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# A corn-inspired structure design for an iron oxide fiber/reduced graphene oxide composite as a high-performance anode material for Li-ion batteries†

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In this paper, we successfully synthesized iron oxide (Fe<sub>2</sub>O<sub>3</sub>) fiber/reduced graphene oxide (rGO) composites with a "corn" structure by an electrospinning technique assisted by annealing treatment and a far infrared reduction process. The special structure consists of Fe<sub>2</sub>O<sub>3</sub> fibers as the "corn cob" completely protected by multilayer rGO as the "sepal". Natural void space between the Fe<sub>2</sub>O<sub>3</sub> fibers and rGO allows for the expansion of Fe<sub>2</sub>O<sub>3</sub> upon lithiation; the good surface area and unblocked channels in the Fe<sub>2</sub>O<sub>3</sub> fiber facilitates fast diffusion of Li<sup>+</sup>. An electrode with such structure shows excellent capacity (1085.2 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup>), and cycle life (407.8 mA h g<sup>-1</sup> at 5 A g<sup>-1</sup> for 1500 cycles with good coulombic efficiency). This is the longest cycle life for Fe<sub>2</sub>O<sub>3</sub>-based anode materials with excellent rate capability (e.g., >400 mA h g<sup>-1</sup> at 5 A h g<sup>-1</sup>). In addition to Fe<sub>2</sub>O<sub>3</sub>, this "corn" structure can also be applied to other high capacity anode materials for next generation Li-ion batteries to improve cycle life and coulombic efficiency.

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## 1. Introduction

Recently, lithium-ion batteries (LIBs) have attracted much attention due to the rapid development of portable electronic devices, electric vehicles (EVs), and hybrid electric vehicles (HEVs).<sup>1–3</sup> At present, most commonly used anode materials for commercial LIBs are based on graphite. However, graphite suffers from an inherently low theoretical charge storage capacity (372 mA h g<sup>-1</sup>) and often operates at significantly low rates (typically, <1C) that in turn limits the achievable power densities.<sup>4,5</sup> Therefore, the design and synthesis of new anode materials is necessary to offer the promise of high performance lithium-ion batteries with high efficiency, great energy density and long-lasting duration to meet various energy storage demands. For the purpose, nanostructure transition metal oxides have received great interest in lithium-ion batteries, and scientists have made great efforts to explore alternative anode materials with high capacity from them, such as SnO<sub>2</sub>, FeO<sub>x</sub>, CoO<sub>x</sub>, MnO<sub>x</sub>, CoFe<sub>2</sub>O<sub>4</sub>, and Co<sub>3</sub>V<sub>2</sub>O<sub>8</sub>.<sup>6–13</sup> Among these anode materials investigated for LIBs, Fe<sub>2</sub>O<sub>3</sub> have been widely studied

as anode materials due to their high theoretical capacity value (1070 mA h g<sup>-1</sup>), low cost, natural abundance, nontoxicity and the highest electrical conductivity (~2 × 10<sup>-4</sup> S m<sup>-1</sup>) than other metal oxides.<sup>14–16</sup>

However, it remains great challenges in the application of Fe<sub>2</sub>O<sub>3</sub> to commercial LIBs, especially the obstacles of poor cycling stability and inferior rate capability. The large volume expansion and severe collapse occurs in the host matrix of Fe<sub>2</sub>O<sub>3</sub> during the cycling processes give rise to pulverization, which results in the breakdown of electrical connection of these anode materials from current collectors and rapid capacity fading upon cycling. To overcome these drawbacks, several strategies have been employed such as Fe<sub>2</sub>O<sub>3</sub> nanotubes, nanorods/rGO, nanoropes/rGO, hollow nanobarrels, hollow nanoparticles/rGO, hollow spheres, and hollow-structured tubular nanostructures.<sup>17–28</sup> Chaudhari *et al.*<sup>26</sup> reported a hollow-structured α-Fe<sub>2</sub>O<sub>3</sub> nanofibers electrode with a reversible capacity of 1293 mA h g<sup>-1</sup> at a current density of 60 mA g<sup>-1</sup>. Fe<sub>2</sub>O<sub>3</sub> hollow nanoparticles/N-doped graphene aerogels were prepared by Liu *et al.*,<sup>27</sup> and the grapheme/Fe<sub>2</sub>O<sub>3</sub> aerogels exhibit high rate capability and excellent cyclic stability (729 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup> for 300 cycles). Zhu *et al.*<sup>28</sup> reported the graphene oxide/Fe<sub>2</sub>O<sub>3</sub> composite exhibiting 1027 mA h g<sup>-1</sup> at a current density of 100 mA h g<sup>-1</sup> after 50 cycles. These results suggested that incorporating nanoscale iron oxide into rGO has a great beneficial impact on the electrochemical performance of Li-ion batteries.

More recently, some core-shell nanostructure materials, which was originally used in semiconductors, have been

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imported to the field of Li-ion batteries. Some efforts were made to investigate Li-ion battery materials with core-shell nanostructure,<sup>29–33</sup> such as Si, alloys, and transition metal oxides with carbon shells, and graphene was also introduced as a shell material. For example, Yang *et al.* have been fabricated graphene-wrapped metal oxides particles by electrostatic self-assembly. This unique core-shell structure has suppressed the aggregation of oxide nanoparticles, accommodated the volume change during the discharge-charge processes, and kept the high electrical conductivity of the electrode. The obtained graphene-wrapped  $\text{Co}_3\text{O}_4$  hybrids delivered very high reversible capacity of about  $1100 \text{ mA h g}^{-1}$  in the initial 10 cycles and  $1000 \text{ mA h g}^{-1}$  after 130 cycles at  $74 \text{ mA g}^{-1}$ . However, further exploration and rational fabrication of iron oxide composite electrode materials with high-rate performance and long cycle life will have a significant impact on its practical utilization in Li-ion batteries.

Herein, we fabricated a novel core-shell structure  $\text{Fe}_2\text{O}_3$  fiber/rGO anode materials by electrostatic self-assembly and the negatively charged graphene layers were wrapped on the positively charged  $\text{Fe}_2\text{O}_3$  nanofiber. As shown in Fig. 1, the core-shell structure of  $\text{Fe}_2\text{O}_3$  fiber/rGO composite is very similar with that of corn;  $\text{Fe}_2\text{O}_3$  nanofiber can be regarded as the “corn cob”, and the wrapping multilayer reduced graphene oxide as the “sepal”. This unique composite with corn-like structure has several advantages for LIB anodes. First, the rGO layers are a stable framework, and the void space between the  $\text{Fe}_2\text{O}_3$  fiber and the rGO layers allows for the  $\text{Fe}_2\text{O}_3$  to expand upon lithiation. Second, the rGO layers prevent the electrolyte from reaching the  $\text{Fe}_2\text{O}_3$  surface inside the rGO layers completely, and lithiation of the  $\text{Fe}_2\text{O}_3$  occurs by Li diffusion through the rGO into the  $\text{Fe}_2\text{O}_3$  fiber. Third, the rGO layers are both electronically and ionically conducting, which allows for good kinetics in  $\text{Fe}_2\text{O}_3$  fiber/rGO anode. Due to the cohesiveness and good conductivity of rGO,  $\text{Fe}_2\text{O}_3$ /rGO anode is applied for LIBs without binder and conductive agent as dopant. As a result, the synergistic effect between rGO and  $\text{Fe}_2\text{O}_3$  fiber could reduce the initial capacity loss as well as improve the high rate capability ( $1085.2 \text{ mA h g}^{-1}$  at  $0.1 \text{ A g}^{-1}$ ) and cyclability ( $407.8 \text{ mA h g}^{-1}$  at  $5 \text{ A g}^{-1}$  for 1500 cycles). This is the longest cycle life for the

$\text{Fe}_2\text{O}_3$ -based anode materials with excellent rate capability (*e.g.*,  $>400 \text{ mA h g}^{-1}$  at  $5 \text{ A h g}^{-1}$ ).

## 2. Experimental section

### 2.1 Preparation of $\text{Fe}_2\text{O}_3$ fibers

$\text{Fe}_2\text{O}_3$  fibers were synthesized by electrospinning technique assisted with anneal treatment. In a typical experiment, 2.4 g poly(vinyl pyrrolidone) (PVP,  $M_w = 1\,300\,000$ , Sigma) was dissolved in 15 ml *N,N*-dimethylformamide (DMF, AR, Sigma) and 15 ml ethanol solution, magnetic stirring for 3 h. Then, 2.4, 4.8, or 7.2 g ferric chloride (AR, Aladdin, China) was added to the solution and then vigorous stirring for 2 h, and  $\text{FeCl}_3$  concentrations to the whole solution are 6, 12 and 18 wt%, respectively. The as-prepared samples were designated as PVP/ $\text{FeCl}_3$  (I), PVP/ $\text{FeCl}_3$  (II) and PVP/ $\text{FeCl}_3$  (III), respectively. Next, the precursor solution was loaded into a plastic syringe that was equipped with a stainless steel needle of 0.8 mm in diameter and electrospun at a DC voltage of 15 kV and a flow rate of  $0.6 \text{ ml h}^{-1}$ . The electrospun fibers were collected on aluminum foil and the distance between the needle and collector was 15 cm. The as-electrospun PVP/ $\text{FeCl}_3$  composite fibers were placed in a vacuum oven for 12 h at room temperature in order to remove the solvent residuals, and calcined for 3 h in air at  $600 \text{ }^\circ\text{C}$  (the heating rate,  $1 \text{ }^\circ\text{C min}^{-1}$ ) in a tube furnace, respectively. Finally the  $\text{Fe}_2\text{O}_3$  fibers obtained were designated as  $\text{Fe}_2\text{O}_3$  (I),  $\text{Fe}_2\text{O}_3$  (II) and  $\text{Fe}_2\text{O}_3$  (III), respectively.

### 2.2 Preparation of $\text{Fe}_2\text{O}_3$ /rGO composites

Graphene oxide was synthesized from natural graphite by a modified Hummers method described in detail previously.<sup>34</sup> To prepare  $\text{Fe}_2\text{O}_3$ /rGO composites, a homogeneous suspension of graphene oxide (GO) and  $\text{Fe}_2\text{O}_3$  fibers was carefully prepared. A total of 20 ml of alcoholic GO ( $1 \text{ mg ml}^{-1}$ ) was sonicated for 30 min to form a stable solution. Subsequently, 0.01 g  $\text{Fe}_2\text{O}_3$  fibers was mixed with alcoholic GO and sonicated for another 30 min to form a homogeneous dispersion. Standing for 24 h, the  $\text{Fe}_2\text{O}_3$ /GO composites were collected by centrifugation. The collecting solid was dried for 24 h by vacuum at  $60 \text{ }^\circ\text{C}$ . Finally, the  $\text{Fe}_2\text{O}_3$ /GO composites were put in home-use

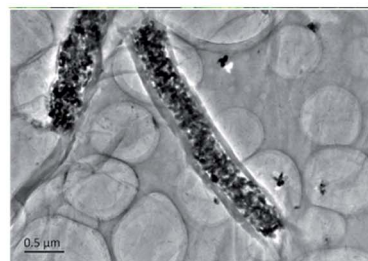
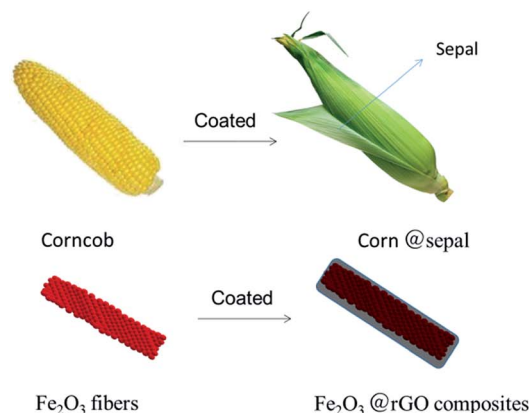


Fig. 1 Schematic of the materials design.



convection oven and irradiated by far infrared light for 5 min, in which the mixture color changed from bright red to dark red. Then Fe<sub>2</sub>O<sub>3</sub> (I)/rGO, Fe<sub>2</sub>O<sub>3</sub> (II)/rGO and Fe<sub>2</sub>O<sub>3</sub> (III)/rGO Fe<sub>2</sub>O<sub>3</sub>/rGO composites were obtained.

### 2.3 Characterization

The morphology and diameter of samples were characterized using scanning electron microscope (SEM, FEI Quanta200F) and transmission electron microscope (TEM, FEI Tecnai G2 F20, 200 kV). The crystalline structural characterization of the all samples was carried out by X-ray diffraction (XRD) using a diffractometer (Bruker D8 Focus X-ray diffractometer), and the diffraction patterns were recorded at room temperature in the  $2\theta$  range between 5° and 80°. The chemical structure of fibers was conducted with a Fourier transform infrared (FT-IR) reflection spectroscopy (NICOLET 380, Wisconsin, USA). Weight loss behavior was tested by thermogravimetric (TG) analysis (TGA/DSC 3+, Mettler Toledo, Zurich, Switzerland) (air, 10 °C min<sup>-1</sup>).

### 2.4 Electrochemical performance evaluation

The electrochemical performance of the Fe<sub>2</sub>O<sub>3</sub> fibers and Fe<sub>2</sub>O<sub>3</sub>/rGO composites were analyzed by constructing a 2025-type coin cell. The active material and a certain amount of EtOH were mixed to prepare slurry, and the resulting slurry was attached onto copper foils. The anodes were dried in a vacuum furnace at 65 °C for 24 h. The mass loading of active materials per electrode is about 0.4 mg cm<sup>-2</sup>, in which the mass of Fe<sub>2</sub>O<sub>3</sub>/rGO composites for the working electrodes was obtained by a Sartorius scale (0.01 mg) and the area of copper sheets were about 2 cm<sup>2</sup>. The cells were assembled in a high purity argon atmosphere inside a glove box (Mbraun lab Master130, Germany). Lithium ribbon (0.3 mm thick) was used as the counter electrode and Celgard® 2325 was used as the separator and the

electrolyte was a solution of 1 M LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC) : dimethyl carbonate (DMC) (1 : 1 vol%). Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed using electrochemical workstation (PARSTAT 2273, Princeton, USA) at 0.1 mV s<sup>-1</sup> scan rate between 0.0 and 3.0 V. Charge and discharge were conducted using an a multi-channel battery test system (NEWARE, Shenzhen, China) at several different current densities between cutoff potentials of 0.02 and 3.00 V. The capacities were calculated on the basis of the weight of Fe<sub>2</sub>O<sub>3</sub> fibers or Fe<sub>2</sub>O<sub>3</sub>/rGO composites.

## 3. Results and discussion

The fabrication process of the flexible Fe<sub>2</sub>O<sub>3</sub> fiber/rGO composite is illustrated in Fig. 2 and S1 (ESI†). Typically, a homogeneous viscous solutions with FeCl<sub>3</sub> dissolved in poly(vinyl pyrrolidone) was electrospun into fibers, following with annealing process at 600 °C in air. Then, the Fe<sub>2</sub>O<sub>3</sub> fibers were sonicated with alcoholic GO solution and formed a homogeneous dispersion; during the process, the negatively charged graphene oxide was uniformly wrapped on positively charged Fe<sub>2</sub>O<sub>3</sub> nanofiber. In the next step, the Fe<sub>2</sub>O<sub>3</sub>/GO composites were collected by centrifugalization. Finally, the Fe<sub>2</sub>O<sub>3</sub>/GO composites was reduced to Fe<sub>2</sub>O<sub>3</sub>/rGO by the thermal decomposition of graphene oxide (GO) in air at a relatively low temperature of ~200 °C in under 5 minutes through far infrared (FIR) irradiation *via* a home-used convection oven.

To understand the influence of FeCl<sub>3</sub> concentration on the PVP/FeCl<sub>3</sub> fibers, three different weights PVP to FeCl<sub>3</sub> in DMF solution (FeCl<sub>3</sub> contents of 6, 12 and 18 wt%, respectively) were applied by electrospinning processes. The as-prepared fibers were designated as PVP/FeCl<sub>3</sub> (I), PVP/FeCl<sub>3</sub> (II) and PVP/FeCl<sub>3</sub> (III), respectively. Fig. 3 shows the SEM images of PVP/FeCl<sub>3</sub>

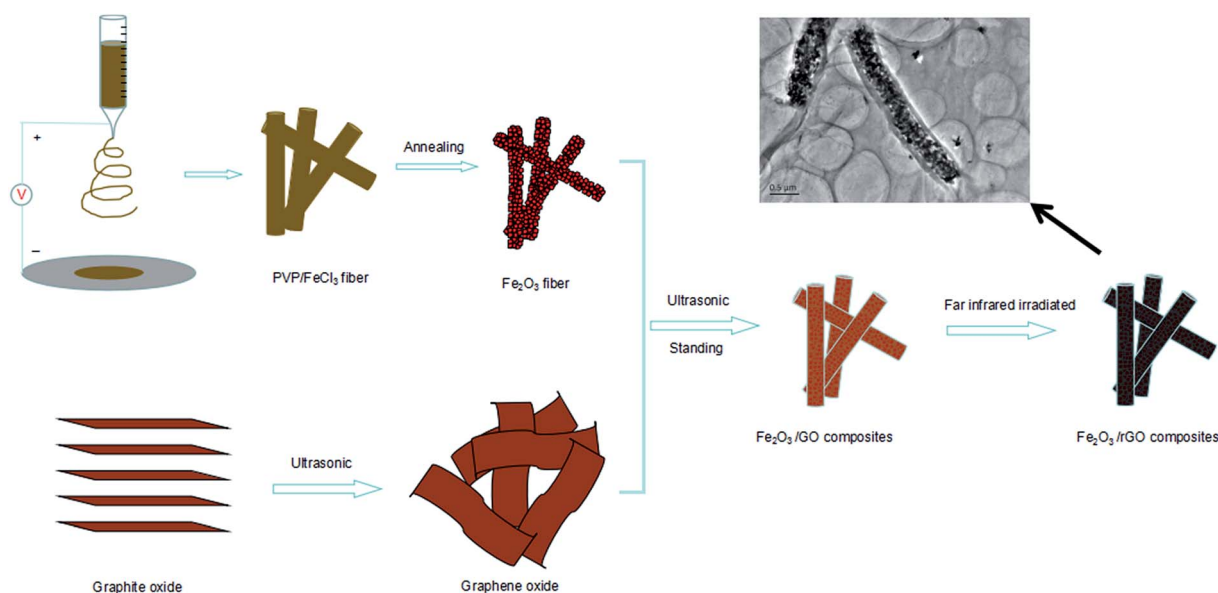


Fig. 2 Schematic diagram for the fabrication of Fe<sub>2</sub>O<sub>3</sub>/rGO composites.



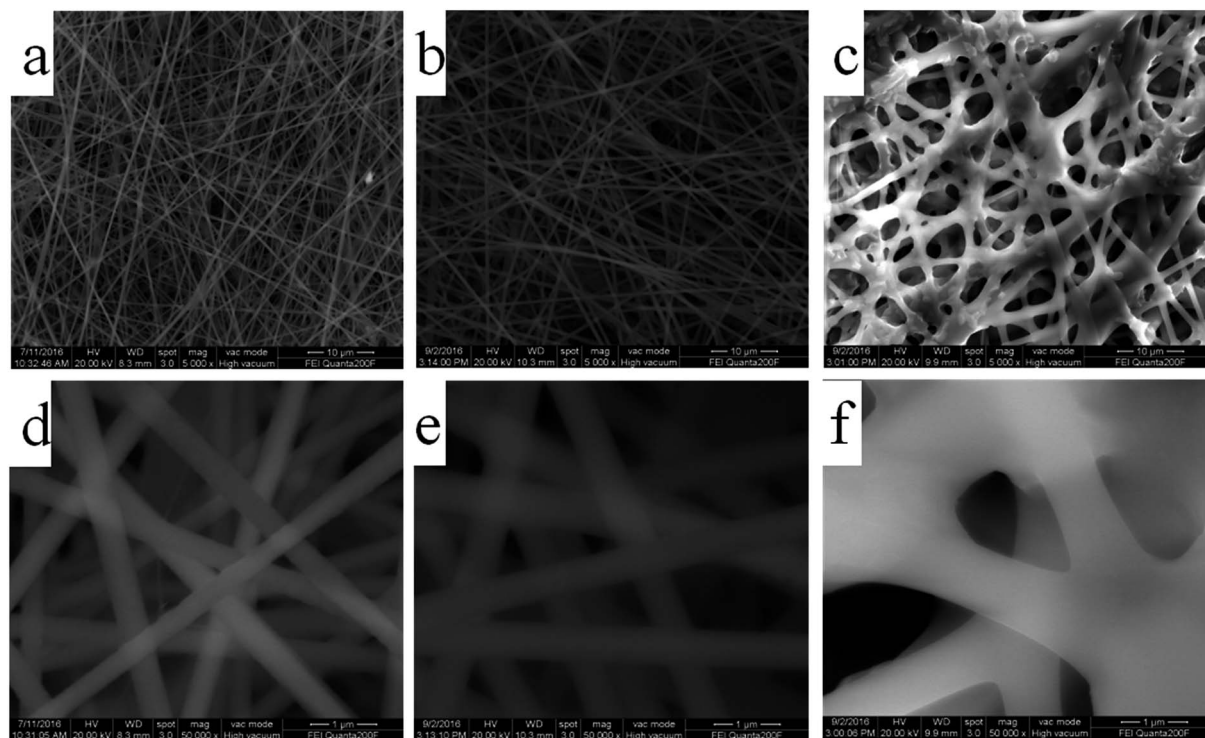


Fig. 3 SEM images of (a and d) PVP/FeCl<sub>3</sub> (I), (b and e) PVP/FeCl<sub>3</sub> (II) and (c and f) PVP/FeCl<sub>3</sub> (III).

fibers with different FeCl<sub>3</sub> contents. All electrospinning PVP/FeCl<sub>3</sub> fibers are straight and exhibit an interconnected pore structure and homogeneously distributed diameters. The fiber diameter increases from ~400 nm to ~1500 nm with the increasing of the contents of FeCl<sub>3</sub> increased from 6 to 18 wt%. However, PVP/FeCl<sub>3</sub> (III) shows junction between single fiber and the larger size. This phenomenon can be explained that the fibers have a lower viscosity at higher concentration of FeCl<sub>3</sub> which results in the junctions morphology.<sup>35</sup>

To obtain the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> fibers with good crystallinity, the FTIR spectra and X-ray diffraction spectra have been analyzed by calcining under different temperatures. Fig. 4a shows the FTIR spectra of the PVP/FeCl<sub>3</sub> fibers and calcined in air at 200–800 °C for 3 h. There are two peaks appearing at 463 and 551 cm<sup>-1</sup> which are assigned to the Fe–O vibration of the Fe<sub>2</sub>O<sub>3</sub> fibers from 400 to 800 °C. Due to the decomposition of PVP, the peaks at about 1621 cm<sup>-1</sup> and 3369 cm<sup>-1</sup>, corresponding to –N–C(=O)–, –O–H, respectively, disappear upon calcination at 600 °C, which indicates the formation of pure Fe<sub>2</sub>O<sub>3</sub>. Fig. 4b shows the X-ray diffraction patterns of the PVP/FeCl<sub>3</sub> fibers calcined in air at 200–800 °C for 3 h. The observed diffraction peaks at  $2\theta$  (°) = 24.14, 33.16, 35.62, 40.86, 49.46, 54.07, 57.61, 62.43, 63.99, 71.96 and 75.45 correspond to the planes of (012), (104), (110), (113), (024), (116), (018), (214), (300), (1010) and (220), respectively, which all match with the rhombohedral phase of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS 33-0664).<sup>26,27</sup> The sharp diffraction peaks clearly indicate the good crystallinity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase. The diffraction peaks of the Fe<sub>2</sub>O<sub>3</sub> fibers were observed above 400 °C in sintering processes, and enhanced upon calcinations at 600 °C, which was in accordance with the FTIR results.

Fig. 5 show the SEM and TEM images of Fe<sub>2</sub>O<sub>3</sub> (I), Fe<sub>2</sub>O<sub>3</sub> (II) and Fe<sub>2</sub>O<sub>3</sub> (III) after heat treatment at 600 °C. As can be seen from the figures, the average diameter of these fibers greatly shrank because of the weight loss resulting from the removal of PVP after heat treatment. The average diameters of Fe<sub>2</sub>O<sub>3</sub> (I), Fe<sub>2</sub>O<sub>3</sub> (II) and Fe<sub>2</sub>O<sub>3</sub> (III) fibers were found to be approximately 200, 400, 800 nm, respectively. It is obvious in Fig. 5 that corn-cob-like fibers were formed through the above approach and their surface became rough and porous due to some decomposition of the organic components.

Based on these Fe<sub>2</sub>O<sub>3</sub> fibers obtained, the Fe<sub>2</sub>O<sub>3</sub>/rGO composites have been prepared after a far infrared (FIR) irradiation process. To prove the reduction effect of GO in the composite, the Raman spectrum of the Fe<sub>2</sub>O<sub>3</sub>/rGO samples before and after reduction was shown in Fig. S2.† It is found that two broad peaks locate at 1345 and 1589 cm<sup>-1</sup>, which correspond to the A<sub>1g</sub> vibration mode of the disordered carbon (D-bond) and the E<sub>2g</sub> vibration mode of the ordered graphitic carbon (G-bond), respectively. The intensity ratio value of I<sub>D</sub>/I<sub>G</sub> for the samples increase from 0.92 to 0.97, which shows the graphene oxide has been reduced to rGO by far infrared irradiation reduction process. The higher I<sub>D</sub>/I<sub>G</sub> value indicates more defects and edges in the reduced graphene structure which may results in more porous structure. Interestingly, the D peaks of in the nanocomposites show the slightly red-shift, revealing the stronger interactions between Fe<sub>2</sub>O<sub>3</sub> nanofiber and graphene after reduction process. This phenomenon usually derives from the dielectric confinement effect of transition metal oxide on graphene.<sup>36,37</sup> Further, X-ray photoelectron spectroscopy (XPS) measurements also provide direct evidence of the reduction of



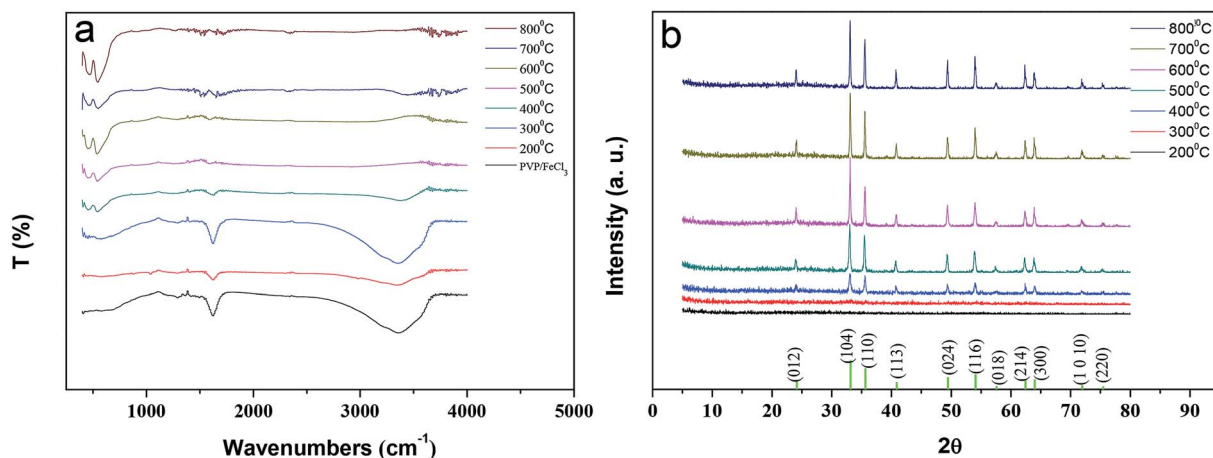


Fig. 4 (a) FTIR spectra of PVP/FeCl<sub>3</sub> (II) fibers and calcined in air at 200–800 °C; (b) X-ray diffraction patterns of the PVP/FeCl<sub>3</sub> (II) fibers calcined in air at 200–800 °C for 3 h.

GO under FIR irradiation and chemical state of Fe<sub>2</sub>O<sub>3</sub> in composites, as shown in Fig. S3.† The survey scan spectrum displays the peaks of iron, oxygen and carbon, showing a high purity of as-prepared Fe<sub>2</sub>O<sub>3</sub>/rGO composites. The C 1s XPS spectra of Fe<sub>2</sub>O<sub>3</sub>/rGO composites indicates that, for Fe<sub>2</sub>O<sub>3</sub>/GO samples, four different peaks centered at 285.0, 286.8, and 288.1 eV were observed, corresponding to the presence of C–C/C=C in aromatic rings, C–O (epoxy and alkoxy), C=O groups, respectively. After FIR irradiation reduction treatment, the intensities of all the C 1s peaks of the carbons binding to

oxygen, decrease obviously. It suggests that the GO have been reduced to rGO in a certain degree. And for the XPS spectra of the Fe 2p for Fe<sub>2</sub>O<sub>3</sub>/GO composites, binding energies of Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> are 711.4 eV and 724.9 eV respectively for Fe<sub>2</sub>O<sub>3</sub>/GO composites before and after reduction, in good agreement with crystalline Fe<sub>2</sub>O<sub>3</sub>. The satellite peak locating at 719.9 eV between the Fe 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks was assigned to its purely trivalent nature, implying that the oxidation state of Fe element in the composites were of Fe<sup>3+</sup> only.<sup>38</sup> Furthermore, the weight content of reduced graphene oxide can be obtained by comparing with

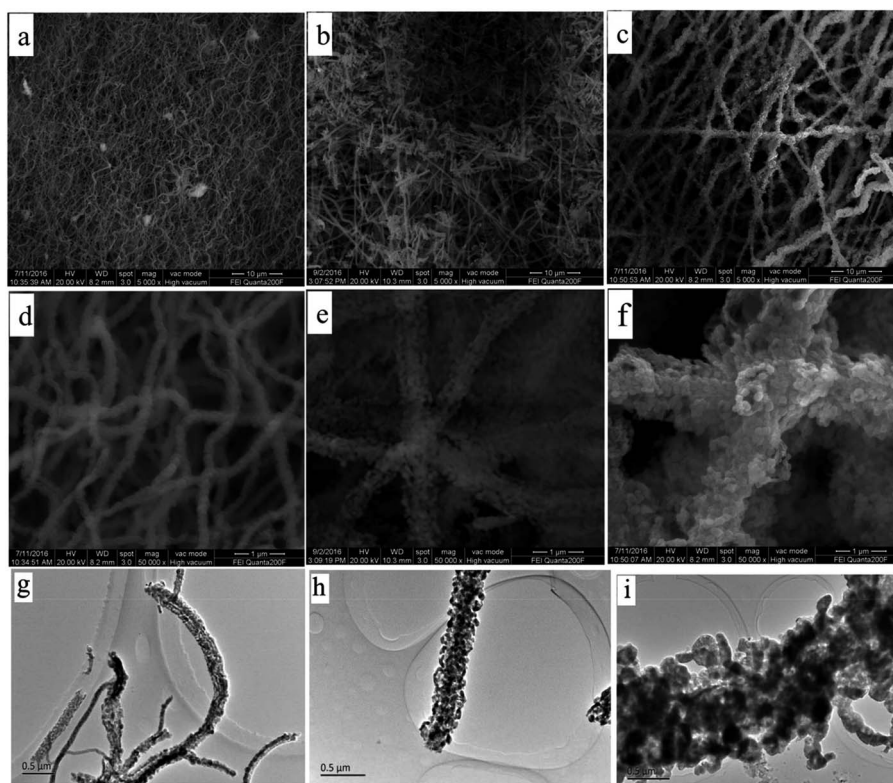


Fig. 5 SEM and TEM images of (a, d and g) Fe<sub>2</sub>O<sub>3</sub> (I), (b, e and h) Fe<sub>2</sub>O<sub>3</sub> (II) and (c, f and i) Fe<sub>2</sub>O<sub>3</sub> (III).



the thermal weight loss behaviors between pure  $\text{Fe}_2\text{O}_3$  fibers and  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites, as shown in Fig. S4.† For the sample of  $\text{Fe}_2\text{O}_3$  fibers, it can be seen that the weight losses could be attributed to the evaporation of moisture and crystal water below 200 °C in the curves. With the temperature increasing, there is no weight loss for the sample of pure  $\text{Fe}_2\text{O}_3$  fibers, which shows that  $\text{Fe}_2\text{O}_3$  crystalline phase has good thermal stability. Instead, there are significant weight loss above 200 °C in the curve for the samples of  $\text{Fe}_2\text{O}_3$  fibers/rGO composites: the weight loss between 200 to 300 °C corresponds to the further reduction process of reduced graphene oxide; the weight loss between 300 °C and 500 °C could be attributed to the complete combustion of graphene; and no further weight loss above 500 °C indicated the pure  $\text{Fe}_2\text{O}_3$ . Therefore, the weight percentage of  $\text{Fe}_2\text{O}_3$  in the composite samples can be estimated by about 50%.

To further investigate the morphological structure of the as-prepared  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites, the SEM and TEM images were shown in Fig. 6. A typical morphology of  $\text{Fe}_2\text{O}_3/\text{rGO}$  hybrid fibers and porous structure have been clearly observed in Fig. 6a and b. The elemental mapping (Fig. 6c) showed that the  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites were uniformly distributed with carbon, oxygen, and iron. Fig. 6d demonstrates  $\text{Fe}_2\text{O}_3$  fiber was uniformly coated by graphene oxide, which looks like a corn, even *via* a reduction of far infrared light irradiation (Fig. 6e). It is obvious that the surface of  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites has

a smooth film, which indicates  $\text{Fe}_2\text{O}_3$  was coated in the rGO sheets. This phenomenon can be explained as follows: the oxygen-containing functional groups (hydroxyl, carbonyl and carboxyl groups) on the GO make it negatively-charged and they can act as anchor sites that interact strongly with the covered species;<sup>39</sup> when treating the mix solution of negatively charged GO and positively charged  $\text{Fe}_2\text{O}_3$  fibers with ultrasound, the positively-charged  $\text{Fe}_2\text{O}_3$  fiber may be absorbed on the negatively-charged surface of GO, which may promote the coating of  $\text{Fe}_2\text{O}_3$  fibers by GO. A regular diffraction spot ring is observed from the selected-area electron diffraction (SAED) pattern (Fig. 6d and e, inset). The SAED pattern of rGO (Fig. 6d) shows the ring pattern obviously, and Fig. 6e shows the typical hexagonally ordered lattice of carbon in graphene, which indicated the  $\text{Fe}_2\text{O}_3/\text{GO}$  was transformed into  $\text{Fe}_2\text{O}_3/\text{rGO}$  completely. In addition, the reduction effect is also confirmed by XRD patterns (Fig. 6f). As shown in Fig. 6f, the sharp X-ray diffraction peak of GO (at  $2\theta \approx 10^\circ$ ) appears in  $\text{Fe}_2\text{O}_3/\text{GO}$  composites before far infrared irradiation, and after far infrared irradiation, the composites obtained appear the new diffraction peak of rGO (at  $2\theta \approx 24^\circ$ ) and disappear the peak of GO (at  $2\theta \approx 10^\circ$ ), indicating the  $\text{Fe}_2\text{O}_3/\text{GO}$  was transformed into  $\text{Fe}_2\text{O}_3/\text{rGO}$  completely. In the meantime, crystalline  $\alpha\text{-Fe}_2\text{O}_3$  and graphene layers are also confirmed by XRD patterns (Fig. 6f) and HRTEM (Fig. S5†). As estimated by the HRTEM images, the lattices with a lattice fringe spacing of 0.22 nm are indexed to

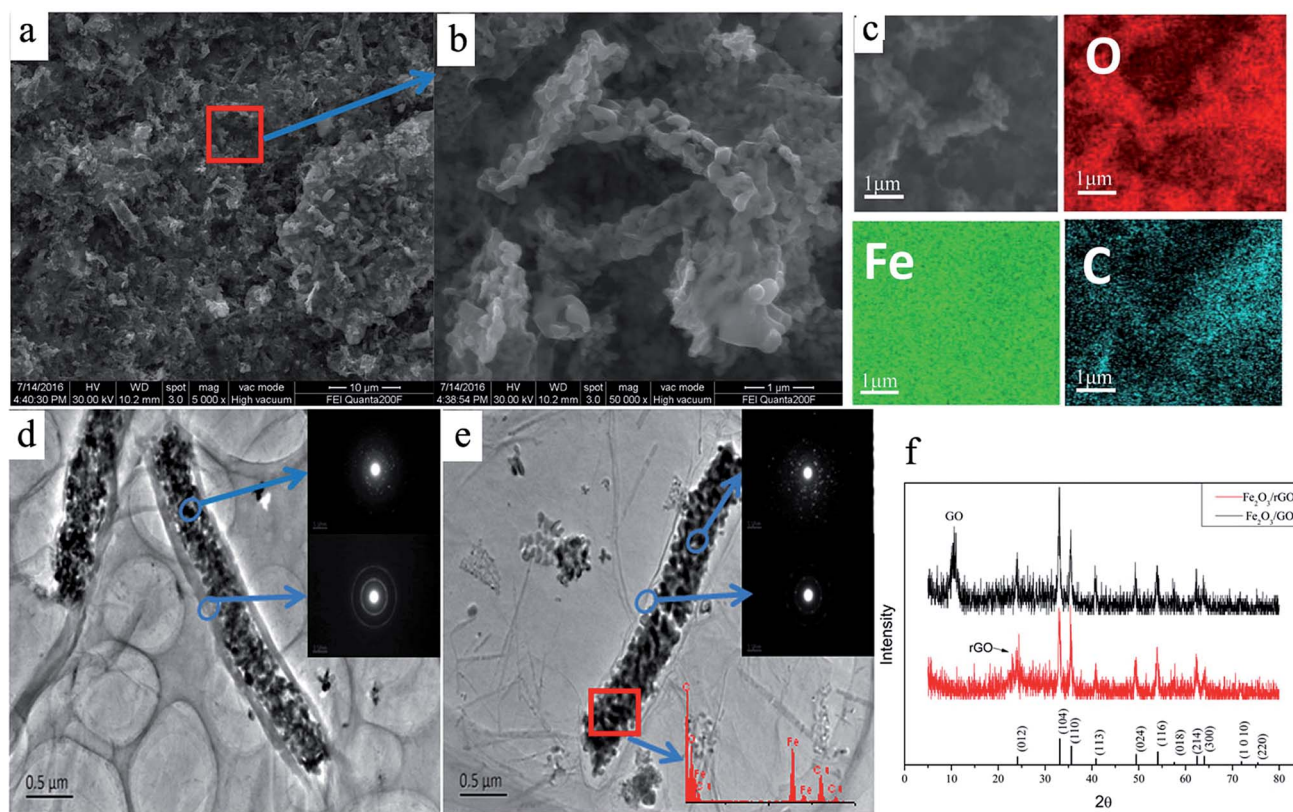


Fig. 6 (a and b) SEM images and (c) element mapping patterns of  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites; (d and e) TEM and SAED images of  $\text{Fe}_2\text{O}_3/\text{GO}$  composites and  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites; (f) X-ray diffraction patterns of the  $\text{Fe}_2\text{O}_3/\text{GO}$  composites and  $\text{Fe}_2\text{O}_3/\text{rGO}$  composites after far infrared light irradiation.



the (113) plane of  $\alpha$ - $\text{Fe}_2\text{O}_3$ , and the thickness of rGO layer is about 3 nm.

Subsequently, the porous characteristics of the  $\text{Fe}_2\text{O}_3$  fiber/rGO composite were investigated by the nitrogen isothermal adsorption–desorption measurement. As displayed in Fig. S6,<sup>†</sup> the pore size distribution of the  $\text{Fe}_2\text{O}_3$  fiber/rGO composite is almost consistent with pure  $\text{Fe}_2\text{O}_3$  nanofiber, which give the evidence that the inside channels in  $\text{Fe}_2\text{O}_3$  fiber remained unblocked after graphene sheets wrapping. The BET specific surface area of  $\text{Fe}_2\text{O}_3$  fiber/rGO composites was estimated as  $150.9 \text{ m}^2 \text{ g}^{-1}$  from the result of nitrogen adsorption data, and a more than 43% increase in specific surface area is found by comparing with pure  $\text{Fe}_2\text{O}_3$  nanofiber. The major increase of the specific surface area can be attributed to the wrapped graphene nanosheets with relatively high specific surface area. It indicates that the graphene sheets working as a robust support can effectively suppress the self-aggregation of  $\text{Fe}_2\text{O}_3$  nanofiber and thus further maintain the surface area of the  $\text{Fe}_2\text{O}_3$  fiber/rGO material. At the same time, the synergistic effect of the unblocked channels and good surface area in the  $\text{Fe}_2\text{O}_3$  fiber/rGO composite will facilitate fast diffusion of  $\text{Li}^+$  when large area of active sites was provided for the lithiation and delithiation reactions.

Therefore, the as-prepared “corn” structure materials of  $\text{Fe}_2\text{O}_3$  fiber/rGO composites with  $\text{Fe}_2\text{O}_3$  fiber as the “corn cob” and multilayer reduced graphene oxide as the “sepal” will be expected to relieve the pulverization originated from the large volume change during the charge/discharge cycles, and further improve the electronic conductivity of  $\text{Fe}_2\text{O}_3$  composites electrode, which contribute to high rate capability, and superior cyclability as Li-ion anode.

To investigate the possibility of the  $\text{Fe}_2\text{O}_3$ /rGO composites used as advanced anode materials, the coin-type Li half-cells has been assembled and their electrochemical performance were studied. The initial cyclic voltammetry (CV) curves at a scan rate of  $0.1 \text{ mV s}^{-1}$  for the first five cycles were shown in Fig. 7a. In the first scan, irreversible reduction peaks were observed at 1.57, 0.90 and 0.60–0.75 V for the  $\text{Fe}_2\text{O}_3$ /rGO, respectively. The irreversible peak of 1.57 V is attributed to the lithium intercalation into  $\text{Fe}_2\text{O}_3$  fiber:  $\text{Fe}_2\text{O}_3 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_2\text{O}_3$ , disappearing at subsequent cycles. The cathodic peak of 0.90 V was ascribed to the phenomenon that hexagonal  $\text{Li}_x\text{Fe}_2\text{O}_3$  is transformed to cubic  $\text{Li}_2\text{Fe}_2\text{O}_3$ :  $\text{Li}_x\text{Fe}_2\text{O}_3 + (2-x)\text{Li}^+ + (2-x)e^- \rightarrow \text{Li}_2\text{Fe}_2\text{O}_3$ . The strongest peak of (0.60–0.75 V) corresponds to the stepwise reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and  $\text{Fe}^0$  and the formation of the SEI layer:<sup>40</sup>  $\text{Li}_2\text{Fe}_2\text{O}_3 + 4\text{Li}^+ + 4e^- \leftrightarrow 2\text{Fe}^0 + 3\text{Li}_2\text{O}$ . The disappearance of the strongest peak in the subsequent cycle was due to the irreversible reactions induced by the formation of an SEI layer on the electrode in the first cycle. At the same time, the peaks at 1.57 V and 0.90 V disappeared indicating that lithium insertion and phase transformation from  $\text{Li}_x\text{Fe}_2\text{O}_3$  to  $\text{Li}_2\text{Fe}_2\text{O}_3$  are irreversible.<sup>41</sup> On the other hand, the two anodic peaks at 1.64 and 1.86 V in the first scan corresponded to the oxidation process of  $\text{Fe}^0$  to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .<sup>42</sup> The broad peak appear in the subsequent cycles and their intensities remains almost the same, as observed from anodic curves, indicating enhanced stability during lithiation and delithiation processes.

Fig. 7b shows the charge–discharge curves of the  $\text{Fe}_2\text{O}_3$  (I)/rGO composites anode at various cycles, which were tested at a current rate of  $100 \text{ mA g}^{-1}$  within a voltage range of 0.02–3.0 V. It is found that the  $\text{Fe}_2\text{O}_3$  (I)/rGO composite electrode exhibits discharge and charge plateaus at  $\sim 0.9$ – $0.8 \text{ V}$  and  $\sim 1.5$ – $1.9 \text{ V}$

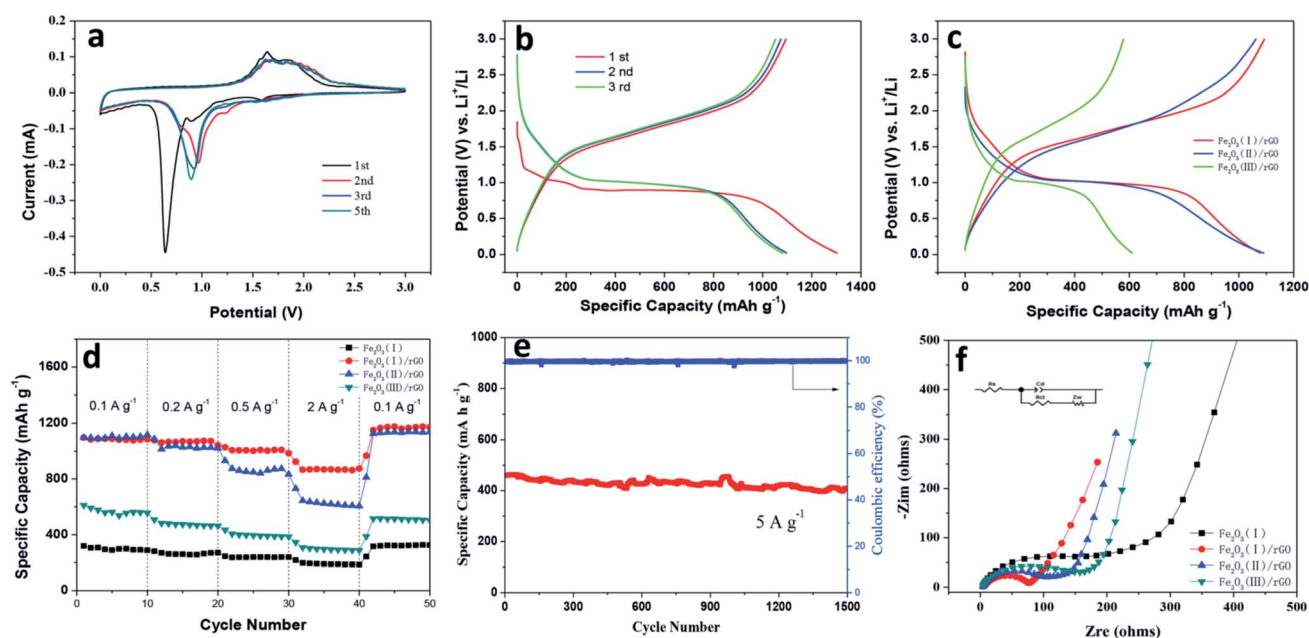


Fig. 7 (a) CV curves of  $\text{Fe}_2\text{O}_3$  (I)/rGO composites at  $0.1 \text{ mV s}^{-1}$ ; (b) Initial discharge–charge curves of  $\text{Fe}_2\text{O}_3$  (I)/rGO composites at  $0.1 \text{ A g}^{-1}$ ; (c) second-cycle discharge and charge curves of the  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO composites at  $0.1 \text{ A g}^{-1}$ ; (d) Rate performance of  $\text{Fe}_2\text{O}_3$  (I) fiber,  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO composites; (e) long term cycling performance and coulombic efficiency of  $\text{Fe}_2\text{O}_3$  (I)/rGO composites at  $5 \text{ A g}^{-1}$ ; (f) electrochemical impedance spectroscopy of the different electrodes.



that are typical for  $\text{Fe}_2\text{O}_3$  based materials, which is in agreement with the charge–discharge process as shown in Fig. 7a. It is also observed that the initial charge and discharge capacities are around 1095.3 and 1303.7  $\text{mA h g}^{-1}$ , and the initial coulombic efficiencies are 84%. In the second and third cycles, although the discharge capacities decrease gradually to about 1098.8 and 1081.6  $\text{mA h g}^{-1}$ , the coulombic efficiencies are all above 97%. Furthermore, the typical second discharge–charge curves of the  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO composites at a current rate of 100  $\text{mA g}^{-1}$  within a voltage range of 0.02–3.0 V are shown in Fig. 7c. The discharge capacity of the  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO composite was 1093.6, 1062.3 and 578.7  $\text{mA h g}^{-1}$ , respectively. From the comparison, the  $\text{Fe}_2\text{O}_3$  (I)/rGO with a smallest diameter show obvious improved specific capacity and higher  $\text{Fe}_2\text{O}_3$  utilization.

To compare the nobility of  $\text{Fe}_2\text{O}_3$ /rGO composites of electrochemical characteristics, the rate capabilities of  $\text{Fe}_2\text{O}_3$ /rGO composites of  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO and  $\text{Fe}_2\text{O}_3$  fibers as anodes were examined at the various current densities of 0.1, 0.2, 0.5, 2 and 0.1  $\text{A g}^{-1}$  (Fig. 7d). The  $\text{Fe}_2\text{O}_3$  (III)/rGO electrode exhibited the lowest rate capability for three samples, significantly decreasing from 610.5  $\text{mA h g}^{-1}$  at 0.1  $\text{A g}^{-1}$  to 287.9  $\text{mA h g}^{-1}$  at 2  $\text{A g}^{-1}$ . By contrast, the  $\text{Fe}_2\text{O}_3$  (I)/rGO electrode exhibited a more stable cyclic performance than others at high current rates and delivered capacities of 1085.2, 1065.1, 974.5, 866.1, and 1170.9  $\text{mA h g}^{-1}$  at 0.1, 0.2, 0.5, 2 and 0.1  $\text{A g}^{-1}$ , respectively.

Then, the cyclic stability of the  $\text{Fe}_2\text{O}_3$  (I)/rGO was investigated as shown in Fig. 7e. It were cycled under an high current density of 5  $\text{A g}^{-1}$ , and the  $\text{Fe}_2\text{O}_3$ /rGO composites show high stability with a specific capacity of 407.8  $\text{mA h g}^{-1}$  after 1500 cycles compared to the  $\text{Fe}_2\text{O}_3$  at the same test conditions and

the excellent coulombic efficiency of higher than 99%. Most notably, the cyclability and rate performance of  $\text{Fe}_2\text{O}_3$ /rGO are better than most of the lately reported  $\text{Fe}_2\text{O}_3$ -based anode materials, such as porous  $\text{Fe}_2\text{O}_3$  nanotubes,<sup>11</sup> nanoropes,<sup>13</sup> hollow nanobarrels/rGO<sup>14</sup> and hollow nanoparticles/rGO.<sup>15</sup>

In order to understand the fast ion transport in the composite electrodes, electrochemical impedance spectroscopy (EIS) measurements were conducted on the fresh cell with  $\text{Fe}_2\text{O}_3$  (I) fiber,  $\text{Fe}_2\text{O}_3$  (I)/rGO,  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO composite electrodes (Fig. 7f). The Nyquist plot shows a depressed semicircle, which generally describes two components: charge transfer resistance<sup>43</sup> and interfacial resistance.<sup>44</sup> The straight line in the low frequency region is the Warburg constant, which is assigned to the diffusion and transport of the  $\text{Li}^+$  ion from the electrolyte to the surface of the electrode. The electrochemical system can be simply modeled by a Randles equivalent circuit, where  $R_s$  is the ohmic resistance,  $C_d$  is the double-layer capacitance,  $R_{ct}$  is the charge transfer resistance, and  $Z_w$  is the Warburg impedance describing the solid-state diffusion of  $\text{Li}^+$  in  $\text{Fe}_2\text{O}_3$ .<sup>45</sup> The resistance of the depressed semicircle of  $\text{Fe}_2\text{O}_3$  (I)/rGO is lower than that of  $\text{Fe}_2\text{O}_3$  (II)/rGO and  $\text{Fe}_2\text{O}_3$  (III)/rGO, which is 78, 118 and 163  $\Omega$ , respectively. It suggests that the  $\text{Fe}_2\text{O}_3$  (I)/rGO composite have a much lower electrolyte resistance and charge transfer resistance than other samples. These results confirm that such special structure for the  $\text{Fe}_2\text{O}_3$  (I)/rGO composites with  $\text{Fe}_2\text{O}_3$  fiber as the “corn cob” and multilayer reduced graphene oxide as the “sepal” is beneficial to further reduce the electronic conductivity of composites. Also, the low impedance can be attributed to higher surface area, uniform  $\text{Fe}_2\text{O}_3$  nanofiber distribution in graphene layer, and better electrolyte wettability associated with porous structure of the  $\text{Fe}_2\text{O}_3$ /rGO composite material.

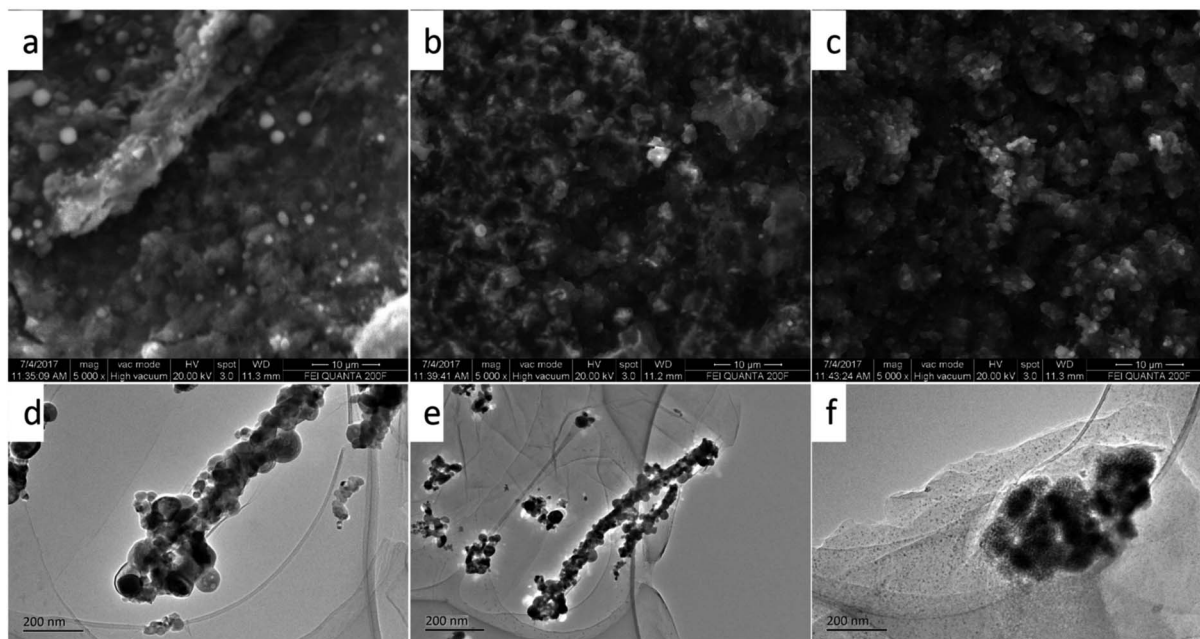


Fig. 8 The SEM (a–c) and TEM (d–f) images of  $\text{Fe}_2\text{O}_3$ /rGO composites after different cycles: (a and d), 100 cycles; (b and e), 500 cycles; (c and f), 1000 cycles.





Finally, to further understand the excellent rate and long cycle performance of the Fe<sub>2</sub>O<sub>3</sub>/rGO composite electrodes based on above results, the structural and morphological evolution of the electrodes were measured by SEM and TEM, respectively in different cycle stages: 100th cycle, 500th cycle and 1000th cycle. As shown in Fig. 8(a and d) and (b and e), it is found that the film electrodes have maintained the fiber morphology before 500 cycles though some Fe<sub>2</sub>O<sub>3</sub>/rGO composite fiber have fractured and some fiber diameters get thin during the discharge-charge process from 100 to 500 cycles. At the 1000<sup>th</sup> cycle, the nanowires are intermixed with each other and begun to get together (Fig. 8c and f), but these Fe<sub>2</sub>O<sub>3</sub> nanoparticles are still homogeneously distributed on the graphene sheets, which maintains the reversible the high specific capacity of the electrode material. In the meantime, the electrochemical impedance spectroscopy (EIS) measurements after initial, 500, and 1000 cycles have also confirmed the stability of Fe<sub>2</sub>O<sub>3</sub>/rGO composite electrode (Fig. S7†). The charge transfer resistance of the Fe<sub>2</sub>O<sub>3</sub> (I)/rGO composite anode are 78, 101 and 195 Ω, respectively. It suggests that the Fe<sub>2</sub>O<sub>3</sub> (I)/rGO composite have low charge transfer resistances, though the values become larger with the cycle number for initial to 1000 cycles gradually. The low charge transfer can be derived from the Fe<sub>2</sub>O<sub>3</sub> nanofibers or nanoparticles encapsulated in the high conductive graphen network.<sup>46,47</sup> In short, the aforementioned factors of as-prepared Fe<sub>2</sub>O<sub>3</sub> fiber/rGO composites translate to greater accessibility to active sites for the lithium ions, shorter diffusion distances and quicker lithium ion diffusion, thereby explaining the significantly better rate capability and excellent cycling performance of the Fe<sub>2</sub>O<sub>3</sub> fiber/rGO composite electrodes.

## 4. Conclusions

In summary, we have designed and fabricated a “corn” structure for a scalable and electrochemically stable Fe<sub>2</sub>O<sub>3</sub>/rGO electrode. The fabrication process is carried out by an electrospinning technique assisted with anneal treatment and far infrared reduction process. The “corn” structure consists of Fe<sub>2</sub>O<sub>3</sub> fibers completely protected by multilayer rGO. Natural void space between the Fe<sub>2</sub>O<sub>3</sub> fibers and rGO allows for the expansion of Fe<sub>2</sub>O<sub>3</sub>; and the good surface area and unblocked channels in the Fe<sub>2</sub>O<sub>3</sub> fiber facilitates fast diffusion of Li<sup>+</sup>. Interestingly, this electrode shows excellent capacity (1085.2 mA h g<sup>-1</sup> at 0.1 A g<sup>-1</sup>), long cycle life (407.8 mA h g<sup>-1</sup> at 5 A g<sup>-1</sup> for 1500 cycles), and high coulombic efficiency (99%). In addition to Fe<sub>2</sub>O<sub>3</sub>, this “corn” structure can also be applied to other high capacity anode materials for next generation Li-ion batteries to improve cycle life and coulombic efficiency.

## Conflicts of interest

There are no conflicts to declare.

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