



General and facile synthesis of metal sulfide nanostructures: *In situ* microwave synthesis and application as binder-free cathode for Li-ion batteries



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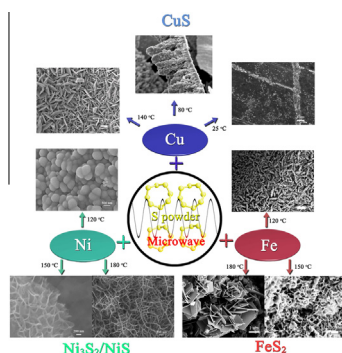
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HIGHLIGHTS

- A general and facile microwave irradiation approach is developed for metal sulfides.
- Morphology control is achieved for three types of metal sulfides.
- CuS exhibits superior electrochemical properties as a binder-free cathode for Li-ion battery.

GRAPHICAL ABSTRACT

A general and facile microwave irradiation approach is reported for *in situ* synthesis of several types of transition metal sulfides on metal foils with morphology control. The Cu foil supported CuS exhibits superior electrochemical properties as a binder-free cathode for lithium ion battery.



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ABSTRACT

Several transition metal sulfides (CuS, NiS/Ni₃S₂, FeS₂, Co₉S₈) with various morphologies are *in situ* synthesized on the corresponding metal foils in the presence of sulfur by a facile single-mode microwave irradiation approach. The irradiation temperature is found to be a key parameter to tune product morphologies for various metal sulfides (CuS nanoparticle at 25 °C; CuS nanobud at 80 °C, CuS nanosheet at 140 °C; NiS/Ni₃S₂ nanoparticle at 120 °C, NiS/Ni₃S₂ interlinked nanosheet at 150 and 180 °C, FeS₂ nanoparticle at 120 °C, FeS₂ interlinked nanosheet at 150 °C, and FeS₂ nanosheet at 180 °C). In general, the particle product is obtained at a low irradiation temperature, while nanosheet and interlinked porous nanosheet are obtained at higher temperatures. As a proof of concept, Cu foil supported CuS nanosheets and nanobuds are also directly used as cathode materials for lithium ion battery without addition of conductive agent and binder material. The CuS nanosheet exhibits an initial reversible capacity of 588 mAh g⁻¹ at 56 mA g⁻¹ with a small capacity fading rate of 0.17% per cycle during 100 cycles and a good high-rate capability (463 mAh g⁻¹ at 2.8 A g⁻¹).

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1. Introduction

Transition metal sulfides have been widely investigated due to their attractive properties and applications in versatile fields such as energy storage properties [1–8], microwave absorption properties [9], photocatalytic properties [10,11], optical properties [12] and electrochemical capacitor [13–15]. They usually exhibit higher electrical conductivity and mechanical stability than their corresponding metal oxides. Several approaches have been developed including templating method [16,17], solvothermal/hydrothermal method [18–25], microwave irradiation [26–28] and calcination method [29,30] for the synthesis of metal sulfide with various morphologies such as particle [6,7,20,23,25,29,30], nanosheet [2,3,11,14,16,26–28,31–32], flower [8–10,17,18,24,26,27,32], nanowire/nanorod [4,5,33], and microsphere [33–35]. In particular, sulfur and metal sulfides have been suggested as promising electrodes for Li-ion batteries basically because the active sulfur element can deliver a large theoretical Li-storage capacity of 1675 mAh g^{-1} [36–38]. Previous efforts have found that there is strong correlation between metal sulfide nanostructures and their Li-storage electrochemical properties [20–30,36–38]. Moreover, most of the used methods are still complicated for the control of metal sulfides morphologies. To realize future promise of various metal sulfide nanostructures, a general, reliable, fast, cost-effective and environmentally-benign preparation method with easily-tuned experimental parameters is highly desirable.

Herein, we report a general and facile microwave-assisted approach to obtain four kinds of metal sulfides with tuned morphologies by varying irradiation temperatures. The metal foil and sulfur were simply irradiated for only 20 min in a single-mode microwave reactor. The obtained metal sulfide films consist of building blocks with different morphologies (nanoparticle, nanobud, nanosheet, and interlinked nanosheet) and were formed directly on the corresponding metal foils. As a proof for concept, Cu foil supported CuS nanostructures were also explored as binder-free and conductive agent-free cathode materials for Li-ion battery.

2. Experimental

2.1. Material preparation

0.045 g sulfur powder (Alfa Aesar) was dispersed in 20 ml N-methyl-2-pyrrolidinone (NMP) at room temperature ($\sim 25^\circ\text{C}$). A circular metal foil (Cu, Ni, and Fe) with a diameter of 12 mm was

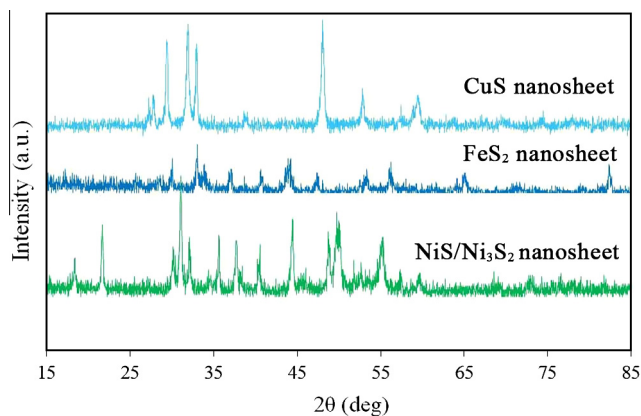


Fig. 1. XRD patterns of copper sulfide nanosheet prepared at 140°C , iron sulfide nanosheet prepared at 180°C , and nickel sulfide interlinked nanosheet prepared at 180°C .

then put into the above suspension. The mixture was sealed in a 40 ml specialized glass tube ($\sim 3 \text{ cm}$ in diameter and 6 cm in height) under microwave irradiation for 20 min at different temperatures varying from 25°C to 180°C in a single mode microwave reactor (Nova, EU Microwave Chemistry). The microwave power fluctuates in a range of ~ 20 – 200 W to maintain the temperature. Metal sulfides products were obtained on the corresponding metal foil after cooling the system to room temperature naturally, washing with absolute ethanol and drying at 60°C overnight. In addition, cobalt powder was also used to synthesize cobalt sulfide (Co_9S_8) nanoparticle on cobalt foil under microwave irradiation for 20 min at 180°C .

2.2. Material characterizations

The obtained four types of metal sulfide products were peeled off from metal foil substrate and characterized by X-ray diffraction (XRD, Rigaku D/max-2550V, Cu K α radiation), field-emission scanning electron microscopy (FE-SEM, JSM-6700F) with an energy dispersive X-ray (EDX) spectrometer, and transmission electron microscopy (TEM, JEOL JEM-200CX) in the Instrumental Analysis and Research Center of Shanghai University. The X-ray photoelectron spectroscopy (XPS) measurement was carried out by a Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System.

2.3. Electrochemical measurements

To evaluate electrochemical performances of copper sulfide materials, Swagelok-type cells were fabricated in an Ar-filled glove box. The working electrodes were the as-synthesized copper foil supported copper sulfide without adding conductive agent and binder materials. Lithium foil (China Energy Lithium) was used as the counter electrode. The electrolyte was 1 M lithium bis(tri fluoro-methane-sulfonyl)imide (LiTFSI) dissolved in 1:1 v/v 1, 2-dimethoxyethane (DME) and 1, 3-dioxolane (DOL). Electrochemical measurements were performed on a LANDCT2001 test system. All half-cells were discharged (lithium insertion) and charged (lithium extraction) at a constant current (0.1, 0.2, 0.5, 1, 2 and 5 C, $1\text{C} = 560 \text{ mA/g}$) in 1–3 V. Cyclic voltammetry (CV) measurements was fulfilled on a CHI660D electrochemical workstation at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

Powder X-ray diffraction (XRD) patterns of three types of metal sulfides (in the absence of metal foils) are shown in Fig. 1. The diffraction peaks of the obtained copper sulfide and iron sulfide can be well indexed to the standard CuS (PDF: 65-7111) and FeS_2 (PDF 65-2567). Various diffraction peaks of nickel sulfide can be indexed to the mixture of Ni_3S_2 (PDF: 44-1418) and NiS (PDF: 12-0014). Powder X-ray diffraction (XRD) patterns of the products with other morphologies are shown in Fig. S1, Supporting information, which can be also indexed to the corresponding metal sulfides.

Fig. 2 shows scanning electron microscope (SEM) images for CuS at different temperatures for microwave irradiation. When the reaction temperature is 25°C , the obtained products are CuS nanoparticles, which tend to align to form line-like structure, as shown in Fig. 2a and b. SEM images of Fig. 2c and d show CuS nanobud array products, which are obtained at 80°C . These CuS nanobuds are composed of numerous CuS particles. When the temperature is further increased to 140°C , CuS nanosheets are obtained (Fig. 2e and f). These leaf-like nanosheets seem to stand on the Cu foil with similar orientation, forming an interconnected nanosheet-assembled network. A single CuS nanosheet is shown in

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