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ARTICLE TYPE

Fe₂O₃@SnO₂ Nanoparticles Decorated Graphene Flexible Films as High-performance Anode Material for Lithium-ion Batteries

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A flexible graphene film decorated with spindle-like Fe₂O₃@SnO₂ nanoparticles was fabricated through vacuum filtration of Fe₂O₃@SnO₂ and GO mixing solution, followed by thermal reduction. The core-shell structured Fe₂O₃@SnO₂ nanoparticles were synthesized through a facile hydrothermal route, which avoided agglomeration of Fe₂O₃ and SnO₂ nanoparticles and was beneficial for electrolyte diffusion. Microstructure characterizations showed that the spindle-like Fe₂O₃@SnO₂ nanoparticles were uniformly dispersed between layered graphene nanosheets, forming a sandwich-like structure. The unique interleaved structure was favorable for lithium ion diffusion and electron transfer. As binder-free electrodes for lithium-ion batteries, the flexible Fe₂O₃@SnO₂/GS films exhibited discharge and charge capacities of 2063 and 1255 mA h g⁻¹ respectively, with excellent cycling performance of 1015 mA h g⁻¹ even after 200 cycles. The specific capacity of Fe₂O₃@SnO₂/GS electrode is higher than that of both Fe₂O₃/GS and SnO₂/GS electrodes, indicating a positive synergistic effect of Fe₂O₃ and SnO₂ on the improvement of electrochemical performance.

Introduction

With the rapid development of portable electronics and hybrid electric vehicles, high performance electric energy storage devices are urgently needed¹⁻⁵. Lithium-ion batteries have attracted worldwide attention as the dominant energy storage devices due to their convenience in operation, but they suffer from limited gravimetric capacity of the electrode materials. For instance, the gravimetric capacity of standard commercialized carbon-based anode material is only about 372 mA h g⁻¹, which can't meet the demand for high efficiency energy storage. In recent decades, transition-metal oxides, such as Co₃O₄⁶, Fe₂O₃⁷, MnO₂⁸ and SnO₂⁹ *et al*, have received tremendous interests as anode materials for Lithium-ion batteries due to their high theoretical specific capacity. Among these materials, Fe₂O₃ is especially attractive because of its abundance in natural resources and low cost. However, just like other transition-metal oxide electrode materials, the tremendous volume change associated with Li-ion insertion/extraction often leads to the pulverization and subsequent fall off of the active material from the electrode, resulting in significant capacity fading. Although the use of nanosized materials can effectively accommodate the volume change induced strain and to some extent alleviate this problem, capacity fading is still inevitable in long term cycling, because of the electrochemical aggregation effect of the nanoparticles. This together with the poor electrical conductivity of the material seriously limits the cyclability and rate performance improvement of the electrode, being the major drawback to hinder its practical application.

In order to address the above issues, several strategies have been taken. One strategy is to combine Fe₂O₃ with other metal oxides to form hybrid nanostructures, such as Fe₂O₃@SnO₂

nanocapsules¹⁰, Co₃O₄/Fe₂O₃ nanowires^{11, 12}, Fe₂O₃@NiO nanorods¹³ and TiO₂@Fe₂O₃ nanoarrays^{14, 15}. The formation of such hybrid nanostructures can effectively prevent Fe₂O₃ nanoparticles from electrochemical aggregation, shorten the Li⁺ insertion/extraction pathways^{11, 16, 17} and well accommodate the strain accompanied with volume change. Many researches indicated that the synergistic effects of the above factors can lead to a significant improvement in cyclability and capacity of the material.

Another strategy for electrochemical performance improvement of Fe₂O₃ is to integrate it with an electrical conducting matrix such as amorphous carbon¹⁸⁻²⁰, graphene^{21, 22} or carbon nanotubes (CNTs)^{23, 24} to enhance the structural stability and electric conductivity of the electrode. Particularly, graphene is an ideal electrical conducting matrix, owing to its high theoretical specific area, excellent electronic conductivity and remarkable mechanical flexibility²⁵⁻²⁸. Nowadays, the integration of graphene with transition metal oxides for use as Li-ion battery electrode has been intensively studied with many promising results^{6, 29-35}. Ruoff and Guo found that a rational combination of graphene with Fe₂O₃ could greatly improve the electrical conductivity and structural stability of the electrode, leading to significant improvement in its electrochemical performances^{36, 37}. What's more interesting, due to the high aspect ratio and mechanical flexibility of graphene, the graphene/transition metal oxide hybrid materials can be made into free-standing films and directly used as Li-ion battery electrodes³⁸⁻⁴². In comparison with conventional electrodes with metal current collectors, such electrodes show much reduced weight, which is very helpful for increase the capacity to weight ratio of the electrode.

In the present work, Li-ion battery anode based on core-shell

structured $\text{Fe}_2\text{O}_3@\text{SnO}_2$ hybrid nanoparticle decorated graphene film was designed through a combination of the above two strategies. We hope that the combination of nanoparticle hybridization and graphene incorporation may result in a synergistic effect in further improving the electrical performance of the material. According to this design concept, free-standing $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ films electrodes were prepared by vacuum filtration of $\text{Fe}_2\text{O}_3@\text{SnO}_2$ spindle-like nanoparticle and graphene oxide (GO) mixing solution, followed by thermal reduction. It was found that the spindle-like $\text{Fe}_2\text{O}_3@\text{SnO}_2$ nanoparticles were uniformly distributed among graphene sheet (GS) layers, forming a sandwich-like structure. Due to the strong interaction between the SnO_2 shell and the Fe_2O_3 core as well as the GS conductivity enhancing agent, the electrochemical performance of the electrode was remarkably improved. It showed a high stable capacity of more than 1000 mA h g^{-1} over 200 charge/discharge cycles along with good rate capability.

Experimental

Material synthesis

All chemicals used were analytical grade without further purification. The fabrication process involves: (1) synthesis of $\text{FeOOH}@\text{SnO}_2$ nanospindles; (2) fabrication of $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ film.

Synthesis of $\text{FeOOH}@\text{SnO}_2$: Nanospindle-like FeOOH precursor was synthesized based on a previously reported hydrolysis method.⁴³ SnO_2 porous shell was coated on the surface of FeOOH by a simple surfactant-free hydrothermal method. Specifically, 0.085g FeOOH was dispersed in a mixing solution of 20 mL distilled water and 30 mL ethanol, then 0.115 g $\text{Na}_2\text{SnO}_3 \cdot 4\text{H}_2\text{O}$ and 0.75 g urea were successively added. After ultrasonication for an hour, the resulting solution was transferred into a Teflon-lined stainless steel autoclave and kept at 170°C for 36 h, then cooled down to room temperature. The resulting $\text{FeOOH}@\text{SnO}_2$ nanoparticles were collected by centrifugation, washed with distilled water and dried at 50°C for 4 h in vacuum.

Fabrication of $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ film: Aqueous GO solution with GO concentration of 0.9 wt% was prepared by a modified Hummer's method⁴⁴. $\text{FeOOH}@\text{SnO}_2$ solution was prepared by dispersing $\text{FeOOH}@\text{SnO}_2$ into water. With the aid of magnetic stirring, an appropriate amount of GO solution was added into the $\text{FeOOH}@\text{SnO}_2$ solution to form a mixing solution, which was then further dispersed through ultrasonication for 5 minutes using a Sonifier (SK250HP, 52Hz). Afterwards, 15 ml of the mixing solution was vacuum filtered using inorganic filter paper with pore diameter of 220 nm. The deposit was dried and peeled off from the filter paper to get a $\text{FeOOH}@\text{SnO}_2/\text{GO}$ film. Finally, the film was annealed at 500°C in Ar flow for 2 h to convert it into $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ film. To optimize the electrochemical performance of the film, the mass proportion of graphene in the film was controlled at $\sim 40\%$. For comparison, $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS films were also fabricated by replacing $\text{FeOOH}@\text{SnO}_2$ with FeOOH and SnO_2 , respectively, according to the same fabrication procedure above.

Characterization

Morphologies of samples were characterized by scanning electron microscopy (SEM, JSM-6700F) at an acceleration voltage of 10.0 kV. Transmission electron microscopy (TEM,

JEM-2100F, JEOL, Tokyo, Japan) was operated at an acceleration voltage 200 keV. X-ray diffraction (XRD) was carried out on a D/max 2550 V diffractometer with $\text{Cu-K}\alpha$ irradiation at $\lambda=1.5406 \text{ \AA}$. Thermal gravimetric analysis (TGA) was conducted in air using Du Pont Instruments TGA 2950 from room temperature to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$. Raman spectroscopy was recorded on a DXR Raman Microscope with a 532 nm excitation length, Thermal Scientific Corporation, USA. X-ray photoelectron spectroscopy (XPS) analysis was conducted in the region of 0-1200 eV using a $\text{Mg K}\alpha$ (1253.6 eV) monochromatic X-ray source (Axis Ultra DLD, Kratos). N_2 adsorption/desorption isotherms were determined using a Micromeritics ASAP2010 Analyzer (USA).

Electrochemical measurements

The synthesized $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ films were directly used as working electrodes without any binder and additive. For electrochemical performance testing, the $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ films were dried in vacuum at 120°C for 2h and assembled into CR 2025 type coin cells with lithium metal as counter electrodes. Mass loading of the film electrode was controlled at about $\sim 1.9 \text{ mg cm}^{-2}$, including graphene and the metal oxides. The specific capacity was calculated based on the total mass of the electrode. Cyclic voltammetry (CV) was carried out in the voltage range of 0-3.0 V with a scan rate of 0.5 mV s^{-1} . The galvanostatic discharge-charge was characterized on a CT2001 battery tester. Electrochemical impedance spectroscopy (EIS) measurements of cells were performed on a CHI660D electrochemical workstation with a sine wave of 5 mV over a frequency range of 100 kHz-0.01 Hz. Cells were assembled in an Ar-filled glovebox with concentrations of moisture and oxygen below 1.0 ppm. The electrolyte used was LiPF_6 (1.0 M) in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume).

Results and discussion

Fig. 1 shows the SEM and TEM images of the FeOOH and $\text{FeOOH}@\text{SnO}_2$ nanoparticles. The FeOOH nanoparticles were spindle-like in morphology and highly dispersed (Fig. 1a). The diameter and length of the nanospindles were about 40-70 nm and 200-400 nm, respectively. After hydrothermal treatment in Na_2SnO_3 and urea mixing solution, SnO_2 layer of 10-12 nm in thickness was uniformly coated on the FeOOH particle surface, forming a core-shelled structure. The core-shell structured $\text{FeOOH}@\text{SnO}_2$ nanoparticle well inherited the spindle-like morphology of FeOOH (Fig. 1b). However, its specific surface area ($96 \text{ m}^2 \text{ g}^{-1}$) showed a great increase over that of FeOOH ($39 \text{ m}^2 \text{ g}^{-1}$, Fig.S1, Supporting Information), because of the coating of extremely fine SnO_2 nanoparticles on its surface, which were less than 5 nm in size.

In order to deep understand the microstructure of the core-shelled $\text{FeOOH}@\text{SnO}_2$ nanoparticles, high resolution TEM (HRTEM) and selected area electron diffraction (SAED) were conducted at the core/shell interface region marked by a square in Fig. 1d. The HRTEM image was shown in Fig. 1e. For the core, only one kind of lattice fringe could be observed and the typical spacing of the adjacent lattice planes was 0.52 nm, corresponding to the (200) crystal plane of FeOOH . For the shell, two kinds of lattice fringes with interplanar spacings of 0.33 nm and 0.26 nm were observed, which were in good accordance with the (110)

and (101) crystal planes of tetragonal SnO₂. In corresponding, selected area electron diffraction of the core-shell interface region showed two sets of diffraction patterns formed by bright diffraction spots and diffraction rings, respectively. The sharp diffraction spots were attributed to the spindle FeOOH, while the bright diffraction rings originated from SnO₂ nanoparticles. Both the HRTEM and SAED results indicated a well crystallinity of the core-shelled FeOOH@SnO₂ nanoparticle in the whole, with the FeOOH core being single crystal in nature.

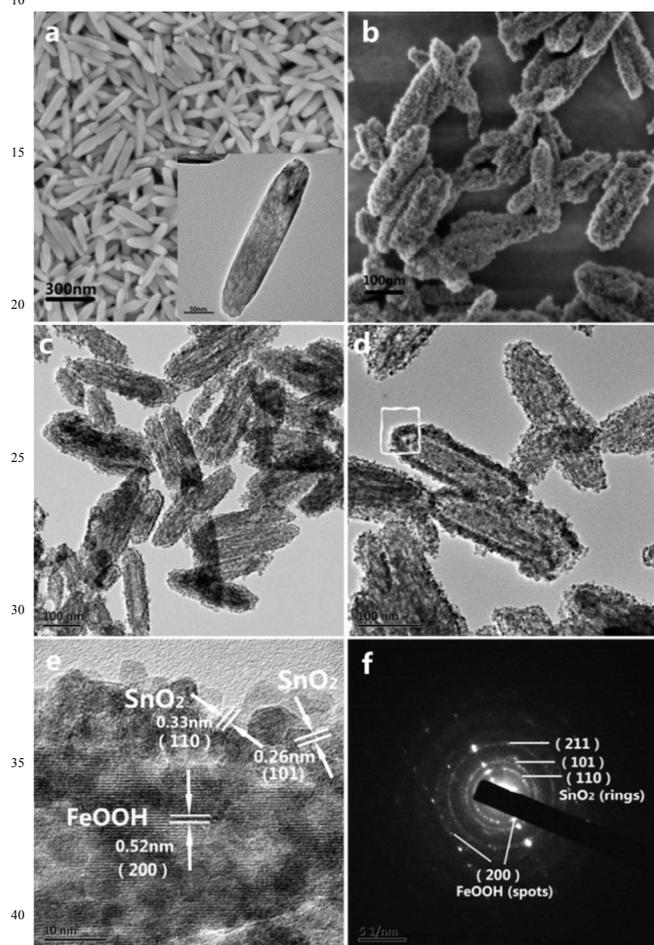


Fig. 1 (a) SEM image of FeOOH nanoparticle; the inset in (a) corresponds to TEM image of FeOOH. (b) SEM image of FeOOH@SnO₂; (c) TEM image of FeOOH@SnO₂; (d) magnified TEM image of FeOOH@SnO₂; (e) HRTEM image of FeOOH@SnO₂; (f) SAED pattern of FeOOH@SnO₂.

Based on the successful synthesis of FeOOH@SnO₂ nanospindles, two dimensional Fe₂O₃@SnO₂/GS films were fabricated according to the fabrication procedure illustrated in Scheme 1. In brief, the FeOOH@SnO₂ nanospindles were mixed with GO solution, and vacuum-filtered to obtain a flexible free-standing FeOOH@SnO₂/GO film. Finally, the FeOOH@SnO₂/GO was reduced to Fe₂O₃@SnO₂/GS by a simple annealing treatment. Owing to the outstanding dispersibility of FeOOH@SnO₂ nanoparticles in GO solution (Fig. S2), flexible Fe₂O₃@SnO₂/GS films could be successfully obtained, and the spindle-like morphology of FeOOH@SnO₂ nanoparticles allowed

for their proper orientation in the graphene films⁴⁵.

The phase assemblages of the products before and after thermal reduction were characterized by XRD (Fig. 2). As expected, the tetragonal FeOOH (JCPDS 75-1594) transformed to Fe₂O₃ (JCPDS 33-0664) after the annealing process, whereas the crystal structure of SnO₂ nanoparticles remained unchanged (Tetragonal, JCPDS 71-0652). Importantly, no diffraction peak characteristic of restacked graphene nanosheets was found at about 25°, indicating the uniform dispersion of graphene nanosheets in the 2D film. SEM cross-section views and top views (Fig. 3) of the Fe₂O₃@SnO₂/GS film showed that the spindle-like morphology of FeOOH@SnO₂ nanoparticles were well preserved after its reduction to Fe₂O₃@SnO₂, as also demonstrated by TEM images in Fig. S3a-b. The Fe₂O₃@SnO₂/GS film took a sandwich-like structure and was about 14 μm in thickness. Fe₂O₃@SnO₂ particles were uniformly embedded within the graphene layers and hereby expanded the interspacing of neighboring graphene layers. Such a structure was helpful for preventing graphene layers from agglomeration and would greatly facilitate electrolyte diffusion when it was used as anode in Li-ion batteries.



Scheme 1 Schematic illustration of the synthesis process of Fe₂O₃@SnO₂/GS film.

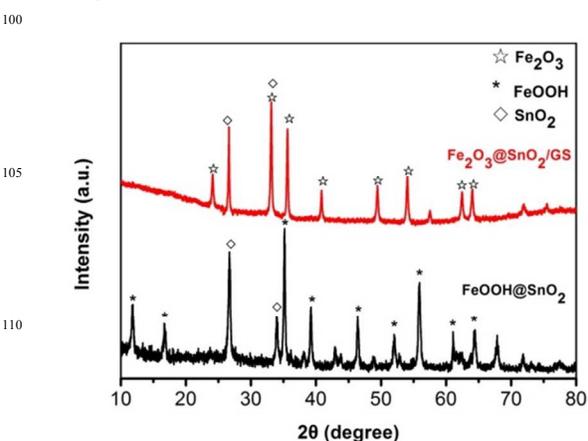


Fig. 2 XRD pattern of FeOOH@SnO₂ nanoparticles and Fe₂O₃@SnO₂/GS film.

For comparison, Fe₂O₃/GS films and SnO₂/GS films were also fabricated as shown in Fig. S4. Similar to the Fe₂O₃@SnO₂/GS film, these two films also possessed a sandwich-like structure consisting of GS and metal oxide particles. However, the metal oxide particle morphologies in the latter films showed a great difference in comparison with the former. It seems that a strong interaction between Fe₂O₃ and SnO₂ nanoparticles exists in controlling their morphologies. The SnO₂ coating on FeOOH particle surface showed a stabilizing effect on the spindle-like morphology of FeOOH when it was reduced to Fe₂O₃. Without this coating, the FeOOH particles were reduced to Fe₂O₃ cubics in Fe₂O₃/GS film. On the other hand, the SnO₂ nanoparticles in the SnO₂/GS film showed a significant increase in agglomeration without the dispersing effect of the FeOOH core.

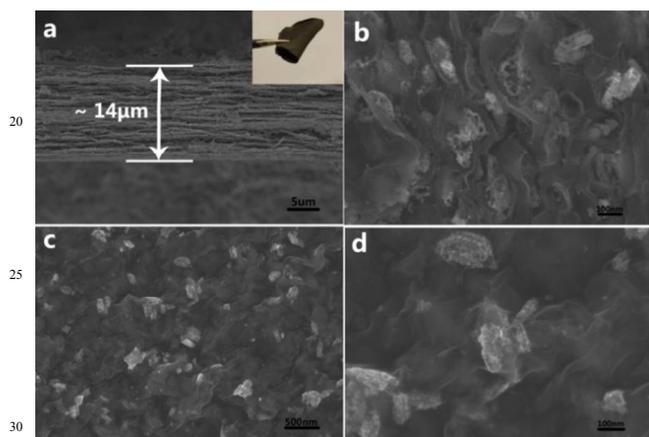


Fig. 3 Cross-section (a, b) and top-view SEM images (c, d) of Fe₂O₃@SnO₂/GS film; the inset in (a) is a digital photograph of a Fe₂O₃@SnO₂/GS film showing good flexibility.

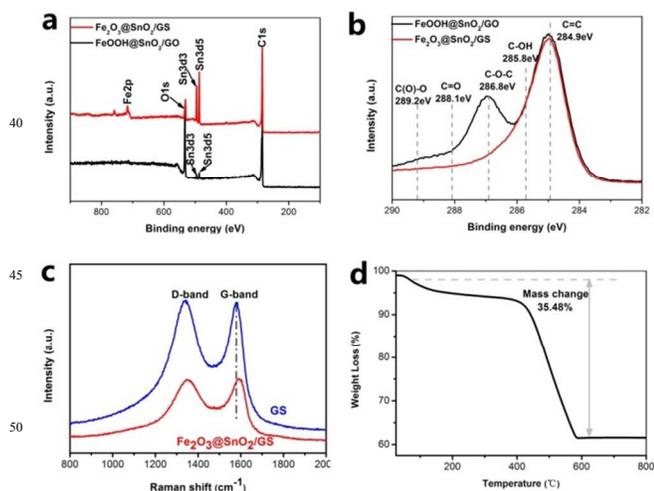
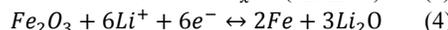
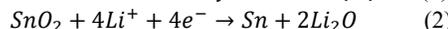
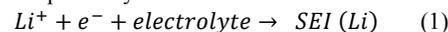


Fig. 4 (a) XPS spectra and (b) C1s spectra of FeOOH@SnO₂/GO and Fe₂O₃@SnO₂/GS films; (c) Raman spectra of GS and Fe₂O₃@SnO₂/GS film; (d) TGA curve of Fe₂O₃@SnO₂/GS film.

Fig. 4a shows the X-ray photoelectron spectrum (XPS) of the Fe₂O₃@SnO₂/GS and FeOOH@SnO₂/GO films. The peaks at 710.7, 725.8, 487 and 495.6 eV in the XPS spectrum of Fe₂O₃@SnO₂/GS film were ascribed to the Fe 2p_{3/2}, Fe 2p_{1/2}, Sn 3d_{5/2} and Sn 3d_{3/2} spinning of Fe₂O₃ and SnO₂, respectively^{37, 46, 24}. The chemical changes in GO before and after thermal reduction could be deduced from the changes in the C 1s spectrum of FeOOH@SnO₂/GO and Fe₂O₃@SnO₂/GS films (Fig. 4b). According to the literature^{26, 47}, five kinds of carbon belonging to C (O)-O, C=O, C-O-C, C-OH and C=C can be detected, and their binding energies are indicated by dashed vertical lines in Fig. 4b. A comparison between the C 1s spectrum of FeOOH@SnO₂/GO and Fe₂O₃@SnO₂/GS films found a sharp decrease in the oxygen-containing functional groups in the latter sample. Accordingly, the atomic ratio of carbon and oxygen (C/O) increased from 3.21 for FeOOH@SnO₂/GO to 7.23 for Fe₂O₃@SnO₂/GS, demonstrating a deep reduction of GO.

Moreover, Raman spectrum of Fe₂O₃@SnO₂/GS film showed a red shift of the G band of graphene from 1590 cm⁻¹ to 1594 cm⁻¹ in comparison with that of bare GS film, indicating an n-type doping effect of Fe₂O₃@SnO₂ particles on GS^{48, 49}. Such an electron donating effect might result from the interaction between the nanoparticles and GS, which would contribute a lot in improving electrochemical performance. Thermogravimetry (TG) analysis of the Fe₂O₃@SnO₂/GS film showed a weight loss of 35.5% at temperature range above 580°C, which was mainly caused by the combustion of GS in air. On this basis, the weight content of Fe₂O₃@SnO₂ in the film could be determined to be around 64.5%.

The Fe₂O₃@SnO₂/GS film was flexible and mechanically robust, and could be folded and twisted without breaking. This plus the good electron transport property endowed by the graphene layers enabled it to serve as a self-supporting electrode. Fig. 5a shows the cyclic voltammetry (CV) behavior of the Fe₂O₃@SnO₂/GS film electrode measured in potential range of 0-3.0 V at a scan rate of 0.5 mV s⁻¹. The CV behavior of the Fe₂O₃@SnO₂/GS anode is closely analogous to a combination of the CV behaviors of Fe₂O₃/GS and SnO₂/GS (Fig. S4), which are generally consistent with the reports in literature^{50, 51}. In the first cathodic scan, three reduction peaks, denoted as peak a_R, b_R and c_R, are observed at about 1.2, 0.45 and 0.06 V, respectively. The broad reduction peak a_R can be ascribed to the formation of Solid Electrolyte Interphase (SEI, Eq. (1)) and reduction of SnO₂ to Sn (Eq. (2))^{52, 53, 55}. The other two characteristic peaks c_R and b_R can be associated with the reversible reaction of Sn and Li⁺ forming Li_xSn alloys (Eq. (3))⁵⁴, and the reduction of Fe³⁺ to Fe⁰ by Li (Eq. (4))⁵⁵ respectively.



Corresponding to the above reduction peaks, three oxidation peaks appeared in the first anodic scan. The oxidation peak a_O at ~1.3 V is thought to be likely resulted from a partially reversibility of reaction (2)⁵⁴, although it is generally acknowledged that reaction (1) and (2) are irreversible and often lead to a large irreversible capacity loss in the first cycle. As to the oxidation peaks b_O and c_O at ~1.65 V and ~0.75 V, they can

be attributed to the oxidation of Fe^0 to Fe^{3+} and the dealloying process of $\text{Li}_x\text{Sn}^{21,53}$.

Furthermore, it is observed from the initial five CV cycles that there is substantial difference between the first and subsequent cycles. Particularly, the peak b_R and b_O in the first cycle shifted to b'_R and b'_O in the subsequent cycles, suggesting the occurrence of structure and electrochemical property variation in the electrode⁵⁶. While in the subsequent cycles, the CV curves became almost completely overlapped, indicating the structure and electrical properties of the electrode became relatively stable. At this time, reactions (3) and (4) were the main reactions that contributed to the capacity of the electrode because of their high reversibility.

The galvanostatic charge and discharge of the electrode were evaluated at a current density of 100 mA g^{-1} between $0.01\text{-}3.0 \text{ V}$ vs Li^+/Li . As shown in Fig. 5b, the nonlinear multi-plateau nature of the charge/discharge curves coincides well with the CV results, and are closely related with the occurrence of multistep intercalation/deintercalation of lithium-ions in the electrode³⁶. The first cycle discharge and charge capacities reached respective value of 2063 and 1255 mA h g^{-1} , much higher than the theoretical capacities of Fe_2O_3 (1007 mA h g^{-1}), SnO_2 (782 mA h g^{-1}) and graphene (372 mA h g^{-1}). Although a big capacity loss of 39.1% occurred in the first cycle because of the SEI film formation and the irreversible reactions of lithium ions with oxygen-containing functional groups on graphene surface *et al*⁵⁷, the capacity loss narrowed hereafter. After 30 charge/discharge cycles, the discharge capacity still remained up to $980.8 \text{ mA h g}^{-1}$. It is believed that the high capacity should be associated with the large surface area of the electrode with more active sites for Li storage, which were mainly nanosized Sn and Fe_2O_3 . Although graphene in the electrode could also contribute to the capacity, this contribution was nearly negligible in comparison with that of Sn and Fe_2O_3 nanoparticles. Galvanostatic charge/discharge measurement of bare graphene electrode found a very low capacity of about 67 mA h g^{-1} after 5 cycles (Fig. S6), which was much lower than that of the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode^{41,42}.

Fig. 5c shows the cycling performance of the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode along with those of $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes at a current rate of 100 mA g^{-1} . Generally, capacity loss caused by irreversible Li insertion process and the strain induced pulverization and subsequent fall off of active materials from current collector can be observed in lithium-ion batteries after long term cycling. However, benefiting from the unique core-shelled morphology of $\text{Fe}_2\text{O}_3@/\text{SnO}_2$ nanoparticles, the electrochemical agglomeration and growth of Fe_2O_3 and Sn metallic particles during cycling can be effectively retarded. This well accommodated the strain induced by Li-ion insertion and extraction, and made the active material particles more resistant to strain induced pulverization, rendering the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode with excellent cyclability. Obvious capacity loss with cycling was only observed in the first 20 cycles, afterwards the capacity became stable at about 1000 mA h g^{-1} . In comparison with the $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes, the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode showed great superiority not only in capacity but also cyclability. The first cycle discharge capacities of the $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes were about 1620 mA h g^{-1} and 1344 mA h g^{-1} , respectively (Fig. 5c). Upon further cycling, the capacities of these electrodes declined rapidly. After 200 cycles, the

$\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes showed respective capacity of $401.2 \text{ mA h g}^{-1}$ and $468.5 \text{ mA h g}^{-1}$, which were less than half of the remnant capacity of $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode (1015 mA h g^{-1}), despite that the active material loadings of these electrodes were nearly the same (Fig. S7).

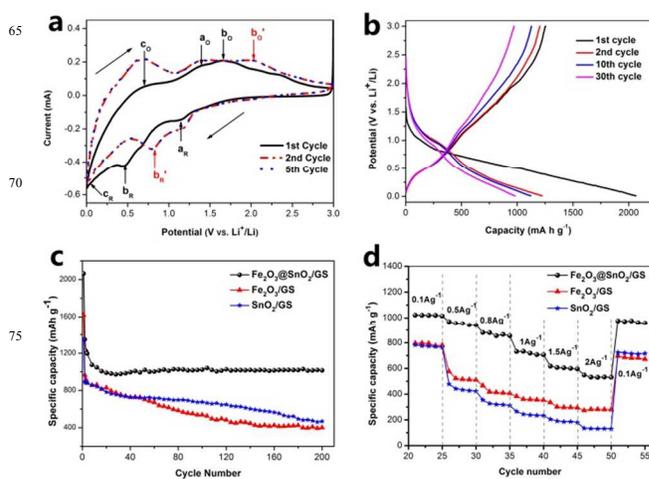


Fig. 5 (a) Cyclic voltammograms of the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ film anode at a scan rate of 0.5 mV s^{-1} over potential range of $0\text{-}3.0 \text{ V}$ vs. Li^+/Li ; (b) charge-discharge profiles of the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ film anode at a current density of 100 mA g^{-1} ; (c) cycling performance of the different electrodes at a current density of 100 mA g^{-1} ; (d) rate capability of the different electrodes at various current densities.

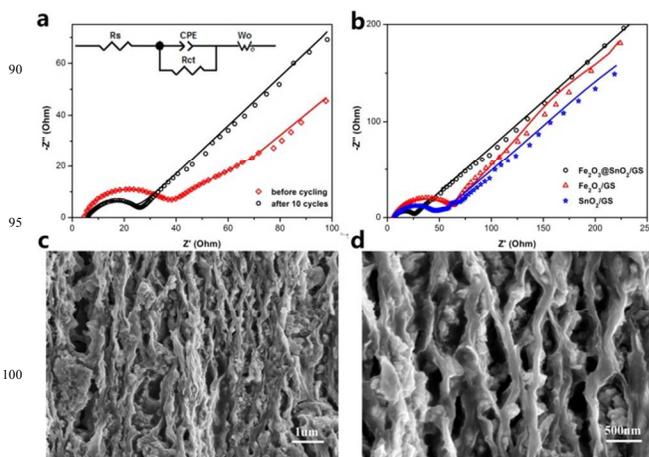


Fig. 6 (a) EIS spectra of the $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ electrode before and after ten cycles of charge/discharge; (b) EIS spectra of all the three electrodes after ten cycles of charge/discharge; (c-d) SEM images of $\text{Fe}_2\text{O}_3@/\text{SnO}_2/\text{GS}$ film after 50 cycles of discharge/charge. The solid lines in (a) and (b) represent the fitting results of EIS spectra using an equivalent circuit shown as the inset in (a). All the cells are charged and discharged at a current density of 100 mA g^{-1} . The geometrical surface areas of the electrodes used in these cells are all about 1 cm^2 .

Fig. 5d shows the rate capabilities of the electrodes, which were measured after the electrodes were activated through galvanostatic cycling at 0.1 A g^{-1} for 20 cycles to make their

electrical performance relatively stable. The $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ electrode exhibits reversible capacities of 1019, 955, 720, 605 and 535 mA h g^{-1} at current densities of 0.1, 0.5, 1, 1.5 and 2 A g^{-1} , respectively. The capacity retention was up to 53% when the current density was increased by twenty folds from 0.1 to 2 A g^{-1} . In contrast, under the same conditions, the $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes showed respective capacity retention of 35% and 17%. The rate capability of the $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ electrode was much improved over that of the other two electrodes, which was mainly attributed to enhanced electrochemical reaction kinetics of the electrode.

To gain insights into the electrochemical reaction kinetics of different electrodes, electrochemical impedance spectra of samples measured and are given in Fig. 6 a-b in the form of Nyquist plot. The impedance spectrum of each sample is comprised of one compressed semicircle at high-frequency region and a straight line at low frequency region. The impedance data were fitted using an equivalent electrical circuit shown as inset in Fig. 6a, where R_s stands for bulk resistance of the electrochemical system, R_{ct} for the charge transfer resistance, CPE for the constant phase element and W_o for the Warburg impedance of electrolyte ion diffusion behavior^{37, 58}. The formation of SEI film during cycling as shown in Fig. 6 c-d hindered charge transfer speed, and caused an increase in R_{ct} of the $\text{Fe}_2\text{O}_3/\text{GS}$ electrode (Fig. S8). However, benefiting from the formation of metallic Sn on the electrolyte/ Fe_2O_3 interface, which enhanced the electronic conductivity, the R_{ct} of $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ electrode was found to be significantly reduced from 34.31 to 22.57 Ω after 10 cycles of charge and discharge (Fig. 6a). Actually, the $\text{Fe}_2\text{O}_3@\text{SnO}_2/\text{GS}$ electrode showed the lowest post-cycling charge transfer resistance ($R_{ct} = 22.57 \Omega$) compared with $\text{Fe}_2\text{O}_3/\text{GS}$ electrode ($R_{ct} = 66.54 \Omega$) and SnO_2/GS electrode ($R_{ct} = 41.46 \Omega$). This would facilitate rapid charge transfer and result in improved electrochemical reaction kinetics and rate capability of the electrode. In addition, it is worth to note that aside from the enhanced electronic conductivity, the electrochemical agglomeration retarding effect of the unique core-shelled $\text{Fe}_2\text{O}_3@\text{SnO}_2$ nanoparticles and the highly porous structure of the total electrode can also contribute to the improved electrochemical reaction kinetics by providing more active sites for Li storage and rapid channel for electrolyte diffusion, resulting in not only better cyclability but enhanced rate capability as well.

Finally, SEM observation indicated that the electrode showed a good stability. Except the formation of SEI film on graphene sheet surface, no obvious change in its microstructure occurred even after charge and discharge for 50 cycles. This good structural stability could partially account for the superior cyclability of the electrode.

Conclusions

In summary, free-standing graphene film decorated with $\text{Fe}_2\text{O}_3@\text{SnO}_2$ nanoparticles was successfully fabricated for use as Li-ion battery anode. The electrode showed a sandwich-like structure with core-shell structured $\text{Fe}_2\text{O}_3@\text{SnO}_2$ nanoparticles homogeneously attached on graphene layers. Due to the synergistic effect of Fe_2O_3 and SnO_2 on retarding electrochemical aggregation of the nanoparticles, as well as the good electronic

conductivity and rapid electrolyte diffusion channel provided by the three-dimensional interconnected porous graphene networks, this electrode showed great improvement in capacity, cyclability and rate capability over the $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes. Although significant capacity fading was observed in the initial stage of cycling, owing to the occurrence irreversible Lithium storage reactions in it, the capacity became stable at about 1000 mA h g^{-1} after charging and discharging for 20 cycles. A high reversible discharge capacity of 1015 mA h g^{-1} still remained at the 200th cycle, which was almost over two times of the remnant capacity of $\text{Fe}_2\text{O}_3/\text{GS}$ and SnO_2/GS electrodes.

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Notes and references

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