Tailoring Iron Oxide Nanostructures for High-Capacity Lithium Storage

Yao Yao, Jiantao Li, Qinyou An, Liqiang Mai,* and Liang Zhou*

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, Hubei 430070, China

Iron oxides, such as hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$), have been considered as alternative anode materials for lithium-ion batteries (LIBs) due to their high theoretical capacity, abundant reserves, low cost, and non-toxicity. However, their practical application has been hampered by the large volume expansion, which leads to rapid capacity fading. Nanostructure engineering has been demonstrated to be an effective avenue in tackling the volume variation issue and boosting the electrochemical performances. Herein, recent advances on nanostructure engineering of iron oxides for lithium storage are summarized. These nanostructures include 0D nanoparticles, 1D nanowires/nanorods/nanofibers/nanotubes, 2D nanoflakes/nanosheets, as well as 3D porous/hollow/hierarchical architectures. The structure-electrochemical performance correlations are also discussed. It is believed that the performance optimization strategies summarized here might be extended to other high-capacity LIB anode materials.

Keywords iron oxide, nanostructure, nanocomposite, lithium storage, anode

Introduction

The global concerns of energy shortage and environmental pollution make the clean and sustainable energy an urgent need. With high energy density and long lifespan, rechargeable lithium-ion batteries (LIBs) are one of the most promising energy storage devices for portable electronics and electric vehicles. However, the current state-of-the-art LIBs can’t meet the ever increasing demands on energy density. The current commercialized graphite-based anode suffers from low specific capacity (372 mAh·g$^{-1}$) and poor safety. Therefore, exploring alternative anode materials with high capacity and good safety has attracted growing attention.

Transition metal oxides (TMOs) represent a promising family of high-capacity anode materials for LIBs. Based on a conversion reaction mechanism, they are able to provide a specific capacity of 700–1000 mAh·g$^{-1}$, which is two to three times to that of graphite. Among the various TMOs, iron oxides, such as hematite ($\alpha$-Fe$_2$O$_3$), maghemite ($\gamma$-Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$), have attracted particular attention due to their high theoretical capacity, abundant reserves, low cost, and non-toxicity. Take the Fe$_3$O$_4$ as an example, each formular of Fe$_3$O$_4$ is able to react with 6 Li$^+$, providing a high theoretical capacity of 1007 mAh·g$^{-1}$. However, the high specific capacity is accompanied by a large volume change (~96%) during lithiation/de-lithiation.

Such a large volume variation results in the notorious problems of active material pulverization, electrode disintegration (loss of electrical contact between active material and current collector), and unstable solid electrolyte interphase (SEI) film formation, eventually leading to rapid capacity fading upon cycling. To achieve high specific capacity without compromising the cyclability, the volume change associated with repeated lithiation/de-lithiation should be better accommodated.

Nanostructure engineering has been demonstrated to be an effective avenue in tackling the volume expansion issue of high-capacity anode materials. The strain induced by lithiation/de-lithiation can be effectively alleviated by proper nanostructure design. Especially, if sufficient pores/voids were introduced in the active material, the volume change of electrode materials can be accommodated as well. Other benefits of nanostructured electrode materials include reduced Li$^+$ diffusion lengths and high electrode/electrolyte contact area for Li$^+$ flux. This review provides a comprehensive summarization of the recent advances on nanostructure engineering of iron oxides for lithium storage. These nanostructures include 0-dimensional (0D) nanoparticles, 1D nanowires/nanorods/nanofibers/nanotubes, 2D nanoflakes/nanosheets, and 3D porous/hollow/hierarchical structures. The structure-electrochemical performance correlations are also discussed.

$\alpha$-Fe$_2$O$_3$ based anode materials

Hematite, also known as $\alpha$-Fe$_2$O$_3$, is the most thermodynamically stable form of iron oxide under ambient conditions. It has a corundum structure, in which oxygen adopts a hexagonal close packed structure with Fe occupying two-thirds of the octahedral vacancy sites. Although the long-term cycling performances were not provided, these studies suggest that $\alpha$-Fe$_2$O$_3$ nanorods could be used as high-capacity LIB anode.

$\alpha$-Fe$_2$O$_3$ based 1D nanostructures

1D nanowires, nanorods, nanofibers, and nanotubes possess multiple merits in lithium storage, including large electrode-electrolyte contact area, facile strain relaxation, and efficient 1D electron transport pathways. In 2006, Xie et al. reported the first discharge/charge profiles of $\alpha$-Fe$_2$O$_3$ nanorods. Later, Tang’s group reported the initial discharge/charge curves of $\alpha$-Fe$_2$O$_3$. Although the long-term cycling performances were not provided, these studies suggest that $\alpha$-Fe$_2$O$_3$ nanorods could be used as high-capacity LIB anode. Wang et al. studied the electrochemical performances of single crystalline $\alpha$-Fe$_2$O$_3$ nanorods with diameters of 60–80 nm.
Tailoring Iron Oxide Nanostructures

α-Fe$_2$O$_3$ nanorods demonstrated a high reversible capacity of 955 mAh·g$^{-1}$; the capacity decreased to 763 mAh·g$^{-1}$ after 30 cycles. Recently, Mullins et al. studied the lithium storage performances of hydrothermally synthesized single-crystalline α-Fe$_2$O$_3$ nanorods with average diameters of ~40 nm and lengths of ~400 nm. The sample exhibited a stable capacity of ~930 mAh·g$^{-1}$ from the 2nd to the 30th cycle.

Introducing porosity in α-Fe$_2$O$_3$ 1D nanostructures can further boost their electrochemical performances due to their volume change accommodation and strain relaxation abilities. Liu et al. prepared porous single-crystalline α-Fe$_2$O$_3$ nanorod array on Ti foil by a hydrothermal method followed by annealing. The α-Fe$_2$O$_3$ nanorod array could be directly used as additive-free LIB anode, delivering a capacity of 562 mAh·g$^{-1}$ after 50 cycles. Liu, Xu, and co-workers synthesized α-Fe$_2$O$_3$ porous nanorods with diameters of 30–60 nm (Figure 1a) through thermal decomposition of FeC$_2$O$_4$·2H$_2$O nanorods. The α-Fe$_2$O$_3$ porous nanorods delivered a high discharge capacity of 916 mAh·g$^{-1}$ after 100 cycles at 1C (1C = 1000–1007 mAh·g$^{-1}$). Recently, Mao and co-workers fabricated a series of α-Fe$_2$O$_3$ 1D nanostructures, including hierarchical nanotubes, porous nanotubes, and ladder-like nanostructures (Figures 1b, 1c), by a template-engaged redox reaction followed by thermal treatment. The α-Fe$_2$O$_3$ ladder-like nanostructure delivered a stable capacity of over 1100 mAh·g$^{-1}$ at 0.1 C. Even at a high rate of 5C, the sample exhibited a capacity of 645 mAh·g$^{-1}$ after 1200 cycles.

![Figure 1](image_url)  
**Figure 1** SEM image of α-Fe$_2$O$_3$ porous nanorods (a); SEM (b) and TEM (c) images of α-Fe$_2$O$_3$ ladder-like nanostructure; TEM images of α-Fe$_2$O$_3$ nanotubes (d); schematic illustration (e) and TEM image (f) of α-Fe$_2$O$_3$-carbon composite nanofibers constructed by α-Fe$_2$O$_3$ nanobubbles dispersed in an amorphous carbon matrix; digital photo of a flexible α-Fe$_2$O$_3$-SWCNT membrane (g); TEM image of α-Fe$_2$O$_3$-SWCNT (h); TEM image of Fe$_3$O$_4$ nanoparticle filled CNT (i).

Nanotubes with efficient Li$^+$ diffusion channels and sufficient free space for volume expansion have also been demonstrated to be a promising electrode structure. In 2005, Chen’s group studied the lithium storage performances of α-Fe$_2$O$_3$ nanotubes prepared by hard templating. The α-Fe$_2$O$_3$ nanotubes delivered an initial discharge capacity of 1415 mAh·g$^{-1}$; the capacity decreased to 510 mAh·g$^{-1}$ after 100 cycles. Using ZnO nanowire array as the template, Liu and co-workers synthesized vertically aligned α-Fe$_2$O$_3$ nanotubes on alloy substrate through a “sacrificial template-accelerated hydrolysis” approach. This synthetic strategy could be extended to the preparation of α-Fe$_2$O$_3$-So$_2$ nanotube array on stainless steel substrate. The obtained nanotube arrays could function as additive-free LIB anode materials. Using Cu nanowires as the sacrificial templates, Lou et al. prepared α-Fe$_2$O$_3$ nanotubes with diameters of 50–200 (Figure 1d). The as-obtained α-Fe$_2$O$_3$ nanotubes exhibited a high specific capacity of over 1000 mAh·g$^{-1}$ at 0.5 C with excellent cycling stability. Chaudhary and Srinivasa synthesized α-Fe$_2$O$_3$ hollow nanofibers by electrospinning, which showed a high reversible capacity of 1293 mAh·g$^{-1}$ at 0.06 C with good cycling stability.

Composing the 1D α-Fe$_2$O$_3$ nanostructures with conductive carbon would integrate the advantages of both materials, further boosting the lithium storage performance. For example, α-Fe$_2$O$_3$-carbon nanofibers (α-Fe$_2$O$_3$-CNT) were prepared via electrospinning and evaluated as LIB anode materials by different groups. The α-Fe$_2$O$_3$-carbon composite nanofibers prepared by Fan et al. demonstrated a stable capacity of ~820 mAh·g$^{-1}$ at 0.2 C for 100 cycles. The α-Fe$_2$O$_3$-carbon composite nanofibers prepared by Kang’s group were constructed by numerous α-Fe$_2$O$_3$ nanobubbles uniformly dispersed in an amorphous carbon matrix (Figures 1e and 1f). This novel nanostructure delivered a high specific capacity of ~820 mAh·g$^{-1}$ after 300 cycles at 1C. Fe$_3$O$_4$-carbon nanotube (Fe$_3$O$_4$-CNT) composites have also been constructed and evaluated as LIB anode materials. The Fe$_3$O$_4$ nanoparticles can be either decorated on or confined in the CNTs. For example, Li et al. designed an α-Fe$_2$O$_3$ nanoparticle decorated single-walled carbon nanotube (α-Fe$_2$O$_3$-SWCNT) membrane with a high Fe$_2$O$_3$ loading of 88 wt% (Figures 1g and 1h). The α-Fe$_2$O$_3$-SWCNT membrane can function as a flexible, binder-free, and current-collector-free LIB anode, demonstrating a high reversible capacity of 1243 mAh·g$^{-1}$ at 0.05 C and a specific capacity of 801 mAh·g$^{-1}$ after 90 cycles at 0.5 C. Liu et al. constructed an Fe$_3$O$_4$ nanoparticle filled CNT composite (Fe$_3$O$_4$-CNT) with α-Fe$_2$O$_3$ as the major phase and γ-Fe$_2$O$_3$ as the minor phase (Figure 1i). A capacity of 811 mAh·g$^{-1}$ could be achieved after 100 cycles at 0.035 C. The superior electrochemical properties of the Fe$_3$O$_4$-CNT could be attributed to its unique configuration, where the CNT shell not only improved the electronic conductivity but also prevented the aggregation and exfoliation of the Fe$_3$O$_4$ nanoparticles during repeated discharge/charge processes.

**α-Fe$_2$O$_3$ based 2D nanostructures**

2D nanoflakes/nanosheets/nanodiscs are able to expand/contract in the direction parallel to the normal of the basal plane during lithiation/delithiation. In 2006, Chowdari et al. reported the preparation of α-Fe$_2$O$_3$ nanoflakes (Figure 2a) on Cu foil via a thermal treatment method. The α-Fe$_2$O$_3$ nanoflakes exhibited a stable capacity of ~700 mAh·g$^{-1}$ at 0.065 C with no noticeable capacity fading for 80 cycles. Using a solvothermal method with subsequent annealing, Lou et al. grew porous α-Fe$_2$O$_3$ nanosheets (Figure 2b) on various metallic substrates. With highly porous and ultrathin features, the Ti foil supported α-Fe$_2$O$_3$ nanosheets provided a specific capacity of 908 mAh·g$^{-1}$ after 60 cycles at 0.1 C.

Graphene, a typical 2D material with excellent electronic conductivity, high surface area, mechanical robustness, is an ideal component to couple with α-Fe$_2$O$_3$ for volume change accommodation and conductivity improvement. Therefore, α-Fe$_2$O$_3$-graphene nanocomposites have been extensively investigated for lithium storage. As a typical example, Ruoff’s group prepared an α-Fe$_2$O$_3$-reduced graphene oxide composite (α-Fe$_2$O$_3$-RGO), which manifested a reversible capacity of 982 mAh·g$^{-1}$ with good capacity retention. Li et al. constructed a monolithic α-Fe$_2$O$_3$-graphene hybrid (Figures 2c and 2d) by a hydrothermal approach. The resultant hybrid could be directly used as a free-standing LIB anode, providing a specific
Review

capacity of 810 mAh·g$^{-1}$ after 100 cycles at 0.1 C. In another study, Wang et al. designed an α-Fe$_2$O$_3$-CNT-graphene ternary hybrid (Figure 2e) by a chemical vapor deposition (CVD) method.[43] When applied as the anode material for LIBs, the ternary hybrid manifested high specific capacity (984 mAh·g$^{-1}$), superior cyclability, and high rate capability.

α-Fe$_2$O$_3$ based 3D nanostructures

3D porous/hollow/hierarchical structures are able to integrate the advantages of both nanosized primary particles and micron-sized secondary assemblies.[44] Among the various 3D architectures, hollow structures attracted the most attention due to their unique merits of hollow cavity for volume change accommodation, reduced lengths for Li$^+$ diffusion, and abundant lithium storage sites.[45,46] In 2007, the lithium storage properties of α-Fe$_2$O$_3$ hollow spindles and microspheres were reported by Tang and co-workers.[47] Later, Xie’s group reported the anode performance of α-Fe$_2$O$_3$ hollow spheres with a mesoporous shell.[48] In 2009, Song et al. reported a Kirkendall-effect-assisted strategy for the fabrication of α-Fe$_2$O$_3$ (Figures 3a and 3b) and carbon encapsulated α-Fe$_2$O$_3$ (α-Fe$_2$O$_3$@C) hollow nanoparticle.[49] The synthesis generally involved two steps, the preparation of Fe$_3$C@C nanoparticles via co-carbonization and the controlled oxidation of Fe$_3$C@C nanoparticles. During the controlled oxidation, Fe$_3$C@C was converted into either α-Fe$_2$O$_3$@C (280 °C for 5 h) or pure α-Fe$_2$O$_3$ hollow nanoparticle (280 °C for 24 h) through nanoscale Kirkendall effect. The outer semi-graphitic carbon shell could solve the volume expansion and aggregation issues of α-Fe$_2$O$_3$ effectively. As a result, the α-Fe$_2$O$_3$@C hollow nanoparticles demonstrated significantly improved cyclability when compared to the pristine α-Fe$_2$O$_3$ hollow nanoparticles.

Hierarchical hollow spheres constructed by nanosheets/nanoneedles were fabricated and evaluated in LIBs by several groups.[50-53] Lou’s group developed a quasi-emulsion templating method for the synthesis of α-Fe$_2$O$_3$ hollow spheres with sheet-like building blocks, which delivered a capacity of 710 mAh·g$^{-1}$ after 100 cycles at 0.2 C.[50] The same group also performed a comparative study on the lithium storage performances of hollow and solid α-Fe$_2$O$_3$ urchin-like spheres (Figures 3c and 3d).[51] It was found that the hollow α-Fe$_2$O$_3$ urchin-like spheres manifested better electrochemical performances than the solid counterpart in terms of specific capacity and capacity retention. Zhang, Yan, and co-workers prepared α-Fe$_2$O$_3$ hierarchical hollow spheres constructed by ultrathin nanosheets (Figures 3e and 3f) via a sacrificial templating process.[52] The product provided a reversible capacity of 920 mAh·g$^{-1}$, retaining 815 mAh·g$^{-1}$ after 200 cycles. The superior electrochemical performances were ascribed to the synergistic effect of the hollow structure and ultrathin nanosheets. To further boost the electrochemical performances of α-Fe$_2$O$_3$ hierarchical hollow spheres, Hub and co-workers fabricated α-Fe$_2$O$_3$@polyaniline (α-Fe$_2$O$_3$@PANI) core@shell hierarchical hollow spheres (Figures 3g and 3h) through a simultaneous etching and polymerization process.[53] As expected, the α-Fe$_2$O$_3$@PANI core@shell yielded significantly enhanced electrochemical performances in terms of cyclability and rate capability, when compared to pristine urchin-like α-Fe$_2$O$_3$ hierarchical hollow spheres.

Figure 2  SEM image of α-Fe$_2$O$_3$ nanoflakes on Cu foil (a),[40] SEM image of α-Fe$_2$O$_3$ nanosheets on Ti foil (b),[47] digital photo of the monolithic α-Fe$_2$O$_3$-graphene hybrid (c), SEM image of the α-Fe$_2$O$_3$-graphene hybrid (d),[48] SEM image of the α-Fe$_2$O$_3$-CNT-graphene ternary composite (e).[53]

Figure 3  TEM images of α-Fe$_2$O$_3$ hollow nanoparticles (a),[60] SEM (c) and TEM (d) images of hollow α-Fe$_2$O$_3$ urchin-like spheres,[61] SEM (e) and TEM (f) images of α-Fe$_2$O$_3$ hierarchical hollow spheres constructed by ultrathin nanosheets,[72] SEM (i), TEM (j) images and cycling performances of α-Fe$_2$O$_3$ multi-shelled hollow spheres.[74]

Despite the multiple merits, hollow structures usually suffer from low tap density, which would sacrifice the volumetric energy density when applied in LIBs. In this regard, multi-shelled hollow structures are advantageous over the single-shelled counterparts. Recently, Zhou et al. developed a simple spray drying method for the preparation of α-Fe$_2$O$_3$ multi-shelled hollow spheres using cheap, widely available iron nitrate and sucrose as the only precursors.[54,55] The obtained α-Fe$_2$O$_3$ presented a unique quadruple-shelled hollow spherical structure with sizes of 300–3000 nm (Figures 3i and 3j). The non-equilibrium heat treatment induced heterogeneous contraction was responsible for the formation of the multi-shelled hollow structures. When evaluated as the LIB anode material, the α-Fe$_2$O$_3$ MSHHSs delivered stable high capacities of 1000 and 900 mAh·g$^{-1}$ with no noticeable capacity fading up to 50 cycles at 0.4 and 1.6 C, respectively (Figure 3k). Similar α-Fe$_2$O$_3$ multi-shelled hollow structures could be achieved by hard templating[56] and spray pyrolysis.[57]

Other α-Fe$_2$O$_3$-based 3D architectures employed in LIBs include mesoporous α-Fe$_2$O$_3$,[58,59] porous α-Fe$_2$O$_3$,[60,61] α-Fe$_2$O$_3$@graphitic carbon microspheres,[62] α-Fe$_2$O$_3$@C hierarchical tubular structures,[63] α-Fe$_2$O$_3$@C hollow nanohorns on CNT (Figure 4b),[64] hierarchical SnO$_2$-Fe$_2$O$_3$ heterostructures,[65] hierarchical TiO$_2$@α-Fe$_2$O$_3$ hollow structures (Figure 4c),[66] branched TiO$_2$-β-(α-Fe$_2$O$_3$) heterostructures (Figure 4d),[67] branched SnO$_2$@α-Fe$_2$O$_3$ heterostructures (Figure 4e),[68] and branched β-MnO$_2$@α-Fe$_2$O$_3$ heterostructures (Figure 4f).[69] All these 3D architectures demonstrated impressive lithium storage performances.
Tailoring Iron Oxide Nanostructures

γ-Fe$_2$O$_3$ based anode materials

γ-Fe$_2$O$_3$ adopts a cubic crystal structure with Fd3m space group. In the unit cell, the Fe$^{3+}$ ions occupy the octahedral 16d and tetrahedral 8a sites with different chemical states. Compared to the numerous publications on α-Fe$_2$O$_3$ based anode materials, the reports on γ-Fe$_2$O$_3$ based anode materials are much less, probably due to its poor stability.

Gamma-Fe$_2$O$_3$ based 1D nanostructures

The 1D γ-Fe$_2$O$_3$ based anode materials include Fe$_2$O$_3$ nanotubes, Fe$_2$O$_3$-CNT hybrids, and γ-Fe$_2$O$_3$-carbon nanofiber. Son reported the synthesis of 1D Fe$_2$O$_3$ nanotubes (γ-Fe$_2$O$_3$ as the dominant phase and α-Fe$_2$O$_3$ as the minor phase) with particulate walls using microporous organic tubes as the templates. The Fe$_2$O$_3$-NT nanocomposite showed a specific capacity of 786 mAh·g$^{-1}$ after 40 cycles. Cheng and co-workers fabricated two types of γ-Fe$_2$O$_3$-CNT hybrids, γ-Fe$_2$O$_3$ nanoparticle-filled CNT (Figure 5a) and γ-Fe$_2$O$_3$ nanoparticle-coated CNT (Figure 5b). The γ-Fe$_2$O$_3$ nanoparticle-coated CNT with an Fe$_2$O$_3$ mass ratio of 45% exhibited a reversible capacity of 1092 mAh·g$^{-1}$ at 50 mAh·g$^{-1}$, the capacity decreased to 867 mAh·g$^{-1}$ after 16 cycles. Meanwhile, the γ-Fe$_2$O$_3$ nanoparticle-filled CNT with a Fe$_2$O$_3$ weight ratio of 20% delivered a reversible capacity of 1144 mAh·g$^{-1}$, the capacity tended to stabilize at 964 mAh·g$^{-1}$ after 16 cycles. By combining electropinning, hydrothermal treatment, and post annealing, Reddy et al. fabricated a γ-Fe$_2$O$_3$-carbon nanofiber hybrid. At a current density of 50 mAh·g$^{-1}$, the γ-Fe$_2$O$_3$-CNF hybrid delivered a specific capacity of 830 mAh·g$^{-1}$ after 40 cycles.

γ-Fe$_2$O$_3$ based 2D nanostructures

The reports on γ-Fe$_2$O$_3$ based 2D nanostructured anodes are relatively rare. Lee et al. reported a γ-Fe$_2$O$_3$-C porous microdisc anode material (Figure 5c). The synthesis involved two steps: hydrothermal synthesis of α-Fe$_2$O$_3$ porous discs and CVD post-treatment in acetylene atmosphere. During the CVD treatment, the α-Fe$_2$O$_3$ was converted into γ-Fe$_2$O$_3$ and a thin carbon shell was coated onto the surface of the sample. The combination of abundant porosity and thin carbon coating provided fast diffusion for both Li$^+$ and electrons. A high capacity of over 900 mAh·g$^{-1}$ could be achieved after 40 cycles at 0.1 C. A γ-Fe$_2$O$_3$-RGO composite was fabricated by Yushin and co-workers (Figure 5d). The γ-Fe$_2$O$_3$-RGO composite exhibited a high specific capacity of 900 mAh·g$^{-1}$ after 100 cycles at 0.5 C.

γ-Fe$_2$O$_3$ based 3D nanostructures

A variety of γ-Fe$_2$O$_3$ based 3D architectures have been applied in lithium storage, including γ-Fe$_2$O$_3$ microspheres, N-doped carbon coated γ-Fe$_2$O$_3$ spheres (Figure 5e), γ-Fe$_2$O$_3$ hollow nanoparticles, Fe$_2$O$_3$-C hollow microboxes (Figure 5f), hollow γ-Fe$_2$O$_3$@graphene core@shell hybrid, polypyrrole coated γ-Fe$_2$O$_3$-ordered mesoporous carbon, and double-shelled Fe$_2$O$_3$-Co$_3$O$_4$ hollow microcubes. For example, monodisperse γ-Fe$_2$O$_3$ mesoporous spheres were fabricated by a surfactant-free solvothermal method with subsequent thermal transformation. The resultant γ-Fe$_2$O$_3$ mesoporous spheres with an average diameter of 6 μm were composed of numerous irregular shaped nanoparticles. When explored as the anode material for LIBs, the γ-Fe$_2$O$_3$ mesoporous microspheres exhibited a high initial capacity of 1453 mAh·g$^{-1}$, retaining 700 mAh·g$^{-1}$ after 110 cycles. Ding and co-workers designed a N-doped carbon γ-Fe$_2$O$_3$ sphere anode (Figure 5e) with high specific capacity, stable cycling, and excellent rate capability. A high capacity of 870 mAh·g$^{-1}$ could be achieved after 150 cycles at 0.5 C. Lu’s group designed a delicate polypyrrole coated γ-Fe$_2$O$_3$-ordered mesoporous carbon composite. Ordered mesoporous carbon was firstly synthesized via a nanocasting method, and γ-Fe$_2$O$_3$ nanoparticles were then loaded into the mesoporous carbon through wet impregnation and thermal decomposition. The polypyrrole coating was achieved by vapor-phase polymerization. When applied as the LIB anode, this novel nanocomposite delivered a capacity of 785 mAh·g$^{-1}$ after 100 cycles at 0.2 C. The superior anode performance could be ascribed to the synergistic effect of mesoporous carbon matrix and polypyrrole sealing layer.

Magnetite based anode materials

Fe$_3$O$_4$ has an inverse spinel crystal structure. Compared to α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$, Fe$_3$O$_4$ possesses significantly enhanced electronic conductivity, which is only an order of magnitude lower than the minimum metallic conductivity. Theoretically, each formular of Fe$_3$O$_4$ may react with 8 Li$^+$, giving rise to a high capacity of 926 mAh·g$^{-1}$. 

Figure 4  SEM image of α-Fe$_2$O$_3$@C hierarchical tubular structures (a), TEM image of α-Fe$_2$O$_3$@C hollow nanohorns on CNT (b), SEM image of TiO$_2$@α-Fe$_2$O$_3$ hollow structures (c), TEM image of branched TiO$_2$@α-Fe$_2$O$_3$ heterostructures (d), SEM image of branched SnO$_2$@α-Fe$_2$O$_3$ heterostructures (e), SEM image of branched β-MnO$_2$@α-Fe$_2$O$_3$ heterostructures (f).

Figure 5  TEM images of γ-Fe$_2$O$_3$ nanoparticle-filled CNT (a) and γ-Fe$_2$O$_3$ nanoparticle-coated CNT (b), SEM image of γ-Fe$_2$O$_3$-C porous microdiscs (c), TEM image of γ-Fe$_2$O$_3$-graphene composite (d), SEM image of N-doped carbon coated γ-Fe$_2$O$_3$ spheres (e), SEM image of Fe$_2$O$_3$ hierarchical hollow microbox (f).
FeO$_4$-based 0D nanostructures

Important progress has been made in the synthesis and lithium storage performance of FeO$_4$ based nanoparticles during the last decade.[108-113] For example, Guo, Song, and co-workers developed a beaker-in-autoclave setup for the synthesis of highly disperse FeO$_4$ nanoparticles.[108] Although the obtained FeO$_4$ nanoparticles exhibited a reversible capacity of over 600 mAh·g$^{-1}$, the capacity decreased to 30 mAh·g$^{-1}$ after only 30 cycles. After carbon encapsulation, the cycling performance could be significantly enhanced; a stable capacity of above 600 mAh·g$^{-1}$ could be achieved. In another example, Zhao et al. fabricated carbon nanosphere (~60 nm) encapsulated FeO$_4$ nanocrystals (~9 nm) through a facile hydrothermal treatment-annealing process (Figure 6a).[9] The composite nanospheres manifested high specific capacities of 784, 568, and 379 mAh·g$^{-1}$ at 1, 5, and 10 C (1 C = 924 mA·g$^{-1}$), respectively.

![Figure 6](image_url) TEM image and schematic structure (inset) of carbon nanosphere encapsulated FeO$_4$ nanocrystals (a).[9] TEM images of FeO$_4$@C core-shell nanospheres (b), chains (c), and rings (d).[113]

Due to their interesting ferromagnetic properties, the 0D FeO$_4$ based nanoparticles can be further assembled into chains and rings.[112,113] Wang, Su, and co-workers synthesized monodisperse FeO$_4$@C core-shell spheres (Figure 6b) using eccentric FeO$_4$@poly(acrylic acid) core-shell nanoparticles as the precursor.[113] By adjusting the reaction temperature and time, FeO$_4$@C core-shell chains (Figure 6c) and rings (Figure 6d) could also be obtained. When tested as anode materials for LIBs, the FeO$_4$@C core-shell chains and rings delivered capacities of 780–800 mAh·g$^{-1}$ after 100 cycles at 200 mA·g$^{-1}$, much higher than that of FeO$_4$@C core-shell nanospheres.

FeO$_4$-based 1D nanostructures

More than a decade ago, FeO$_4$ had been electrochemically deposited onto Cu nanorod arrays for lithium storage.[107] The self-supported Cu-nanorod FeO$_4$ electrode demonstrated excellent rate capability. When compared to planar electrodes, the power density could be improved by a factor of six. Since then, much attention has been paid to 1D FeO$_4$ based nanostructures for lithium storage.[114-121] FeO$_4$ based 1D nanofibers/nanotubes can be facilely prepared via electrospinning.[122-126] Chen et al. prepared FeO$_4$-C composite nanofibers via electrospinning ferric acetylacetonate and polyacrylonitrile (PAN) with subsequent annealing.[121] A high specific capacity of 1007 mAh·g$^{-1}$ could be obtained after 80 cycles at 200 mA·g$^{-1}$. The electrospinning technique can be easily extended to the fabrication of FeO$_4$-C hollow nanofibers[123,124], FeO$_4$-TiO$_2$ nanofiber[125], and N-doped amorphous carbon coated FeO$_4$-SnO$_2$ coaxial nanofibers (Figure 7a).[126]

Carbon nanotubes (CNTs) have been extensively used as the backbone material to construct FeO$_4$ based 1D nanostructures.[127-131] For example, Dillon et al. designed a binder-free FeO$_4$ nanorod-SWCNT electrode (Figure 7b) through a two-step vacuum filtration-reduction process.[127] Impressively, the binder-free electrode with 95 wt% FeO$_4$ and 5 wt% SWCNT demonstrated high reversible capacities of ~1000, 800, and 600 mAh·g$^{-1}$ at 1, 5, and 10 C, respectively. By integrating CNT drawing and magnetron sputtering, Wang et al. obtained FeO$_4$-CNT electrodes.[128] The FeO$_4$ nanoparticles with sizes of 5–7 nm were uniformly sputtered on aligned CNTs, forming a core-sheath structure (Figures 7c and 7d). The free-standing FeO$_4$-CNT electrode delivered a specific capacity of over 800 mAh·g$^{-1}$ based on the total mass of the electrode. Benefiting from the outstanding electronic conductivity of CNTs, the electrode also demonstrated excellent rate capability.

![Figure 7](image_url) SEM and TEM (inset) images of N-doped amorphous carbon coated FeO$_4$-SnO$_2$ coaxial nanofibers (a);[126] colorized SEM image of FeO$_4$ nanorod-SWCNT composite (b);[127] TEM images of core-sheath structured FeO$_4$-CNT composites (c, d).[128] SEM image and schematic illustration of FeO$_4$-TiO$_2$-C composite nanofibers (e);[132] and TEM image of porous FeO$_4$-VO$_2$-graphene ternary nanowires (f).[136]

Cellulose nanofibers and other 1D nanostructures can also be employed as the scaffold material or sacrificial templates to prepare 1D FeO$_4$ based nanofibers/nanowires/nanotubes.[123-134] Huang et al. constructed FeO$_4$-TiO$_2$-C composite nanofibers (Figure 7e) by employing natural cellulose as the scaffold.[123] The ternary composite exhibited a stable capacity of ~525 mAh·g$^{-1}$ at 100 mA·g$^{-1}$. By anchoring FeO$_4$ nanoparticles on bacterial cellulose nanofiber followed by carbonization, Luo and co-workers obtained a flexible, binder-free FeO$_4$-carbon nanofiber electrode.[133] By electrochemical deposition of FeO$_4$ on CuO nanoneedle arrays, Yan et al. obtained coaxial CuO/FeO$_4$ hybrid nanowire electrode.[134] Lu’s group reported the synthesis of carbon coated FeO$_4$ nanotubes by using α-MoO$_3$ nanorods as the hard template.[135] An et al. synthesized porous FeO$_4$-amorphous vanadium oxide-graphene (FeO$_4$-VO$_2$-graphene) ternary nanowires (Figure 7f) by reducing graphene decorated iron vanadate (FeVO$_2$-1.1H$_2$O) nanowires in 5%/95% H$_2$/Ar.[136]
Fe$_3$O$_4$-based 2D nanostructures

Fe$_3$O$_4$-graphene nanocomposite is the most extensively studied Fe$_3$O$_4$-based 2D nanostructures. In 2010, Cheng’s group designed a graphene nanosheets wrapped Fe$_3$O$_4$ anode. In the constructed Fe$_3$O$_4$-graphene composite, the graphene nanosheets not only buffered the volume change of Fe$_3$O$_4$, but also reduced the restacking of graphene; meanwhile, the porosity between Fe$_3$O$_4$ and graphene provided efficient Li$^+$ diffusion channels. As a result, the resultant Fe$_3$O$_4$-graphene nanocomposite delivered a specific capacity of 580 mAh g$^{-1}$ after 100 cycles at 700 mA g$^{-1}$ (Figure 8c). More recently, an intriguing Fe$_3$O$_4$-graphene ternary composite was reported by Liu, Xie, and co-workers (Figures 8d and 8e). The Fe$_3$O$_4$-TiO$_2$-Graphene ternary composite delivered a reversible capacity of $\approx 330$ mAh g$^{-1}$ at 1000 mA g$^{-1}$ (Figure 8f).

Fe$_3$O$_4$-based 3D nanostructures

Due to their multiple structural merits, Fe$_3$O$_4$-based hollow structures, such as hollow spheres and hollow cubes, have demonstrated promising lithium storage performances. As a typical example, Lou et al. prepared uniform Fe$_3$O$_4$ hierarchical hollow spheres comprised of nanoplate building blocks (Figures 9a and 9b) by an ethylene glycol-mediated solvothermal method. The product delivered a reversible capacity of 640 mAh g$^{-1}$ at 200 mA g$^{-1}$, retaining 580 mAh g$^{-1}$ after 100 cycles (Figure 9c). In another study, the same group synthesized monodisperse Fe$_3$O$_4$ hollow spheres organized by ultrathin nanosheets (Figures 9d and 9e), which demonstrated a high reversible capacity of 1046 mAh g$^{-1}$ without noticeable capacity fading over 100 cycles. Such unique structures also led to remarkable rate capability, showing capacities of 992, 853, 716, and 548 mAh g$^{-1}$ at 1, 2, 4, and 8 A g$^{-1}$, respectively (Figure 9f).

With desirable free spaces for volume change accommodation, yolk@shell structures have also been fabricated to boost the electrochemical performances of Fe$_3$O$_4$. Guan et al. constructed Fe$_3$O$_4$@C yolk@shell spheres (Figure 10a) showing a specific capacity of 680 mAh g$^{-1}$ at 5 A g$^{-1}$. Paik et al. reported the synthesis of Fe$_3$O$_4$@C yolk-shell microrods (Figure 10b) via an “etching-in-a-box” strategy. The Fe$_3$O$_4$@C yolk-shell boxes with an optimized etching time of 2 h demonstrated the best anode performance in terms of specific capacity, cycling stability, and rate capability. Guo et al. designed a novel yolk@shell structure with a Fe$_3$O$_4$@Fe$_3$C core@shell yolk and a carbon nanospindle shell (Figure 10c). This intricate yolk@shell structure demonstrated significantly enhanced electrochemical performances when compared to bare Fe$_3$O$_4$ and Fe$_3$O$_4$@C core-shell structures. To study the effects of void size on the electrochemical performances, Yu, Zhou, and co-workers prepared a series of Fe$_3$O$_4$@C yolk@shell structures (Fe$_3$O$_4$ as the dominant phase) with tailored void space (Figure 10d). Only with an optimized void size, the Fe$_3$O$_4$@C yolk@shell structures demonstrated the best cycling performance (Figure 10e).
FeO₃-based hierarchical structures also demonstrate high lithium storage performances. Long, Ling, and co-workers reported the preparation of FeO₃-C micro-flowers constructed by nano flakes (Figures 11a and 11b). The FeO₃-C micro-flowers delivered high specific capacities of 920–1030 mAh·g⁻¹ for 150 cycles. Hyeon et al. reported a bottom-up self-assembly approach for the fabrication of FeO₃-C hierarchical spheres comprised of nanoparticles (11–12 nm). Compared to random FeO₃ nanoparticle aggregates, the assembled hierarchical spheres demonstrated better cyclability and higher Coulombic efficiency.

Porous carbon materials are considered as an ideal host material to encapsulate electrochemically active FeO₃ for lithium storage. By coating α-Fe₃O₄ nanospheres with glucose-derived carbon-rich polysaccharide followed by carbothermal reduction, carbon coated FeO₃ nanoparticles (FeO₃@C) were prepared by Wan, Guo, and co-workers (Figure 11c). By chemical vapor deposition of acetylene on α-Fe₃O₄ nanorods, Zhu et al. obtained FeO₃@C nanorings (Figure 11d); during the CVD, carbon deposition and α-Fe₃O₄ reduction occurred simultaneously. Through a hydrothermal method followed by carbonization, Xue et al. prepared mesoporous carbon sphere encapsulated FeO₃ nanoparticles (Figure 11e). By impregnating Fe(NO₃)₃ into mesoporous carbon via a “host-guest” approach, Lee, Kim, and co-workers synthesized mesoporous carbon foam encapsulated FeO₃ nanocrystals (Figure 11f). All these FeO₃-porous carbon nanocomposites demonstrated superior electrochemical lithium storage performances. Especially, the FeO₃ nanoparticle embedded in mesoporous carbon spheres exhibited stable capacities for 290 cycles at various current densities ranging from 0.5–10 A·g⁻¹.

**Conclusions**

This review provides a comprehensive summary on the nanostructure engineering of iron oxides (FeO₃, FeO₂, and γ-Fe₂O₃) for high-capacity lithium storage. Various iron oxide nanostructures, including 0D nanoparticles, 1D nanowires/nanorods/nanofibers/nanotubes, 2D nanoflakes/nanosheets, as well as 3D porous/hollow/hierarchical architectures, have been constructed for lithium storage. These delicate nanostructures show not only reduced ion/electron diffusion lengths but also sufficient free space for volume change accommodation and strain relaxation, leading to enhanced cycling stability and rate capability. Moreover, the combination of nanostructured iron oxide with conductive carbon integrates the advantages of both components, further boosting the structural stability and electrochemical performances.

**References**

Tailoring Iron Oxide Nanostructures


www.genchemistry.org 179