FeF₃/8.8%G (b) 67.7%FeF₃/32.3%G.

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