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Sulfurization of FeOOH Nanorods on a Carbon Cloth and their Conversion into Fe$_2$O$_3$/Fe$_3$O$_4$-S Core-Shell for Lithium Storage

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Fe$_2$O$_3$/Fe$_3$O$_4$-S Core-Shell nanorods were fabricated on a carbon cloth by sulfurization of FeOOH and post annealing. The prepared electrode exhibited remarkable cyclic stability and attractive rate capability for lithium storage.

Lithium-ion batteries (LIBs) have been invented and developed in the past decades.\(^1\) As a successful commercial product, LIBs have been widely used in portable electronic devices. Because LIBs possess the advantages of high energy density, long working life and environmental benignity and so on;\(^3\) they are considered as an important energy storage way to solve the energy crisis and much research attention has been paid to them.\(^5\) To develop the next generation of LIBs for the demands of electric vehicles and large scale electrical energy storage grid, the anode materials of LIBs owing outstanding electrochemical performances play a key role.\(^7\) Among the explored materials, iron-based materials (Fe$_2$O$_3$ and Fe$_3$O$_4$, mainly), which have many advantages, such as higher capacity (~1000 mAh g$^{-1}$), low cost, high safety and nontoxicity, will be the most promising candidate for the replacement of carbon anode (whose capacity is relatively low 372 mAh g$^{-1}$).\(^8\) However, low intrinsic electric conductivity and fast capacity fading still seriously hamper iron-based materials for practical using.\(^9\)

In order to solve the above issues, a large number of methods have been proposed. Depending on the main characteristic of these methods, they can be divided into four kinds. First, design the nanostructure of the iron-based materials (particle size and morphology).\(^2,\)\(^11\) Second, utilize the iron-based materials to construct hybrid with other materials.\(^12,\)\(^13\) Third, dope other element in the iron-based materials.\(^13,\)\(^14\) And lastly, coat carbon materials on the external of the iron-based materials.\(^15,\)\(^16\) On one hand, taking into consideration the individual properties of both Fe$_2$O$_3$ and Fe$_3$O$_4$, the combination of these oxides as LIB anode through a facile fabrication method are less reported.\(^17,\)\(^18\) Thus, we proposed that the iron-based materials which consist of both Fe$_2$O$_3$ and Fe$_3$O$_4$ will possess high electrochemical performances and might be an effective way to overcome the problems hindering iron-based materials for practical using.

In this communication, we report a simple method to synthesize high performance Fe$_2$O$_3$-Fe$_3$O$_4$-S (FFS) core-shell nanorods on a carbon cloth as lithium ion batteries anode materials. On account of the co-contribution of the Fe$_2$O$_3$ and Fe$_3$O$_4$ and the existence of conductive sulfur coated layer, the FFS presents high rate performance and long excellent cycling stability. The FFS core-shell nanorods exhibit 1213 mA h g$^{-1}$, 1090 mA h g$^{-1}$, 892 mA h g$^{-1}$, 728 mA h g$^{-1}$, 587 mA h g$^{-1}$, 414 mA h g$^{-1}$ tested at 0.2 C, 0.5 C, 1 C, 3 C, 5 C and 10 C, respectively (1 C = 1000 mA h g$^{-1}$), and maintains 539 mA h g$^{-1}$ after 100 cycles tested at 5 C.

![Fig. 1. Characterization of the FFS core-shell nanorods. (a) XRD profiles (b) Raman spectrum and (c, d) the high resolution XPS spectra of the S 2p and Fe 2p.](Image)

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**Notes:**

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Firstly, FeOOH flower-like nanorods (Fig. S1) were fabricated on a carbon cloth by simple hydrothermal method according to our previous method (Experimental Section, Supporting Information, SI). The carbon cloth was then immersed in 0.1 M thiocetic acid for 6 h and then annealed in N₂ atmosphere at 300 °C for 60 mins to obtain the FFS core-shell nanorods. Thiocometamide was responsible for the partial reduction of Fe₂O₃ to Fe şO₂ and sulfur coated layer upon annealing. Fig. 1a shows the XRD profile of the FFS nanorods. Intensed peaks of Fe şO₂ and Fe şO₃ were well observed, confirming the co-existence of the two oxides (PDF card no. #33-0644 and #19-0629, respectively). There were no traces of sulfur peaks due to the small amount in thioceticamide. Raman spectra collected for the FFS sample displayed Raman peaks of Fe şO₃ at 225 and 413 cm⁻¹ and Fe şO₂ at 290 and 667 cm⁻¹, further affirming the co-existence of the two oxides (Fig. 1b). The enlarge Raman spectra of the FFS sample displayed in Fig. S2 shows the Raman peak of S at 243 cm⁻¹ in the composite indicating the presence of S in the sample.

X-ray photoelectron spectroscopy (XPS) analyses were carried out to study the composition of the core-shell sample. Fig. 2c shows the high resolution XPS spectra of S 2p analyzed from the XPS survey (Fig. S3). The S 2p spectra of the FFS sample exhibit two peaks at 161.3 and 162.4 eV, which corresponds to S 2p₁/₂ and S 2p₃/₂, respectively of the S²⁻ oxidation state. This demonstrates that the presence S element in the nanorod. As shown in Fig. 1d, the Fe 2p XPS spectrum of the FFS exhibits two peaks at 710 and 724 eV, corresponding to Fe 2p₁/₂ and Fe 2p₃/₂ of the Iron oxides and a satellite peak of Fe şO₂ at 718 eV. Both Fe 2p peaks can further be deconvoluted into two broad peaks, namely Fe O²⁻ and Fe O³⁺, which confirm with the Fe 2p peaks of Fe şO₂ and Fe şO₃. Further authenticating the co-existence of the iron oxides.

To gain an insight about the morphology of the FFS core-shell nanorods, Fig. 2 shows the scanning electron microscope (SEM), transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images of the FFS core-shell nanorods. As shown in Fig. 2a and 2b, the FFS core-shell nanorods were homogeneously distributed on the carbon cloth, with diameters of 150-200 nm. Compared with the FeOOH nanorod, the FFS morphology exhibits a rough surface (Fig. 2b). Fig. 2c clearly reveals that the surface of the Fe şO₂-Fe şO₃ (core) is well coated by the S-layer (shell), and the thickness of the layer is about 10 nm (Fig. 2d). The energy dispersive X-ray spectroscopy (EDS) data revealed that the nanorods consist mainly of Fe, O and S elements, which are uniformly distributed in the nanorod (Figure S4). The enlarge HRTEM image in Fig. 2e shows that the fringe spacing of 0.22 nm agree well with the interplanar spacing (006) plane of the hematite Fe şO₃ (PDF card no. #33-0644) and 0.48 nm, which corresponds with the (111) plane of the magnetite Fe şO₄ (Fig. 2e) (PDF card no. #19-0629).

In order to test the electrochemical performance of the prepared FFS composite for application in lithium ion batteries, several electrochemical analysis were conducted. We used the optimized FFS-6h electrode for further electrochemical test (Fig. S5). Fig. 3a displayed the cyclic voltammetry (CV) of the FFS core-shell nanorod for the 1st, 2nd and 3rd cycles at a scan rate of 0.01 mV s⁻¹ between 0.01 V and 3 V. In the first cathodic process, the sample showed a large peak at 0.7 V, which indicated the transformation from Fe ŞO₂ to Fe ŞO₃ and the formation of solid electrolyte interphase (SEI) layer. As can be seen from the charge-discharge profile, the first-cycle discharge capacity of the FFS composites reaches 1600 mA h g⁻¹ at the current density of 0.2 C and the second-cycle discharge capacity maintain 1280 mA h g⁻¹ (Fig. 3b). Also, an obvious voltage plateau appears at...
about 0.8 V during the initial discharge process, then the plateau moves to about 1.0 V during the second discharge process, which correspond to the result obtained in the CV profiles. Considering the capacity contribution from the carbon cloth, the carbon cloth contributed about 9% of the total capacity as calculated in the Supporting Information. This indicated that the carbon cloth have less capacity contribution to the capacity of the FFS electrode. Meanwhile, the FFS composite was cycled at various current densities for ten cycles ranging from 0.2 to 10 C, then back to the initial current density of 0.2 C. As shown in Fig. 3c, the reversible specific capacities of the FFS composite were 1213 mA h g⁻¹, 1090 mA h g⁻¹, 892 mA h g⁻¹, 728 mA h g⁻¹, and 587 mA h g⁻¹, respectively, even tested at a high current density of 10 C, the composite still delivered a high reversible capacity of 414 mA h g⁻¹. When the current density back to 0.2 C, the capacity of the FFS composite also kept at 1175 mA h g⁻¹, confirming that the FFS electrode exhibiting excellent rate capability and reversibility. This result is higher than some of the recently reported iron oxide-based anode 8, 10, 18 and comparable to some other ones. 11, 22

Besides, we used a high constant current density (5 C) to evaluate the cycling performance of the FFS composite of the same cell after 70 cycles of rate performance test. Fig. 3d showed a highly stable cycling performance profile of the FFS composite. After 100 charge-discharge cycles, a reversible capacity of 538 mA h g⁻¹ can be retained, which is higher and comparable to some other iron-oxide based electrodes. 2, 9, 11, 18, 22 It demonstrated that the FFS composite material can bear high current density, meanwhile it could also deliver high reversible capacity with coulombic efficiency maintained at 100 %. Fig. 3e was the Nyquist plots of the FFS core-shell nanorod before and after cycling at a frequency range between 100 kHz and 0.1 Hz with a perturbation amplitude of 5 mV. It clearly suggested that the electrochemical impedance after cycling was much smaller than the impedance before cycling and because of the reduction of the electrochemical impedance, it made the charge transfer resistance smaller and lead to rapid electron transport during the electrochemical lithium insertion/extraction, which was the reason of the excellent cycling stability of the FFS core-shell nanorods. Such phenomenon is common for many iron-oxide based electrodes. 22 Fig. 3f was the SEM and TEM images of the FFS electrode after 100 cycles at a current density of 5 C. It showed that the nanorod structure of the samples did not have any obvious change but the coated shell disappeared and the nanorod are slightly denser than those of the initial SEM image (Fig. 2a-b), further affirming the excellent structural stability of the FFS nanorods. The excellent performance of the FFS electrode can be attributed to the synergistic effect and co-contribution of the Fe₂O₃ and Fe₃O₄, the coating of the conductive sulfur layer, which could improve the conductivity of the electrode and the mechanical strength and capacity contribution from the carbon cloth substrate.

In summary, we successfully synthesized excellent electrochemical performance Fe₂O₃-Fe₃O₄-S (FFS) core-shell nanorods on a carbon cloth through a simple method and use as anode material for lithium ion batteries. XRD, Raman and XPS characterization results demonstrate that the FFS core-shell nanorods comprises of both Fe₂O₃ and Fe₃O₄ as well as S element. The FFS nanorod composite as anode deliver a high reversible capacity of 1600 mA h g⁻¹ at 0.2 C. Meanwhile, the FFS electrode has a long-term cycling stability with about 95 % capacity retention, maintaining 538 mA h g⁻¹ after 100 cycles at a high current density, of 5 C. We believe that the high reversible capacity and long cycling stability of the Fe₂O₃-Fe₃O₄-S (FFS) nanorod composite attributed to the existence of both Fe₂O₃ and Fe₃O₄ with synergistic effect, S conductive coated layer as well as the carbon cloth support. Moreover, the FFS core-shell nanorods were synthesized on a carbon cloth, which could make the whole system a promising material to be utilized in the flexible lithium ion batteries.

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References