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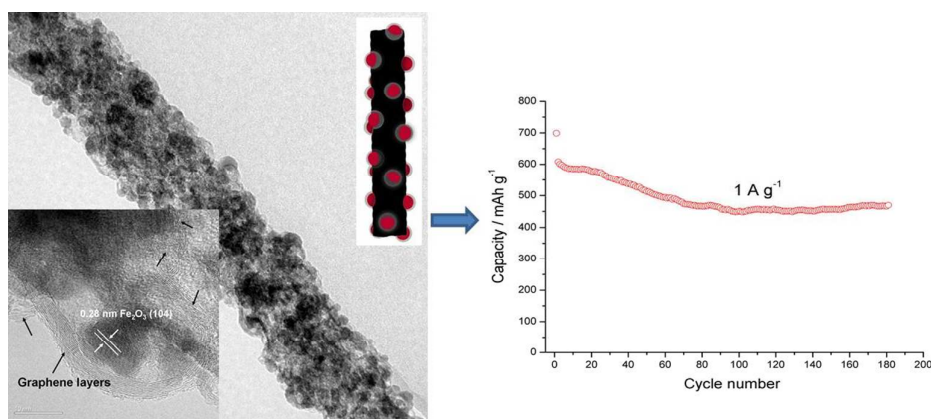
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Graphical Abstract

C/Fe₂O₃/CNF composites are produced through one-pot electrospinning process. The onion-shaped graphene coating layer not only prevents the Fe₂O₃ particles from peeling off from the carbon nanofiber substrate, but also it buffers the volume change of Fe₂O₃ and improves the conductivity of the electrode.



ARTICLE

***In situ* grown graphitic carbon/Fe₂O₃/carbon nanofiber composites for high performance freestanding anodes in Li-ion batteries**

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Conductive carbon nanofiber electrodes containing graphitic carbon coated Fe₂O₃ nanoparticles are synthesized via facile, one-pot electrospinning. The catalytic effect of Fe allows *in situ* formation of onion-shaped graphene layers on Fe₃C nanoparticles upon carbonization, which are transformed into Fe₂O₃ by annealing. The graphene coating offers several important synergies: it not only prevents the Fe₂O₃ particles from peeling off from the carbon nanofiber substrate, but it also buffers the volume change of Fe₂O₃ and improves the conductivity of the electrode. As a consequence, the freestanding composite anode delivers an excellent capacity of 826 mAh g⁻¹ after 105 charge/discharge cycles at 0.1 A g⁻¹ for Li ion batteries.

Introduction

Tremendous efforts have been devoted to developing high performance electrode materials for Li-ion batteries (LIBs) to satisfy the functional requirements of demanding applications like electric vehicles and stationary electricity storage. Graphite—the most popular anode material—suffers from a low theoretical capacity of 372 mAh g⁻¹. In addition, metallic Li may easily deposit on the surface of graphite electrodes at high current densities due to the low plateau of about 50 mV vs. Li/Li⁺, causing serious safety issues.¹ Various anode materials have been investigated as potential substitutes for graphite, including nanocarbon,² Li₄Ti₅O₁₂,³ and transitional metal oxides.⁴ Among them, transitional metal oxides, such as iron oxides and cobalt oxides, have attracted considerable attention because of their high capacities of ~1000 mAh g⁻¹, low material cost, high safety and environmental friendly nature.⁵

One of the main obstacles that prevent successful commercialization of these transitional metal oxides is the large volume change occurring during Li ion insertion/extraction, which results in pulverization of electrodes and fast capacity degradation. Designing diverse nanostructures and incorporation of conductive nanocarbon materials have proven to be most effective in improving the cyclic performance.^{6,7} Combining the above two approaches together with metal oxide

nanoparticles encapsulated into the nanocarbon material may greatly improve the capacity retention. The free space allowed between the well dispersed nanoparticles can accommodate the volume change during the charge/discharge process, while the nanocarbon acts as a buffer layer to alleviate the mechanical strains. Furthermore, the conductive carbon networks provide fast transfer paths for electrons and the nanosized particles shorten the diffusion length for Li ions, leading to an excellent rate performance.⁸

A composite structure containing a thin layer of amorphous carbon coated on the metal oxide/nanocarbon composites has recently been developed to avoid the detachment of active particles from the nanocarbon matrix that also served as the conducting substrate.^{9, 10} For instance, an amorphous carbon layer was coated on a SnO₂/graphene nanocomposite to improve the capacities at high current densities as well as the capacity retention.⁹ An additional processing step was required to deposit the carbon layer after the incorporation of metal oxides into a nanocarbon substrate, inevitably increasing the fabrication cost. In this study, we report a facile, one-pot electrospinning process to fabricate composites consisting of graphitic carbon coated Fe₂O₃ nanoparticles embedded in carbon nanofibers (CNFs). A graphitic carbon layer was *in situ* deposited on the Fe particle surface thanks to the catalytic

effect of Fe. The composite electrodes delivered a high capacity with excellent cyclic performance.

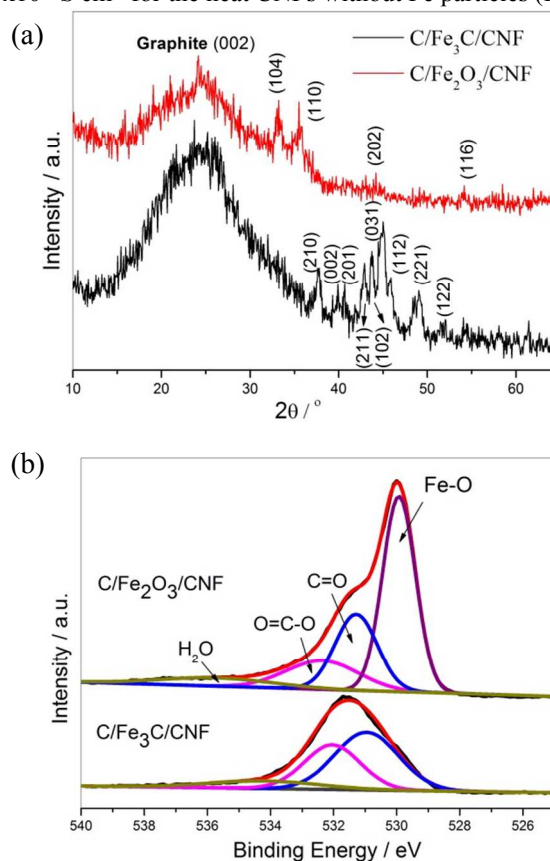
Experimental

Polyacrylonitrile (PAN, Mw=150k, Aldrich) was employed as a carbon precursor for producing CNFs. PAN was dissolved in N-dimethylformamide at 80 °C for 3h and iron (III) acetylacetonate was added into the solution, which was kept stirring overnight. The weight ratio of iron (III) acetylacetonate to PAN was controlled at 3:2. Electrospinning was conducted on an electrospinner (KATO Tech. Co.) at a high voltage of 18 kV and a flow rate of 1.0 ml h⁻¹. After collecting from the drum collector, the PAN fiber film containing Fe particles was stabilized at 220 °C for 3h, and carbonized at 650 °C for 1h in a N₂ atmosphere to obtain *in situ* graphitic carbon coated Fe₃C particles in CNFs (designated as C/Fe₃C/CNF). An optimized carbonization temperature of 650 °C was chosen to maintain a high N content and thus to achieve a high capacity of neat CNFs.¹¹ Fe₃C particles were converted to Fe₂O₃ through two-step annealing of the composite at 250 °C for 6 h and at 300 °C for 0.5 h in air to finally obtain C/Fe₂O₃/CNF. For comparison, the C/Fe₂O₃/CNF composite was further treated at 500 °C in air for 2 h at a ramping rate of 2 °C min⁻¹ to obtain neat Fe₂O₃ particles.

X-ray diffraction (XRD, PW 1830, Philips) analysis was conducted to investigate the crystal structure. The morphology of the composites was examined by scanning electron microscopy (SEM, JEOL 6700F) and transmission electron microscopy (TEM, JEOF 2010). X-ray photoelectron spectroscopy (XPS) analysis (PHI5600, Physical Electronics, Inc.) was conducted using a monochromatic Al K α X-ray at 14 kV. The electrical conductivities of the CNF composite films were measured on a four-probe resistivity/Hall system (HL5500PC, Bio-Rad). The freestanding CNF films of thickness ~150 μ m were cut into 1x1 cm² squares which were used directly as the electrodes in 2032 coin cells for electrochemical tests. The mass loading of each electrode was ~2 mg. The neat Fe₂O₃ particles were mixed with the carbon black conductive additive and polyvinylidene fluoride binder at a weight ratio of 7:2:1 by magnetic stirring in N-methyl-2-pyrrolidone for 4 h. The slurry was coated onto the copper foil and dried in an oven at 80 °C, which was cut into pellets of 12 mm in diameter to obtain the neat Fe₂O₃ electrode. The cells were assembled in an Ar-filled glove box with a Li foil as the counter electrode, 1 M LiPF₆ in ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte and a porous polyethylene film (Celgard 2400) as the separator. The coin cells were charge/discharge between 0 and 3 V on a LAND 2001 CT battery tester. Cyclic voltammetry (CV) tests were carried out on a CHI660c electrochemical work station at a scanning rate of 0.2 mv s⁻¹.

Results and discussion

The crystalline structure of Fe particles after carbonization in N₂ gas was investigated by XRD, as shown in Fig. 1a. The Fe particles were present in the form of Fe₃C instead of FeO_x, which may be ascribed to the inert and reducing atmosphere during carbonization. Because Fe₃C was not an active material for Li ion storage, the composites were further annealed in air to oxidize Fe₃C into Fe₂O₃.¹² All Fe₃C particles were transformed to Fe₂O₃ after annealing (Fig. 1a), which was further confirmed by the XPS spectra (Fig. 1b). Oxygenated functional groups, like C=O and O=C-O, and adsorbed H₂O molecules were identified from the O1s peak of the C/Fe₃C/CNF composite obtained before annealing in air. In contrast, an additional functional group assigned to Fe-O appeared in the C/Fe₂O₃/CNF composite after annealing, indicating the oxidation of Fe₃C.¹³ Along with the oxidation, CNFs was also partially removed after annealing. The TGA curves (Fig. 1c) showed that at above 500 °C there was 68% weight loss in C/Fe₃C/CNF as a result of removal of carbon and oxidation of Fe₃C into Fe₂O₃. It can be estimated that the composite contained about 24wt.% Fe₃C after excluding the weight contribution from the transformation of Fe₃C to Fe₂O₃. Carbon began to burn out at ~300 °C, resulting in the increase of Fe₂O₃ to 44 wt.% in C/Fe₂O₃/CNF after annealing. The concomitant decrease in carbon content was responsible for the marginal reduction in electrical conductivity of the composite films from 0.21 to 0.061 S cm⁻¹ after annealing. Nevertheless, this value was about three orders of magnitude higher than 8.3x10⁻⁵ S cm⁻¹ for the neat CNFs without Fe particles (Fig. 1d).



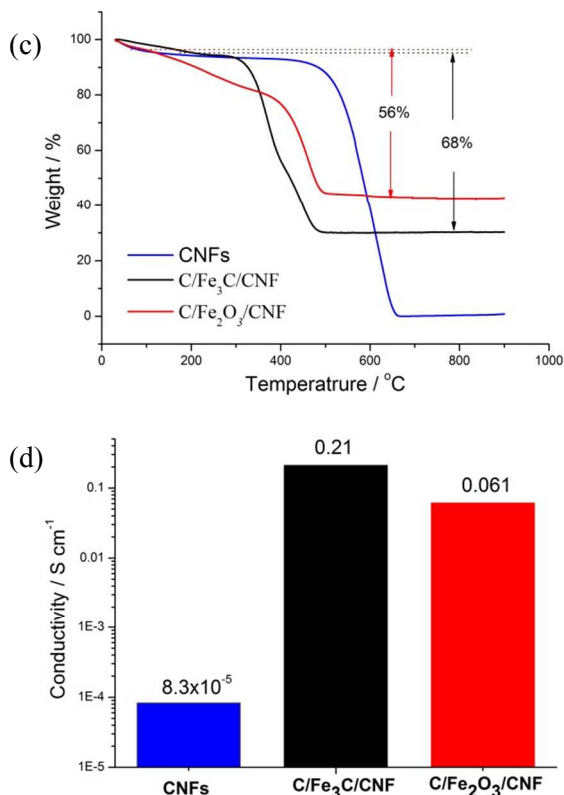


Fig.1 (a) XRD patterns, (b) XPS O1s peaks, (c) TGA curves and (d) electrical conductivities of neat CNF and composite samples.

The C/Fe₃C/CNF composite had a smooth surface with a diameter ranging 100 - 300 nm (Fig. 2a). They looked much the same as the neat CNFs, suggesting little change in fiber structure after the incorporation of Fe.¹¹ After annealing, the C/Fe₂O₃/CNF composite became shorter due to damage induced by the oxidation of carbon (Fig. 2b), in agreement with the TGA curves. The shorter CNF length indicates less entanglement between them with a lower mechanical strength, while the freestanding film can still be maintained. The TEM image (Fig. 2c) shows that the diameter of Fe₃C particles ranged 5-40 nm, and the particles were encapsulated by several graphene layers (Fig. 2e). These graphene layers were *in situ* formed due to the catalytic effect of Fe on graphitization during carbonization of electrospun polymer fibers. The interconnected graphene layers could establish conductive networks within CNFs and resulted in a sharp increase in electrical conductivity. After annealing, the Fe₂O₃ particles tended to aggregate due to the partial loss of carbon between them (Fig. 2d). Nevertheless, the onion-structured graphene layers encapsulating the Fe₂O₃ particles were well preserved (Fig. 2f). In contrast, the neat Fe₂O₃ showed a collapsed fiber structure with the carbon scaffold totally removed and only Fe₂O₃ particles left behind (Fig. S1) after annealing at 500 °C for 2h. The color of the sample was also changed from black to red.

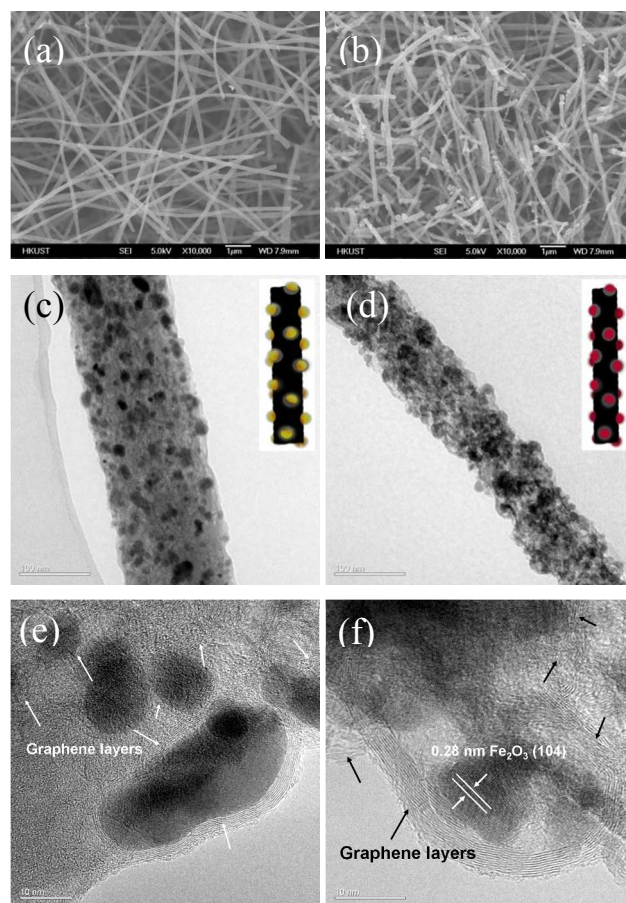


Fig.2 SEM and TEM images of (a)(c)(e) C/Fe₃C/CNF and (b)(d)(f) C/Fe₂O₃/CNF composites

The freestanding films were used directly as electrodes and their electrochemical performance was evaluated, as shown in Fig. 3. The absence of polymer binders and conductive additives could potentially improve the energy densities of LIBs. The CV curves of the C/Fe₂O₃/CNF electrode presented a typical characteristic of Fe₂O₃ anode (Fig. 3a). A pair of peaks at about 0.75 and 1.75 V corresponded to the reduction of Fe³⁺ to Fe⁰ and its reversible oxidation process, respectively. A small cathodic peak at about 1.25 V may be ascribed to the intermediate reduction of Fe₂O₃ to Li_{0.6}Fe₂O₃.¹⁴ The charge/discharge profiles (Fig. 3b) showed a clear discharge plateau at about 0.75 V in the C/Fe₂O₃/CNF electrode, similar to that observed in the neat Fe₂O₃ electrode, but with a lower capacity. In contrast, there was no clear plateau in the C/Fe₃C/CNF electrode owing to the inactive Fe₃C particles for Li ion storage.

Fig. 3c shows that the neat Fe₂O₃ electrode had capacities even higher than the theoretical value of Fe₂O₃ in the first two cycles, which is attributed to the formation of a solid electrolyte interface (SEI).¹⁴ The electrode underwent, however, fast capacity degradation with low coulombic efficiencies of 76.8 and 81.8% for the 1st and 2nd cycles, respectively. The fast capacity fading can be explained by the poor electrical conductivity and large volume change during the Li ion

insertion/extraction cycles. After the encapsulation of Fe_2O_3 particles within the CNF substrate along with the conductive multi-layer graphene coating, the $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ composite electrode delivered excellent capacity retention even at a high current density of 2 A g^{-1} . Moreover, the capacity was restored to its initial value when the current density was reduced back to 0.1 A g^{-1} . An excellent capacity of 826 mAh g^{-1} was maintained after 105 cycles. The neat CNF film itself could make an excellent anode material¹⁵ and has contributed to a high capacity of 540 mAh g^{-1} when discharged at 0.1 A g^{-1} .¹¹ In comparison, only 520 mAh g^{-1} was obtained for the $\text{C}/\text{Fe}_3\text{C}/\text{CNF}$ electrode without annealing, which was even lower than the corresponding value for the neat CNFs. The main advantage of this electrode is a potentially high rate capability due to its higher electrical conductivity (Fig. 1d).

The stability of the $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ composite electrode was evaluated by charging/discharging at 1 A g^{-1} for 180 cycles, where a high capacity of 469 mAh g^{-1} was retained. The capacity obtained in this study is comparable or even higher than similar $\text{FeO}_x/\text{carbon}$ composite electrodes, such as 810 mAh g^{-1} (at 0.1 A g^{-1} for 100 cycles) for $\text{Fe}_2\text{O}_3/\text{graphene}$ hybrid¹³ and 645 mAh g^{-1} (at 0.1 A g^{-1} for 145 cycles) for $\text{Fe}_3\text{O}_4/\text{CNT}$ composites.¹⁶ The high capacity and excellent capacity retention shown by the $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ electrode are attributed to several synergies offered by its unique structure: namely (i) the graphitic carbon coating effectively prevented the Fe_2O_3 nanoparticles from peeling off from the CNF substrate; (ii) the onion-shaped graphene layers functioned as additional stress buffer and conductive paths; and (iii) the interconnected CNFs offered 3D conductive networks for fast charge transfer.

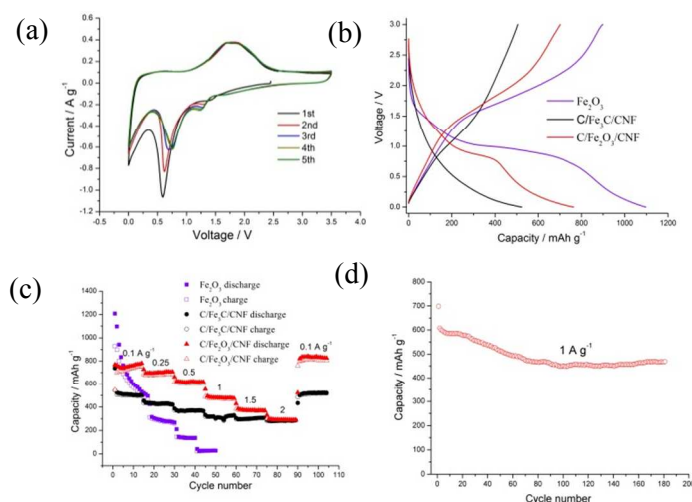


Fig. 3 (a) CV curves of $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ composite electrodes in the first 5 cycles; (b) charge/discharge curves of the 2nd cycle at 0.1 A g^{-1} and (c) rate performance of different electrodes; (d) cyclic performance of $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ electrodes measured at 1 A g^{-1} for 180 cycles.

Conclusions

A facile, one-pot electrospinning process was employed to synthesize composite fibers consisting of graphene layers on

Fe_2O_3 nanoparticles that are embedded in the CNF matrix. Onion-shaped multi-layer graphene coating was in situ formed on Fe_3C nanoparticles upon carbonization thanks to the catalytic effect of Fe. The Fe_3C nanoparticles were annealed to modify into Fe_2O_3 and the $\text{C}/\text{Fe}_2\text{O}_3/\text{CNF}$ composites were employed as the anode for LIBs. The confinement of Fe_2O_3 particles through the graphitic carbon coating and CNF matrix effectively buffered the volume change, while the graphene layers offered additional conductive paths for faster charge transfer, resulting in an excellent capacity of 826 mAh g^{-1} after 105 cycles. The strategy adopted here using Fe or Ni catalyst provides a new insight into synthesizing nanocarbon-based composite electrodes for LIBs with high capacity performance.

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