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**In-situ** Growth of FeS Microsheet Networks with Enhanced Electrochemical Performance for Lithium-Ion Batteries

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A facile solution-based approach has been developed for the preparation of mackinawite FeS microsheet networks directly on Fe foil. It is found that sulfur sources significantly impact the uniformity and purity of the products, while ethylenediamine as a strong donor ligand plays an important role in the formation of FeS microsheet networks. As comparison, numerous FeS microspheres are obtained in the absence of ethylenediamine. The FeS microsheet networks deliver promising Li storage capacity (772 mAh g\(^{-1}\) at the 1\(^{st}\) cycle and 697 mAh g\(^{-1}\) at the 20\(^{th}\) cycle), much higher than that of the FeS microspheres. The enhanced electrochemical performance of the FeS microsheet networks can be attributed to their layered structure and unique morphology, which possesses larger electrode-electrolyte contact area, shorter diffusion length of the ions and easier transportation of the electrons.

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1 Introduction

Layered transition-metal sulfides are theoretically and technologically important materials due to their interesting electronic, 1 electro-chemical 2-5 and optical 6, 7 properties resulting from their low dimensionality. Two-dimensional (2D) nano/micro sheets of these layered-structured metal sulfides can be obtained through direct growth or exfoliation due to their weak interlayer bonds. There have been some pioneer works for the direct growth of ultrathin mackinawite-type FeS nanosheets, 8 greigite-type Fe₃S₄ nanoplatelets 9 and ultrathin MoS₂ sheets 10. However, they are usually harvested in powder form, which is susceptible to dissolve, agglomerate, and sinter when they are used for the fabrication of thin-films. It is necessary to explore a facile approach to grow 2D nanostructured metal sulfides directly on a substrate.

2D nanostructure of some layered-structured metal sulfides such as MoS₂ 11, 12 and WS₂ 13 have been previously studied in energy storage systems due to their unique structural and surface properties. However, the metal elements in these sulfides are relatively heavy, which may limit their theoretical specific energy densities. 14 Among metal sulfides, iron sulfides have attracted great attention due to their cost effectiveness and abundance in nature. They have been explored as a material for microbial fuel cells 15 and as a substrate for the removal of toxic trace metals from water 16. Also, iron sulfides are suitable electrodes for thermal primary batteries 17 and lithium ion batteries (LIBs) 18-20 because of their high theoretical capacities of 609 mA h g⁻¹ for FeS and 894 mA h g⁻³ for FeS₂. 21, 22 However, the main drawback of these electrode materials stems from the huge volume expansion–contraction caused by the lithiation and delithiation processes. For example, the reduction of FeS to Fe and Li₂S leads to a 200% volume expansion, leading to pulverization and thus a loss of electrical contact. 23 2D nanostructured electrodes have been confirmed to well sustain the volume change and thus benefit for the integrity of electrode during cycling. Zheng’s group have reported that the 2D structure and large amounts of mesopores within the nanosheets can effectively improve structural stability, reduce the diffusion length for lithium ions and electrons, and buffer volume expansion during cycling. 24 Xu et al. 14 also confirmed the nanosheets can effectively accommodate large volume changes induced during the charge/discharge process. Furthermore, an intimate electric contact between the electrode and current collector, which can be realized by the direct growth of electrode materials on current collectors, is also extremely important both for fast electrochemical reactions and prolonged cycling behaviour. 25

Herein, we report a facile solution-based approach for the in-situ growth of FeS microsheet networks on iron foil, which exhibits improved lithium storage performance. It was found that the sulfur sources have significant impact on controlling the uniformity and purity of the final products, while ethylenediamine (EDA) as a strong donor ligand plays an important role in the formation of FeS microsheet networks. The formation mechanism of the 2D FeS nanostructured films is proposed according to time-dependent experiments and adjusted synthesis conditions. Benefitted by the 2D layered structures of mackinawite FeS and direct growth of vertically-aligned structures on iron foil, the FeS microsheet networks exhibited notably improved capacity performance for LIBs.

2 Results and discussion

2.1 Microstructure

Fig. 1a shows the XRD patterns of the FeS microsheet networks. All the diffraction peaks can be well indexed as the mackinawite FeS (PDF No. 86-0389), except for three additional peaks corresponding to the iron foil substrate. The strong and sharp diffraction peaks imply that the FeS microsheet networks are highly crystallized. It should be noted that the strongest peak in the FeS microsheet networks is not (001) suggested by the standard PDF card, but (110) and (200), indicating the favored growth orientation of the FeS microsheet networks. In comparison, the FeS microspheres exhibit similar XRD patterns (Fig. 1b) as the FeS microsheet networks, which also match well with the patterns of mackinawite. However, the intensities of most peaks are in consistent with the standard powder mackinawite patterns, indicating that there is no texture or favored orientation for FeS microspheres.

Fig. 1 XRD patterns of the FeS products (a) microsheet networks and (b) microspheres.

The the FeS microsheet networks were further characterized by FESEM and TEM as illustrated in Fig. 2. FeS microsheets are formed in network-like structure on a large scale area (Fig. 2a).
Additionally, a single microsheet is assembled by several nanosheets as depicted in the insert image in Fig. 2a. Typical cross-section FESEM image (Fig. 2b) clearly shows those microsheets nucleate from the Fe substrate and grow up vertically with a height of 20–25 µm. An individual FeS nanosheet with two perpendicular surfaces is clearly shown in TEM image (Fig. 2c). Meantime, the corresponding selected area electron diffraction (SAED) patterns are given as an insert in Fig. 2c, the two perpendicular surfaces could be indexed as (110) and (100) respectively. The HRTEM image of the region highlighted by a black rectangle in Fig. 2c is shown in Fig. 2d. The lattice planes are clearly observed and indexed as (110), (100) and (200). The TEM observation suggests that the FeS microsheets are surrounded by the {110} planes, which is in well agreement with the XRD results that (110) peak of FeS microsheets has an abnormal strong intensity (Fig. 1a). Based on the TEM characterization, the morphology and the growth orientation of the FeS microsheet can be illustrated in Fig. 1e.

Replacing Na₂S and S powder with Tu as the sulfur source in the absence of EDA and keeping other synthesis parameters similar will lead to the growth of FeS microspheres. A panoramic FESEM image in Fig. 3a displays that the diameter of the FeS microsphere is 2–5 µm. The high-magnification FESEM image (Fig. 3b) illustrates that the surface of the FeS microsphere is not smooth and it is built by numerous microsheets. Typical image of an individual FeS microsphere was shown in Fig. 3c. The corresponding SAED patterns consist of several rings, suggesting the polycrystalline characteristics. Fig. 3d shows the HRTEM image of the edge of the microsphere. Several nanograins with different orientation are clearly observed, which also confirms the polycrystalline characteristics of the FeS microsphere.
2.2 Possible growth mechanism of the FeS films

In order to clarify the formation mechanism of the FeS microsheet networks on Fe foil, the products grown for various periods were investigated by FESEM. After reaction for 4 h, a gray film was obtained and many nanosheets appeared clearly on the Fe surface (Fig. 4a). When the reaction time was extended to 6 h, the size and number of nanosheets increased and spread uniformly on the substrate (Fig. 4b). When the reaction time was further increased to 9 h, the microsheets grew larger and fully covered the substrate and became dense to form a net-like film (Fig. 4c), which similar to that obtained at 12 h. The FeS film did not detach from the Fe foil, even after long periods of intense ultrasonication, suggesting that the film strongly adhered to the substrate. This strong adhesion was presumably due to the in-situ growth of FeS nanosheet from the Fe foil.

Similar time-dependent experiments were carried out to investigate the formation and evolution of the FeS microspheres. As shown in Fig. 4d, at the early reaction stage, the products were composed of numerous nanosheets which were uniformly and densely distributed on the substrate. When the reaction time was extended to 6 h, the nanosheets grew larger and tend to aggregate together to form flower-like products (Fig. 4e). When the reaction was further prolonged to 9 h, the microsphere-like product fully formed, as displayed in Fig. 4f. The FESEM observation indicates that the nanosheets gradually aggregated into microspheres with increasing reaction time. These processes seem to obey the Ostwald ripening mechanism, as they were driven by decreasing the surface energy to form a densely packed morphology.

The growth of FeS microsheet networks and FeS microsheets is schematically illustrated in Fig. 4g. The uniform microsheet networks were successfully obtained with Na$_2$S·9H$_2$O and S powder as sulfur sources in the presence of EDA (Fig. 2a). A likely reaction pathway is that Fe$^{3+}$ in precursor solution reacts with Fe foil to form Fe$^{2+}$: 2Fe$^{3+}$ + Fe $\rightarrow$ 3Fe$^{2+}$ (4). Then Fe$^{2+}$ likely reacts with EDA to form [Fe(EDA)$_n$]$^{2+}$ ($m$>$0$). At the same time, some S in solution reacts with Na$_2$S to form S$^2$ and other S steadily supplies S$^2$ in a controllable way. Then, S$^2$ and S$^2$ react with [Fe(EDA)$_n$]$^{2+}$ to form FeS·mEDA nuclei layers for uniform FeS microsheet in the EDA-sufficient precursor. The shape of the crystalline FeS sheets may be directly related to the crystal lattice structure of the mackinawite phase instead of the influence of solvents. Mackinawite adopts a layered structures that are held together through Van Der Waals interactions, leading to the growth within the (001) plane. This is consistent with nanosheets of mackinawite-type FeS that are truncated along the [001] direction, and further indicates that the nanosheet morphology is characteristic of the bulk of the sample.

To investigate the effect of the EDA and sulfur sources on the obtained products, we carried out the synthesis of FeS under different conditions. When we substituted Tu for Na$_2$S·9H$_2$O and S in the presence of EDA, flower-like microsheets products with poor orientation was obtained as shown in Figure S2a. The likely reaction pathway is that thiourea reacts with H$_2$O in the system to produce S$^2$ which bonds with [Fe(EDA)$_n$]$^{2+}$ in solution to form FeS·mEDA. XRD (Figure S2b) studies suggest that the layered structured products contain not only mackinawite FeS, but also

![Fig. 3](a) and (b) FESEM images of FeS microspheres; (c) TEM image of a single microsphere, insert is the corresponding SAED patterns and (d) HRTEM image of the edge of the microsphere.
some impurities (Fe$_{1-x}$S). Wang et al. 28 indicated that the poor orientation of the microsheet and the existence of impurities would be due to the reaction being too fast to control at high temperature when Tu was used as the sulfur source.

It is well-known that solvent plays an important role in determining the final morphology of crystals. Various solvents with different chemical and physical properties can affect the reactivity, solubility and diffusion behavior of the reactants. The coordinating ability and polarity of the solvents have a great influence on the crystal morphology of the final product in particular. 29, 30 The EDA molecules have the strong coordinating ability and function as metal activation (chelation) or mediating the electron transfer in the reaction system. These molecules enable the forming of chemically stable coordinating metal complexes with metal ions and such metal complexes will perform as the intermediate species in the chemical reaction. 31, 32 Furthermore, Lu et al. 33 found that EDA was a strong donor ligand due to its N-chelating behavior and it played an important role in the formation of 2D ZnS nanobelt arrays. As a result, the FeS-EDA molecular precursors may serve as molecular templates in the control of the crystal growth, which is lead to the microsheet networks obtained in the presence of EDA. 31, 34, 35 Replacing EDA with H$_2$O as solvents leads to the change of growth significantly and finally the nanosheet aggregates into sphere to minimize the surface energy. It is found that the sulfur sources and the EDA have a significant effect on the growth mechanism of the FeS nanostructured films, which is schematically illustrated in Fig. 4 (g).
2.3 Electrochemical performance

The electrochemical properties of FeS microsheet networks and microspheres as anode electrodes in lithium-ion storage were tested based on two-electrode coin-type cells with Li metal as the counter-electrode. Fig. 5a shows the cyclic voltammograms (CVs) of the FeS microsheet networks at a scan rate of 0.1 mV s⁻¹ between 0.01 and 3.0 V. At the 1st cycle, three reduction peaks appear obviously at 1.2, 1.15 and 0.5 V, while only one oxidation peak is shown at 2.0 V. The small peak at 1.2 V is related to the formation of Li₂FeS₂. 21, 30 2FeS + 2Li⁺ + 2e⁻ = Li₂FeS₂ + Fe (1) and the sharp peak at around 1.15 V accounts for the conversion reaction 37: FeS + 2Li⁺ + 2e⁻ = Li₂S + Fe (2). The broad peak at 0.5 V is attributed to the decomposition of the electrolyte and formation of a solid electrolyte interlayer (SEI). Fong et al. 38 indicated that the peak at around 2.0 V might correspond to the oxidation of Fe to form Li₃.₅FeS₂ as Fe + Li₂S → 3Li + xFe → Li₁₋ₓFeS₂ (3). The cathodic peak shifts to 1.3 V for the 2nd cycle, which mainly originates from the irreversible insertion reaction during the first lithiation process. 39 The peak at around 2.0 V during the following charge step is attributed to the delithiation process of Li₁₋ₓFeS₂ to form LiₓFeS₂. Worthy of noting, the electrochemical behaviour of the FeS microsheet networks electrode is largely sustained in the following cycles, with gradual changes in intensity of the peaks. Chen et al. 40 indicated that the conversion between Li₁₋ₓFeS₂ and LiₓFeS₂ is reversible, which enables the application of iron sulfides in rechargeable LIBs.

Charge/discharge voltage profiles of FeS microsheet networks electrode at 0.1 A g⁻¹ are shown in Fig. 5b and are in agreement with the CV curves. There are two plateaus during the first discharge, which are similar to those reported previously in the literature. 14 The electrode delivers an initial discharge capacity of 772 mAh g⁻¹ and a charge capacity of 679 mAh g⁻¹, leading to a first-cycle Columbic efficiency of 87.9%. It is well-known that the irreversible capacity loss during the first cycle arises due to inevitable formation of SEI film and electrolyte decomposition. During the second cycle, the FeS microsheet networks electrode delivers a discharge capacity of 697 mAh g⁻¹ and a charge capacity of 674 mAh g⁻¹ with a much higher Columbic efficiency of 96.7%. What is more, FeS microsheet networks exhibit a narrow voltage hysteresis as confirmed by the closer discharge/charge voltage profiles.

The discharge/charge cycling stability of FeS microsheet networks and microspheres electrodes were examined at a current density of 0.1 A g⁻¹ between 0.01 and 3.0 V (Fig. 5c). The discharge capacity of the FeS microsheet networks electrode is 772 mAh g⁻¹ at the 1st cycle and remains at 677 mAh g⁻¹ at the 20th cycle, indicating a stable cycling characteristic. As comparison, FeS microspheres anode delivers a discharge capacity of 743 mAh g⁻¹ at the 1st cycle and a lower capacity of 233 mAh g⁻¹ at the 20th cycle. These results reveal that FeS microsheet networks exhibited much higher lithium-ion storage capacity and much better cyclic performance than FeS microsphere films. FeS microspheres exhibit the poor electrochemical performance, a possible reason is that the poor electric contact between the microspheres and current collector (Fig. 3a), deceasing the amount of effective substance during cycles. The high capacity performance of FeS microsheet is superior to that of most FeS electrodes previously reported, including pristine FeS-embedded carbon microspheres and bare FeS nanocrystals. 14, 21

To better understand the advantage of the FeS microsheet arrays in lithium storage, the rate performance of the FeS microsheet networks electrode is also investigated (Fig. 5d). It depicts tenth-cycle discharge capacities of around 797, 770, 505 and 357 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5 and 1 A g⁻¹, respectively. Even at the current density of 2 A g⁻¹, the FeS microsheet arrays still delivered a tenth-cycle discharge capacity of 150 mAh g⁻¹, which are about two times larger than those reported of the powder FeS electrode at 2 A g⁻¹. 19 As the current density returns to the initial value of 0.1 A g⁻¹, the electrode resume a capacity of 593 mAh g⁻¹, indicating that the electrode has lost some capability and shows a certain decline of performance during high rate discharges.

As shown in Fig. 5e, after 20 cycles, the microsheets are thickened to some degree resulting from the repeating lithiation and delithiation reactions. Part space between the original open-structures between the FeS microsheets is filled with a little reaction products remaining from the lithiation and delithiation process, which may lead to a slight irreversible capacity loss. 40, 41 However, the structural integrity of the FeS microsheet array is well preserved. The enhanced structure stability should be attributed to the unique architecture of net-structured microsheet array.

Compared with FeS microsphere or nanoparticle films, FeS microsheet networks possess a much better electrochemical performance for lithium-ion batteries, which could be deduced from their morphologies and structures due to following advantages:

(1) The microsheet structure greatly shortens the ionic diffusion length and provides sufficient electrode-electrolyte contact area for lithium-storage reactions (Fig. 5f). 39,42,43 Furthermore, the CV peak shape of FeS microsheet networks was sharp and intense (Fig. 5a), demonstrating that the products have low overall resistance and great efficiency of the redox reaction. The low voltage hysteresis (Fig. 5b) should result in faster kinetics and improved energy efficiency.

(2) The FeS microsheets are interconnected with each other to form macropores, which can effectively accommodate large...
volume change induced by the Li$^+$/ diffusion/extraction (Fig. 5f). Therefore, the structural integrity could be well remained during the discharge/charge processes (Fig. 5e). 34,45

3) Compared with the fabrication of the traditional battery electrode, in-situ growth of microsheet networks onto the metal current collector results in good electrical contact of every microsheet with the metal current collector. That should be beneficial for easier transportation for electrons and lithium ions, and good strain accommodation. 46,47 What’s more, no additive is needed for the preparation of electrode.
Fabrication of FeS microsheet networks: FeCl$_3$·6H$_2$O (0.5 mmol) and Tu (2 mmol) were added in 30 mL DI water to form a homogenous solution. Then the solution was added into a 30 mL Teflon-lined autoclave with a piece of clean iron foil-placed standing against the wall. The autoclave was heated at 160 °C for 12 h and cooled down to room temperature. The iron foil was taken out and thoroughly rinsed with distilled water and absolute ethanol, and finally dried for characterization.

Characterization: All observation and characterization were performed and analyzed on the face side. The structural characteristic of the samples was tested by X-ray diffraction diffractometer (XRD, X'Pert PRO) using Cu Kα radiation. The data were collected from 2θ = 10-90° in a step-scan mode. The morphologies of the samples were investigated by a field-emission scanning electron microscopy (FESEM, Hitachi SU-70). The substrate-bound iron sulfide were scraped from the Fe foil mechanically, dispersed in an alcohol solution ultrasonically and then deposited on carbon-coated copper grids for high resolution transmission electron microscope (HRTEM, JEM-2100) characterization.

Electrochemical properties: The coin-type cells were assembled in a glove box filled with pure argon gas directly using the FeS grown on iron substrate as the cathode without any ancillary materials and lithium metal as the anode. Both the cathode and anode were electronically separated by a polypropylene film saturated with 1 M LiPF$_6$ electrolyte solution made up of 1: 1 w/w diethyl carbonate and ethylene carbonate. Charge-discharge cycles were performed in the potential range of 0.01 and 3.0 V at room temperature using a multichannel battery test system (Neware, BST-610). Cyclic voltammetry (0-3 V, scan rate of 1 mV s$^{-1}$) was carried out with an electrochemical workstation (Solartron).

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