Low temperature plasma synthesis of mesoporous Fe₃O₄ nanorods grafted on reduced graphene oxide for high performance lithium storage†

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Transition metal oxide coupling with carbon is an effective method for improving electrical conductivity of battery electrodes and avoiding the degradation of their lithium storage capability due to large volume expansion/contraction and severe particle aggregation during the lithium insertion and desertion process. In our present work, we develop an effective approach to fabricate the nanocomposites of porous rod-shaped Fe₃O₄ anchored on reduced graphene oxide (Fe₃O₄/rGO) by controlling the in situ nucleation and growth of β-FeOOH onto the graphene oxide (β-FeOOH/GO) and followed by dielectric barrier discharge (DBD) hydrogen plasma treatment. Such well-designed hierarchical nanostructures are beneficial for maximum utilization of electrochemically active matter in lithium ion batteries and display superior Li uptake with high reversible capacity, good rate capability, and excellent stability, maintaining 890 mA h g⁻¹ capacity over 100 cycles at a current density of 500 mA g⁻¹.

Introduction

With a multi-billion dollar market value, rechargeable lithium-ion batteries (LIBs) have been the most popular power source for portable electronics due to their superior advantages, such as high energy density, long lifespan, no memory effect and environmental benignity.¹ They are also greatly desired for the continuously surging demand in large-scale energy applications, such as electric vehicles, renewable power plants and electric grids.²,³ This boosts a great deal of effort in the development of high-performance electrode materials that can store more energy efficiently. Fe₃O₄ is a very attractive anode material with high theoretical capacity (ca. 922 mA h g⁻¹), widespread availability, intrinsically enhanced safety, nontoxicity and low cost.⁴,⁵ More importantly, this inverse spinel possesses one of the highest electronic conductivities (σ = 2 × 10⁴ S m⁻¹) of the simple metal oxides, which makes it especially appealing as a high-power electrode material in LIBs, due to significantly reduced electrode polarization.⁶ Despite the substantial merits, a major drawback of Fe₃O₄-based electrodes is the severe electrode pulverization caused by the drastic volume variation (up to 200%) during repeated electrochemical cycling and sluggish kinetics of conversion reaction.⁴,⁷ Macroscopically, this is manifested as poor cycling stability with low lithium storage capacities, especially at a high current rate. One way to improve the electrochemical performance of Fe₃O₄ is to use nanostructures with a short lithium diffusion path, large surface areas and enhanced reactivity, such as the nanoparticles, nanospheres, nanobelts and nanorods.⁸–¹⁰ Despite the observed high capacities of about 500–1000 mA h g⁻¹, lithium storage in most Fe₃O₄ based electrodes remains reversible only at slow rates of 0.1–1 C due to the insufficient structural stability.

A promising approach to further enhance the lithium storage capability of Fe₃O₄ based electrodes is to combine them with carbonaceous materials. The presence of elastic carbon not only serves as a physical buffering layer to cushion the mechanical stress associated with the volume change of Fe₃O₄ upon cycling, but also greatly improves the electronic conductivity of the electrode.⁴,¹⁷–²¹ In some cases, it can even construct a three-dimensional network to facilitate the charge transfer and reinforce the entire electrodes.²²–²⁸ So far, various Fe₃O₄/C composites, including carbon coated nanospindles/nanospheres/nanoparticles, Fe₃O₄/CNT composites, graphene-wrapped particles, carbon-coated Fe₃O₄/graphene hybrids, and 3D hierarchical Fe₃O₄/graphene composites, have been explored as high-performance electrodes in LIBs.²⁹–³² Nevertheless, the fabrication of truly durable Fe₃O₄ based electrodes with
satisfactory cyclability and high-rate performance still remains a significant challenge.

In this work, we report a simple approach for the synthesis of reduced graphene oxide (rGO) decorated with mesoporous Fe₃O₄ nanorods through one-pot reduction of the β-FeOOH/graphene oxide (GO) composite in dielectric barrier discharge (DBD) H₂ plasma under ambient conditions. The method shows superior efficiency for the growth of graphene-based composites due to the low temperature and short time (typically 30 min). Characterization shows that mesoporous Fe₃O₄ nanorods are tightly combined with rGO in high mass loading (79 wt.%). When evaluated for lithium storage capability, the Fe₃O₄/rGO composite exhibits a high capacity of ca. 890 mA h g⁻¹ with exceptional capacity retention for 100 cycles at a current density of 500 mA g⁻¹. Even when cycled at very high current densities of 1000–3000 mA g⁻¹, it may still deliver high reversible capacities of 520–700 mA h g⁻¹ due to the enhanced structural stability, electronic conductivity and kinetics for lithium storage.

Results and discussion

The synthetic strategy for the decoration of mesoporous Fe₃O₄ nanorods on rGO is illustrated in Scheme 1, and the synthesis experimental details are described in the ESI.† Firstly, β-FeOOH nanorods are spontaneously grown on the surface of GO (denoted as β-FeOOH/GO) through the electrostatic adsorption and hydrolysis of Fe³⁺ on GO at 120 °C. Afterwards, β-FeOOH nanorods are easily reduced to mesoporous Fe₃O₄ nanorods by active hydrogen species and high-energy electrons generated in the DBD hydrogen plasma. When bombarded by these energetic species, the polar chemical bonds in the oxygen-containing groups on GO are also distorted and ruptured. As a result, rGO is simultaneously formed to construct the composite with Fe₃O₄.

The crystallographic structure and phase purity of the β-FeOOH/GO sample were determined by X-ray powder diffraction (XRD), as shown in Fig. 1a. All the diffraction peaks can be assigned to tetragonal β-FeOOH (JCPDS no. 34-1266). No apparent signals from GO could be identified, indicating that β-FeOOH particles are efficiently deposited on the surface of GO and suppress the stacking of GO layers. The presence of GO is evidenced by the Raman spectrum, as characterized by the D-band and G-band at Raman shifts of 1373 and 1589 cm⁻¹, respectively (Fig. 1b). A panoramic view by using a scanning electron microscope (SEM) reveals a high density of β-FeOOH nanorods on the surface of GO (Fig. 1c). Such a geometric confinement of metal oxide nanoparticles onto GO layers can enhance their interface contact and protect the particles from dissolution and agglomeration, thereby promoting the electrochemical activity and stability of the composite. Transmission electron microscopy (TEM) characterization further indicates the uniform distribution of β-FeOOH nanorods on GO (Fig. 1d). These nanorods prepared in a higher initial concentration of FeCl₃ (e.g., 0.1 M), with the length of 300–400 nm and the diameter of 30–50 nm, are firmly anchored on GO even after drastic ultrasonication, showing the strong interaction between them. The high-resolution TEM (HRTEM) image validates the single-crystalline structure of β-FeOOH nanorods. In Fig. 1e, the distinct lattice fringes with ca. 0.47 nm spacing correspond to...
the (210) planes of β-FeOOH. We suggest the preferential electrostatic attraction of Fe³⁺ to polar oxygen-containing groups on GO as the governing mechanism. The subsequent hydrolysis of Fe³⁺ and further olation/oxolation of FeO₆ units may be responsible for the heterogeneous nucleation and growth of β-FeOOH nanoparticles on the GO surface. In this process, a lower initial concentration of FeCl₃ (e.g., 0.015 M) results in the growth of sparse and smaller nanospindles on GO (Fig. S1†). Therefore, the size and growing density of β-FeOOH nanorods on GO can be readily tuned to achieve a desirable loading amount of active materials by simply varying the initial concentration of FeCl₃ in solution.

The β-FeOOH/GO composite possesses good structural stability and is robust enough to withstand hydrogen plasma. After the treatment, Fe₃O₄/rGO can be derived from β-FeOOH/GO through the phase transformation of β-FeOOH to Fe₃O₄ (magnetite, JCPDS no. 19-0629) and simultaneous reduction of GO, as confirmed by XRD analysis (Fig. 2a). Due to the n-type doping effect on rGO (electron donating effect), the Raman spectrum of Fe₃O₄/rGO shows a shift of the G-band to 1590 cm⁻¹ (Fig. 2b). It suggests significant charge transfer and strong interactions between closely bonded rGO and Fe₃O₄, which is beneficial to the electrochemical reactions. The bands at 583 and 687 cm⁻¹ can be ascribed to the T₂g and A₁g modes of Fe₃O₄, respectively. SEM and TEM examination shows that the conversion of β-FeOOH to Fe₃O₄ nanorods undergoes a topotactic transformation process due to their structural similarity, as shown in Fig. 2d–f. During the plasma treatment, high porosity is generated in the nanorods as a result of the volume contraction associated with the transformation from low density β-FeOOH (3 g cm⁻³) to denser Fe₃O₄ with a density of 5.17 g cm⁻³. The N₂ adsorption/desorption isotherm of Fe₃O₄/rGO shows a type IV curve with a type H₃ hysteresis loop at relatively high pressure, corresponding to a specific surface area (calculated by the Brunauer–Emmett–Teller (BET) method) of ca. 86 m² g⁻¹ and a mesopore size of 10–50 nm (Fig. 2c). Moreover, the TGA analysis indicates a high loading amount of 79 wt.% for Fe₃O₄ nanorods in this composite after subtracting the weight increase induced by the conversion of Fe₃O₄ to Fe₂O₃ and the loading amount, the size and morphology of Fe₃O₄ can be easily tuned by controlling the initial ratio of GO and Fe source (Fig. S1 and S2†).

Fig. 3a shows representative discharge/charge voltage curves of the Fe₃O₄/rGO composite at a moderate current density of 500 mA g⁻¹ within a cut-off window of 0.01–3.0 V. The initial discharge and charge capacities are found to be 1090 and 845 mA h g⁻¹ based on total sample mass, respectively. The irreversible capacity loss of 22% may be mainly attributed to initial irreversible formation of Li₂O, and other irreversible processes such as trapping of some lithium in the lattice, formation of the solid-electrolyte interphase (SEI) and electrolyte decomposition, which are common for most anode materials, especially nanostructured ones. From the second cycle onwards, they exhibit a high discharge capacity of over 1000 mA h g⁻¹, which then stabilize at about 890 mA h g⁻¹ after 100 cycles with a high coulombic efficiency of around 97–99% (Fig. S3†), corresponding to a capacity loss of 11%. This value is much higher than the theoretical capacity of graphite (372 mA h g⁻¹). Benefitting from its unique structure, the Fe₃O₄/rGO composite also exhibits an excellent cycling response to a
continuously varying current rate. At a low current density of 200 mA g\(^{-1}\), it delivers a higher capacity of ca. 1070 mA h g\(^{-1}\) than the theoretical value of pure Fe\(_3\)O\(_4\) anode (922 mA h g\(^{-1}\)), probably due to surface lithium storage. Even when cycled at very high rates of 1000–3000 mA g\(^{-1}\), high capacity of 700–520 mA h g\(^{-1}\) still remains, as shown in Fig. 3c. Such a remarkable high-rate performance is superior to that of most Fe\(_3\)O\(_4\) based electrodes, conventionals, and other novel MXene materials as well.\(^\text{19–23,38}\) A deep cycling at 3000 mA g\(^{-1}\) for ten cycles, a reversible capacity of ca. 800 mA h g\(^{-1}\) can be restored when cycling at a lower current density of 500 mA g\(^{-1}\). To highlight the superiority of the Fe\(_3\)O\(_4\)/rGO composite in lithium storage, the electrochemical performance of pure Fe\(_3\)O\(_4\) and rGO prepared by the same method as Fe\(_3\)O\(_4\)/rGO without introducing GO or FeCl\(_3\) precursors is also investigated under the same conditions. The pure Fe\(_3\)O\(_4\) particles deliver an initial discharge capacity of ca. 800 mA h g\(^{-1}\) but only ca. 25% of that can be retained after 20 cycles (Fig. 3b). Whereas for rGO, much lower capacities of 300–400 mA h g\(^{-1}\) are delivered due to low theoretical capacity of carbonaceous materials. Under a high rate of 1000–3000 mA g\(^{-1}\), both materials lose almost all of their capacities. Apparently, the tight integration of porous Fe\(_3\)O\(_4\) nanorods and rGO significantly improves the electrochemical properties of their composite.

Moreover, spindle-like Fe\(_3\)O\(_4\) (S-Fe\(_3\)O\(_4\)) can also be obtained by controlling Fe source concentration during the growth of \(\beta\)-FeOOH. The lithium storage performance of rGO decorated with Fe\(_3\)O\(_4\) nanorods (R-Fe\(_3\)O\(_4\)/rGO) and nanospindles (S-Fe\(_3\)O\(_4\)/rGO) was compared in Fig. S4.\(^\text{†}\) Obviously, the cycling performance and specific capacity of S-Fe\(_3\)O\(_4\)/rGO are remarkably lower than that of R-Fe\(_3\)O\(_4\)/rGO, which may be mainly attributed to the relatively poor structural stability of the spindle-like Fe\(_3\)O\(_4\) and/or the improper ratio of Fe\(_3\)O\(_4\) to rGO.

To uncover the electrochemical reaction involved in lithium storage in the Fe\(_3\)O\(_4\)/rGO composite, cyclic voltammetry (CV) is performed within 0.01–3.0 V at a scan rate of 0.1 mV s\(^{-1}\), as shown in Fig. 3d. In the first cycle, the cathodic peak centered at 1.47 V corresponds to the structure transition caused by lithium insertion into Fe\(_3\)O\(_4\) (Fe\(_3\)O\(_4\) + \(x\)Li\(^+\) + \(x\)e\(^-\) \(\rightarrow\) Li\(_x\)Fe\(_3\)O\(_4\)). The intense peaks at ca. 0.71 and 0.96 V can be attributed to the reduction of Fe\(^3+\)/Fe\(^2+\) to Fe\(^0\) (Li\(_x\)Fe\(_3\)O\(_4\) + 8Li\(^+\) + 8e\(^-\) \(\rightarrow\) 3Fe + 4Li\(_2\)O), and the formation of amorphous Li\(_2\)O plus the irreversible reaction with the electrolyte. The broad anodic peak at 1.61–1.95 V corresponds to the restoration of Fe\(_3\)O\(_4\) from Fe\(^0\). The subsequent curves show good reproducibility with a cathodic and anodic peak pair at ca. 0.8 V and 1.6–1.9 V for reversible conversion between Fe\(_3\)O\(_4\) and Fe\(^0\), which is in good agreement with the literature report.\(^\text{10,25}\)

The excellent electrochemical performance of the Fe\(_3\)O\(_4\)/rGO composite can be attributed to their rationally designed architecture. First, the highly elastic and stable rGOS not only serve as separators preventing the Fe\(_3\)O\(_4\) nanostructures from aggregation, but also efficiently accommodate the volume change of Fe\(_3\)O\(_4\) nanorods during electrochemical cycling, which ensures...
the sustained structural integrity of the electrode. Second, the highly conductive rGO network provides an efficient pathway for fast charge transfer. In favor of the presence of rGO, the Fe3O4/rGO composite exhibits much lower resistance than the bare Fe3O4 nanoparticles, as evidenced by the drastically reduced size of the semicircle at high-frequency regions in the electrochemical impedance spectroscopy (EIS) patterns (Fig. S5†). Third, appropriate size and internal porosity of Fe3O4 nanorods make them highly accessible to Li+ in the electrolyte and afford them the maximum structural stability by buffering volume expansion and internal mechanical stress induced by lithiation/delithiation with hollow spaces. This approach has been successfully used to develop silicon-containing anodes. Moreover, Fe3O4 has an inverse spinel structure where 1/3 of the iron ions occupy the tetrahedral sites (all Fe2+), and 2/3 of the iron ions occupy both octahedral and tetrahedral sites (one half is Fe2+ and the other half is Fe3+). The electron exchange between the Fe3+ and Fe2+ endows Fe3O4 with very high electronic conductivities (σ = 2 × 10^4 S m^-1) at room temperature. This feature further facilitates the high-rate performance of the Fe3O4/rGO composite. Apparently, the high structural stability, enhanced electronic conductivity and the fast kinetics of lithium storage reaction determine the excellent electrochemical performance of the Fe3O4/rGO composite.

Conclusions

In summary, a low temperature plasma approach has been developed for the synthesis of mesoporous Fe3O4 nanorods grafted on rGO. The method shows superior efficiency to conventional annealing approaches due to the low temperature and short time (typically 30 min) for the reaction. Characterization shows that mesoporous Fe3O4 nanorods are tightly bonded to rGO and a high mass loading can be achieved. This well-designed nanostructure exhibits a stable high capacity of 890 mAh g^-1 after 100 cycles at a current density of 500 mA g^-1. Remarkably, excellent rate capability is also achieved, delivering high capacities of 700–520 mAh g^-1 at high current densities of 1000–3000 mA g^-1, respectively, which shows a promise of this anode material for high-power LIBs. Additionally, the plasma method has been also proven highly efficient for the production of graphene-based composites.

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Notes and references