TiO$_2$ modified FeS Nanostructures with Enhanced Electrochemical Performance for Lithium-Ion Batteries

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Anatase TiO$_2$ modified FeS nanowires assembled by numerous nanosheets were synthesized by using a typical hydrothermal method. The carbon-free nanocoated composite electrodes exhibit improved reversible capacity of 510 mA h g$^{-1}$ after 100 discharge/charge cycles at 200 mA g$^{-1}$, much higher than that of the pristine FeS nanostructures, and long-term cycling stability with little performance degradation even after 500 discharge/charge cycles at current density of 400 mA g$^{-1}$. Full batteries fabricated using the FeS@TiO$_2$ nanostructures anode and the LiMn$_2$O$_4$ nanowires cathode with excellent stability, and good rate capacities could also be achieved. The enhanced electrochemical performance of the composite electrodes can be attributed to the improved conductivity of the integrated electrodes and the enhanced kinetics of lithium insertion/extraction at the electrode/electrolyte interface because of the incorporation of anatase TiO$_2$ phase.

Lithium-ion batteries, one of the most promising energy-storage devices and providing the power for almost all current portable electronics, have attracted worldwide attention accompanying the increasing concerns about the limited global energy supply and the degradation of living environment$^{1-6}$. The performances of lithium-ion batteries depend largely on the properties and structures of electrode materials for lithium storage$^{7,8}$. Two-dimensional (2D) nanostructures are of great interest in lithium storage due to their shortened paths for fast lithium ion diffusion and large exposed surface offering more lithium-insertion channels$^{9,10}$. Two-dimensional (2D) nanostructures of some layered-structured metal sulfides, such as WS$_2$ and MoS$_2$, have been actively studied as electrode materials in lithium-ion batteries due to their structural advantages in reversible Li storage processes$^{11-14}$. However, the metal elements in these sulfides are relatively heavy, which may limit their theoretical specific energies densities$^{10}$.

Iron sulfides are interesting materials for energy storage applications due to their cost effectiveness and abundance in nature. Furthermore, they have a higher Li-insertion voltage (ca. 1.3 V vs Li$^+/\text{Li}$) than that of commercial graphite anode (below 0.2 V vs Li$^+/\text{Li}$), which can avoid reduction of electrolyte on the surface of the electrode and formation of the solid-electrolyte interphase (SEI) layer (usually occurring below 1.0 V vs Li$^+/\text{Li}$). Several kinds of iron sulfides have been studied as electrodes for lithium-ion batteries, which storage Li via a conversion reaction$^{15,16}$. However, the products after the discharge process in such batteries are insulating polysulfides (Li$_2$S$_x$, 1 < x < 8), which could easily dissolve in liquid electrolyte$^{16}$. Besides losing active material, the dissolved polysulfides also deteriorate the conductivity of the electrolyte and the electrode leading to capacity degradation$^{17-19}$. What’s more, part of the insulating reaction products cover the electrode and prevent its further electrochemical reactions. Recently, carbon-based capping the sulfides into thin wrapping layers is a successful strategy to reduce polysulfides dissolution into the electrolyte. However, because of safety issues concerning carbon materials, great efforts are also directed to carbon-free coatings for achieving superior rate performance, high tap density, and surface stability$^{20}$. At this stage, a novel iron sulfides nanostuctures with 2D morphology for lithium ion transport and uniform carbon-free conducting nanocating layer are still highly desired.

Herein, we successfully exhibit a novel one-dimensional anatase TiO$_2$ modified FeS nanostructure composed of 2D graphene-like FeS nanosheets via a facile hydrothermal growth method followed with the treatment in TiCl$_4$ solution. As expected, the TiO$_2$ modified FeS nanostructure displayed excellent Li storage properties with considerable capacity of 520 mA h g$^{-1}$ after 100 discharge/charge cycles at 200 mA g$^{-1}$, superior cyclic stability (456 mA h g$^{-1}$ even after 500 discharge/charge cycles at 400 mA g$^{-1}$) and improved rate capability compared with those of the pure FeS nanostructures. The enhanced electrochemical performances of the composite electrodes...
can be attributed to the large exposed electrochemical active surface, the improvement of lithium diffusion coefficient, and the electrical conductivity of the overall electrode because of the introduction of anatase TiO\(_2\) phase, which were confirmed by the investigation of the lithium storage performance, electrochemical impedance and the kinetics of lithium ion insertion/extraction.

**Results**

The FeS@TiO\(_2\) nanostructures were synthesized via a facile hydrothermal method combined with a post-treatment process. Figure 1 shows the X-ray diffraction (XRD) patterns of the FeS products before and after TiO\(_2\) treatment. All peaks in Figure 1a can be well indexed as hexagonal FeS (JCPDS Card No. 03-065-3356, space group P-6\(\bar{2}\)c). As for the FeS@TiO\(_2\) sample shown in Figure 1b, all the diffraction peaks of FeS remain unchanged, while the peak located at 25.2° matches well with the (101) plane of anatase TiO\(_2\) (JCPDS Card No. 01-065-9124), indicating the formation of anatase TiO\(_2\). The morphology and microstructures of the as-prepared products were characterized by field-emission scanning electron microscopy (FE-SEM) as illustrated in Figure 2. One-dimensional (1D) wire-like materials with lengths of tens of micrometers on a large scale can be obtained for the FeS@TiO\(_2\) nanostructures (Figure 2a). Further observation of the SEM image in Figure 2b, we can clearly see that the wire-like nanostructures were assembled by numerous 2D nanosheets, being in sharp contrast with the smooth surface of the precursor before calcination (Figure S1), while keeping well with the pure FeS nanostructures (Figure S2), due to the running away of organics in the precursor. The corresponding energy-dispersive X-ray spectroscopy (EDS) (Figure 2c) suggests the existence of Fe, S, Ti and O in the resultant FeS@TiO\(_2\) nanostructures, further confirm the introduction of TiO\(_2\), in good agreement with the XRD result. In the spectrum, the peak of Pt comes from the deposited platinum when prepared for SEM characterization. The corresponding elemental mapping of Fe, S, Ti and O in the FeS@TiO\(_2\) nanostructures is shown in Figure S3, revealing the uniform dispersion of those elements. Besides, the EDS pattern and the corresponding elemental mapping of Fe and S in the pure FeS nanostructures are also depicted in Figure S4 and S5.

Typical TEM image of an individual FeS@TiO\(_2\) nanostructure was shown in Figure 2d, where a lot of nanosheets assemble into the 1D composite nanostructure can be seen. Further observation of the nanosheet (Figure S6) revealed that TiO\(_2\) nanoparticles were implanted on the surface of FeS nanosheet. Figures 2e and 2f show the high-resolution TEM (HRTEM) images of the FeS nanosheet and TiO\(_2\) nanoparticle in the composite nanosheets. The well-resolved periodic lattice fringe with an interplanar distance of 0.48 nm comes from the (101) plane of hexagonal FeS (Figure 2e). Two sets of lattice fringes with inter-plane spacing of 0.24 and 0.35 nm indicated in the HRTEM image (Figure 2f) are attributed to the (004) and (101) planes of the anatase TiO\(_2\) phase, respectively.

For the formation of FeS nanosheets, it is believed that the annealing temperature plays an important role in determining their final shapes. Previously, people reported that nanowires were obtained once the annealing temperature was set at 200–300°C\(^2\). While in our case, we increased the annealing temperature to 500°C and nanosheets assembled nanostructures were thus obtained. At a higher temperature, combined with the evaporation the organics from the precursors, the rapid diffusion process of the atoms may

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**Figure 1** | XRD patterns of the as-synthesized FeS and FeS@TiO\(_2\) nanostructures.

**Figure 2** | (a, b) SEM images, (c) EDS pattern, (d) TEM image and (e, f) HRTEM images of the as-prepared FeS@TiO\(_2\) nanostructures.
take place across the interface (the amorphous layers, grain boundaries, and so on) to allow the formation of the hexagonal FeS nanosheets, which may be attributed to the confined growth within the (001) plane of the hexagonal symmetrical crystals. With the reaction went along, the novel nanostructures assembled by nanosheets were collected.

X-ray photoelectron spectroscopy (XPS) was employed to analyze the information on the surface chemical compositions and the valence states of the FeS@TiO2 nanostructures. Figure 3a shows the XPS spectrum of the S 2p core-level. Two signals at 161.5 and 167.5 eV can be attributed to S 2p3/2 and S 2p1/2, respectively, characteristic peaks of FeS. The core level spectra of Fe 2p are shown in Figure 3b. Peaks corresponding to 708.4 eV and 721.6 eV are attributed to Fe2+ states coming from FeS phase, whereas 710.5 eV and 723.4 eV are ascribed to Fe3+ states, which may be attributed to the Fe3+ formed from iron and oxide elements. The peak of O 1s (Figure 3c) is centered at 530.2 eV, which is attributed to the O2- forming oxide with titanium. Fig. 3d presents the XPS spectra of Ti 2p doublet peaks. The binding energy of Ti 2p1/2 and Ti 2p3/2 was observed at approximately 464.2 eV and 458.5 eV, respectively. The splitting data between the Ti 2p1/2 and Ti 2p3/2 core levels are 5.7 eV, indicating a normal state of Ti4+ in the anatase TiO2. These results indicate that anatase TiO2 phase have been introduced successfully into the FeS nanostructures.

To demonstrate the effect of the introduced anatase TiO2 in improving the lithium storage performance, we investigate the electrochemical properties of the pristine FeS and FeS@TiO2 nanostructures as anode materials for lithium batteries, respectively. Figures 4a and 4b show the discharge/charge voltage profiles of the FeS and FeS@TiO2 nanostructures electrodes at a current density of 200 mA g\(^{-1}\) between 0.01 and 3.0 V. As evidenced in Figure 4c, the composite electrode shows considerable enhanced discharge/charge capacity with respect to the pure FeS electrode during all the 100 cycles. The FeS@TiO2 nanostructures electrode exhibits a discharge capacity of 505 mAh g\(^{-1}\) during the 15 th cycle and remains at 510 mAh g\(^{-1}\) after 100 cycles, which are much higher than those of the pure FeS electrode (320, and 266 mAh g\(^{-1}\) during the 15th and after 100 cycles, respectively). To better understand the advantage of the FeS@TiO2 nanostructures in lithium storage, the rate performance of the FeS@TiO2 nanostructures electrode is also investigated (Figure 4d). Obviously, compared with the pristine FeS electrode, the specific capacities of the composite electrode are substantially increased at all investigated discharge/charge rates from 100 to 4000 mA g\(^{-1}\). It depicts that the
ninth cycle discharge capacities are around 705, 474, 382, 283, and 160 mAh g$^{-1}$ at current densities of 100, 500, 1000, 2000, and 4000 mA g$^{-1}$, respectively, which are about two times larger than those of the pristine FeS electrode (407, 235, 179, 121, and 60 mAh g$^{-1}$). These results reveal that the incorporation of anatase TiO$_2$ into FeS nanostructures can greatly enhance the electrochemical performance for lithium storage.

To get more information about the electrochemical properties of the FeS@TiO$_2$ nanostructures electrode, the cyclic performance was also carried out at current densities of 100, 400, and 800 mA g$^{-1}$ as revealed in Figure 5a. When tested at a low current density of 100 mA g$^{-1}$, the capacity of the composite electrode is as high as 635 mAh g$^{-1}$ after 100 discharge/charge cycles, much higher than that of the C@FeS nanoplates electrode$^{10}$. Importantly, the FeS@TiO$_2$ nanostructures electrode still exhibits an excellent cyclic performance at much higher current densities of 400 and 800 mA g$^{-1}$, and the capacities reach 440 and 355 mAh g$^{-1}$ after 100 discharge/charge cycles. The corresponding coulombic efficiencies of the electrode cycled at 100 to 800 mA g$^{-1}$ were shown in Figure 5b. The coulombic efficiencies (nearly 100%) are still highly expected for the composite electrode, though different discharge/charge current densities are applied, further demonstrating the excellent lithium storage performance of the FeS@TiO$_2$ nanostructures electrode. Furthermore, the composite electrode exhibits satisfactory cycling performance as evidenced in Figure 5c and 5d. The specific capacity of the composite is 430 mAh g$^{-1}$ after 500 discharge/charge cycles at 400 mA g$^{-1}$ with a coulombic efficiency of 99%, demonstrating the high cyclic stability and good reversibility of the FeS@TiO$_2$ nanostructures electrode.

To explore the potential application of the FeS@TiO$_2$ nanostructures as the anode material of full battery, spinel LiMn$_2$O$_4$ nanowires were synthesized and selected as the cathode material because of its three-dimensional tunnel structure for the migration of lithium ions and advantage of fast charging resulted from the stable delithiated structure$^{28}$. All peaks in the XRD pattern of the as-synthesized LiMn$_2$O$_4$ nanowires (Figure S7) can be well indexed as spinel LiMn$_2$O$_4$ (JCPDS Card No. 01-089-8325). Figure S8 shows the SEM image of the as-synthesized LiMn$_2$O$_4$ nanowires with uniform diameter of 200 nm and length of 10 μm. The electrochemical performances of the as-prepared LiMn$_2$O$_4$ nanowires were first evaluated as demonstrated in Figures 6a and 6b. The LiMn$_2$O$_4$ nanowires electrode exhibits impressive specific capacities (82–94 mAh g$^{-1}$ at 500 mA g$^{-1}$), high coulombic efficiency of 99%, and excellent cycling performance with capacity retention more than 87% after 100 charge/discharge cycles. Galvanostatic charge-discharge curves of the half cell based on the LiMn$_2$O$_4$ nanowires electrode (Figure S9) display expected discharge plateau potentials of 4.05 and 3.9 V at 500 mA g$^{-1}$, in accordance with the previous report$^{28}$. As can be seen in Figure 6b, the cathode shows capacities of 89, 85, 78, 70, and 62 mAh g$^{-1}$ at current densities ranged from 100 to 2000 mA g$^{-1}$. The little capacity loss with the increase of the charge/discharge current densities indicates the superior rate capability of the LiMn$_2$O$_4$ nanowires.

To demonstrate the real contribution of the FeS@TiO$_2$ nanostructures electrode to the assembled LiMn$_2$O$_4$/FeS@TiO$_2$ full battery, the over-capacity of the LiMn$_2$O$_4$ nanowires was adopted. Figure 6c shows the charge/discharge voltage profiles of the as-fabricated full battery. As expected from the operating voltages of the FeS@TiO$_2$ nanostructures and LiMn$_2$O$_4$ nanowires, their combination produces a battery with an operating voltage of 2.2 V, and the discharge capacity of the battery is 520 mAh g$^{-1}$ with a coulombic efficiency of 98% at 200 mA g$^{-1}$. The rate performance of the full battery was further inspected, as illustrated in Figure 6d. Remarkably, an acceptable capacity of 350 and 170 mAh g$^{-1}$ at 500 and 1500 mA g$^{-1}$, respectively, during the 5th cycle could be achieved, which are comparable with the rate performance of practical graphite-based full battery, although the rate capacity at high current density is still

![Figure 4](https://www.nature.com/scientificreports/4) | Discharge and charge voltage profiles of (a) FeS, and (b) FeS@TiO$_2$ nanostructures electrodes. Comparison of the cycling performance of FeS and FeS@TiO$_2$ nanostructures electrodes: (c) at 200 mA g$^{-1}$, and (d) at various current densities of 100, 500, 1000, 2000, and 4000 mA g$^{-1}$. 

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**Table 1** | Properties of FeS and FeS@TiO$_2$ Nanostructures Electrodes
| Property | FeS | FeS@TiO$_2$ |
|----------|-----|------------|
| Capacity (mAh g$^{-1}$) | 160 | 355 |
| Stability | Excellent | Excellent |
| Reversibility | High | High |
| Rate Capability | Good | Better |

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**Table 2** | Properties of LiMn$_2$O$_4$ Nanowires Electrode
| Property | Value |
|----------|-------|
| Capacity (mAh g$^{-1}$) | 90 |
| Stability | High |
| Reversibility | High |
| Rate Capability | Good |

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**Figure 5** | Cyclic Performance of FeS@TiO$_2$ Nanostructures Electrodes
- Figure 5a: Cyclic performance at 200 mA g$^{-1}$
- Figure 5b: Cyclic performance at various current densities
- Figure 5c: Specific capacity vs. cycle number
- Figure 5d: Specific capacity vs. cycle number at different current densities

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**Figure 6** | Charge/Discharge Characteristics of LiMn$_2$O$_4$/FeS@TiO$_2$ Full Battery
- Figure 6a: Discharge/Charge profile of LiMn$_2$O$_4$ nanowires electrode
- Figure 6b: Discharge/Charge profile of as-fabricated full battery
- Figure 6c: Discharge/Charge profile of assembled full battery
- Figure 6d: Rate performance of full battery
Figure 5 | (a) Cycling performance and (b) corresponding coulombic efficiency of the prepared FeS@TiO₂ nanostructures electrodes cycled at 100, 400, and 800 mA g⁻¹. (c) Discharge and charge voltage profiles and (d) long cycling performance of the electrode at a current density of 400 mA g⁻¹.

Figure 6 | Cycling performance of the as-synthesized LiMn₂O₄ nanowires electrodes at (a) 500 mA g⁻¹, and (b) various current densities ranged from 100 to 2000 mA g⁻¹. (c) Charge and discharge voltage profiles at 200 mA g⁻¹ and (d) rate performance at current densities between 500 and 1500 mA g⁻¹ of the as-fabricated full battery based on FeS@TiO₂ nanostructures anode and LiMn₂O₄ nanowires cathode.
need to be improved. Further investigations are on-going to improve the capacity of the full cell at high discharge rates to meet the demand of electronic device for high energy density.

Discussion

In order to gain better understanding on the enhanced electrochemical performances of the FeS@TiO2 nanostructures electrodes, we have performed CV measurements to investigate the kinetics of lithium ion insertion/extraction at the electrode/electrolyte interface and rate of lithium diffusion in the film. It is known that the change in peak shape with sweep rate reflects the kinetics of lithium insertion/extraction at the electrode/electrolyte interface and rate of lithium diffusion in the film29. Figures 7a and 7b show the CV curves of the pristine FeS and the FeS@TiO2 nanostructures electrodes recorded at scan rates of 0.1–0.8 mV s\(^{-1}\) in the voltage range of 0.01–3.0 V after 5th, 10th, 15th, and 20th cycles. As the scan rates increase, the cathodic and anodic peaks moved to lower and higher potential, respectively, with the increase of the magnitude of the peak currents. Furthermore, the peak currents of the FeS@TiO2 nanostructures electrodes are higher than those of the pristine FeS electrodes, indicating the incorporation of TiO2 render the composite electrodes much faster lithium diffusion and much higher lithium storage capacity. As evidenced in Figures 7c and 7d, linear correlation was established between the anodic/cathodic peak currents and the square roots of scan rates for both Peak 1 and 2, which suggests diffusion-limited reactions30. In this kind of reaction, the peak currents and scan rates follow the Randles-Sevck equation31:

\[
I_p \sim (2.69 \times 10^5)n^{1/2}AD^{1/2}v^{1/2}\Delta C_0
\]

Where \(I_p\) is the peak current; \(n\) is the number of transfer electrons; \(A\) is the surface area of electrodes; \(D\) is the diffusion coefficient; \(v\) is the scan rate, and \(\Delta C_0\) is the concentration of reaction. It is worth noting that the slopes for peak 1 and peak 2 on the FeS@TiO2 nanostructures were higher than those for the FeS system, revealing that the combination of TiO2 into the FeS nanostructures is benefit to improve the lithium diffusion coefficient, resulting the enhanced electrochemical performance for lithium storage.

To gain insight into the prominent electrochemical properties of the FeS@TiO2 nanostructures with respect to the FeS electrode, we also take the electrochemical impedance spectroscopy (EIS) measurements as shown in Figure 8. The equivalent circuit model of the studied system is also shown in Figure 8 inset to represent the internal resistance of the test battery according to literature32,33. The high-frequency semicircle corresponds to the contact resistance (Rs) and constant phase element of the SEI film (CPE1), the semicircle in the medium-frequency region is assigned to the charge-transfer impedance (Rct) and constant phase element of electrode/electrolyte
Preparation of FeS and FeS@TiO2 nanostructures

Methods

Preparation of FeS and FeS@TiO2 nanostructures. FeS nanostructures were prepared by using solvothermal method, similar to the literature except the anneal temperature. Briefly, FeCl3·6H2O (1.18 g) was mixed with CH3CSNH2 (4H2O (1.18 g) was mixed with CH3CSNH2). Porous carbon nanofiber-sulfur composite electrodes for lithium/sulfur cells. Porous carbon nanofiber-sulfur composite electrodes for lithium/sulfur cells

Fabrication of LiMnO4 nanowires. LiMnO4 nanowires were fabricated via a solid state reaction of β-MnO2 nanowires and lithium hydroxide. The synthesis of β-MnO2 nanowires can be seen in our previous report. Typically, manganese sulfate (0.338 g) and potassium chloride (0.246 g) were dissolved in 25 mL of distilled water under vigorous stirring to form a homogeneous solution. The mixture was then transferred to a Teflon-lined stainless autoclave and kept at 200 °C for 10 h in air, the LiMnO4 nanowires were obtained.

Characterization. The phase purity of the products were characterized by X-ray powder diffraction (XRD) using an X-Ray diffractometer with Cu Kα radiation (λ = 0.154 nm). Scanning electron microscopy (SEM) images and energy dispersive X-Ray spectroscopy (EDS) analyses were obtained using a Sirion 200 microscope.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) observations were carried out on a Philips CM 200 instrument. X-Ray photoelectron spectroscopy (XPS) spectra were performed on a VG Multilab 2000 system with a monochromatic aluminum anode X-ray source.

Electrochemical evaluation. The working electrodes were fabricated by coating a slurry containing 70 wt% active materials (FeS or FeS@TiO2 nanostructures), 20 wt% acetylene black (Super-P), and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone onto a copper foil and dried at 80 °C in vacuum for 12 h before pressing.

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| Table 1 | Impedance parameters derived using equivalent circuit model for FeS and FeS@TiO2 nanostructures electrodes |  |
|---|---|---|---|
| R0 (|  Ω | R1 (|  Ω | Rct (|  Ω |
| FeS | 8.9 | 140.2 | 169.7 |
| FeS@TiO2 | 5.8 | 84.9 | 109 |

mixed with lithium hydroxide with mole ratio of 1 : 0.55. After annealing at 750 °C for 10 h in air, the LiMnO4 nanowires were obtained.
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Author contributions
X.F.W., D.C. and G.Z.S. devised the original concept, designed the experiment, discussed the interpretation of results and co-wrote the paper. X.F.W., Q.Y.X. and L.J.W. performed the experiments. B.L. and T.L. analysed the dates. All authors reviewed the manuscript.

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