



Facile synthesis of metal disulfides nanoparticles encapsulated by amorphous carbon composites as high-performance electrode materials for lithium storage



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ARTICLE INFO

Article history:

Received 5 April 2018

Received in revised form

28 August 2018

Accepted 19 September 2018

Available online 22 September 2018

Keywords:

Metal disulfide

Amorphous carbon layer

Electrode material

Electrochemical performance

Lithium-ion battery

ABSTRACT

With the purpose to settle the aggregation and conductivity issues of the active materials, the metal disulfides (MS_2 , $M = Fe, Co$) nanoparticles in-situ encapsulated by amorphous carbon layers ($MS_2@C$) have been synthesized by directly vulcanizing the iron (III) acetylacetonate or cobalt (II) acetylacetonate, which are both the metal source and carbon source, using sulfur power as S source and dispersant by a facile one-step heating method. A structure that MS_2 nanoparticles are well wrapped by amorphous carbon layer uniformly coated by many ultra-small MS_2 nanoparticles is obtained. Benefiting from the unique multidimensional structure that integrates the advantages of low-dimensional nanostructures and high-dimensional bulk structure, $FeS_2@C$ and $CoS_2@C$ composites evaluated as electrode materials for lithium storage exhibit superior electrochemical performance. After 100 charge-discharge cycles, this novel $FeS_2@C$ architecture delivers a reversible capacity of 829 mAh g^{-1} at 100 mA g^{-1} . Moreover, a high specific capacity of 480 mAh g^{-1} for $FeS_2@C$ at 1000 mA g^{-1} after 500 cycles is obtained. As for $CoS_2@C$ composite, a high specific capacity of 481 mAh g^{-1} at 500 mA g^{-1} after 300 cycles is still displayed. This remarkable cycling property and superior rate capability demonstrate the potential applications for next-generation lithium-ion batteries.

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1. Introduction

Currently, the lithium ion batteries (LIBs) are widely used and remain popular in electrical market [1]. However, the theoretical lithium storage capacity of the commercialized graphite anode is too low to fulfill the ever-growing demanding of burgeoning market [2,3]. And the graphite anode has a low lithiation potential at about 0.2 V (vs. Li/Li^+) close to the potential to form the lithium dendrite, which may cause some safety issues, especially at high current density [4,5]. It is imperative to develop and research competitive electrode materials for high-performance LIBs.

Transition metal dichalcogenides (FeS_2 , CoS_2 , NiS_2), which have

many advantages such as, abundant in nature, inexpensive, and high theoretical capacity, have attracted more and more attentions as promising electrode materials for energy storage [6–9]. Especially, an intrinsically conductive material, CoS_2 with good conductivity can be employed directly as conversion-reaction type electrode materials [10–12]. Similar to CoS_2 , semiconducting FeS_2 also demonstrates excellent electrochemical properties as electrode material for lithium storage [13,14]. However, the quick capacity fading upon cycling hinders their practical applications, which is considered as an identified problem in metal sulfide-based electrodes, and believed to originate from the huge volume change and the generation of polysulfide intermediates during cycling process [15–17].

Designing rational structures has been an effective way to tackle these problems [18–21]. Compared with the bulk materials, the nanostructured materials can deliver better rate capability by shortening the lithium-ion diffusion length and increasing the specific surface area. However, the low tap density and serious

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agglomeration of the nano-scaled materials during cycling limit their application directly as electrode materials [22,23]. Generally speaking, an optimal architecture composed of primary nanoparticles compacted to form 3D hierarchical structures can be an effective strategy to improve the performance of LIBs, which combines the advantages of the nanostructured materials with good rate performance and stable 3D hierarchical structure with enhanced cycling stability and high tap density. This unique structure can be formed by integrating carbonaceous materials with nano-sized materials [24,25]. Carbonaceous materials can not only help increase the electrical conductivity of the composites but also build the nanoparticles together due to the elastic feature of carbon matrix. There is a consistently great interest in low cost and accessible precursors and simple preparation method to obtain the composites combining low-dimensional metal sulfides with high-dimensional carbon layers with enhanced performance for lithium storage.

Herein, a novel structure, with two different sizes of MS_2 (FeS_2 and CoS_2) nanoparticles embedded in 3D continuous carbon network, has been fabricated through direct calcination treatment of metal acetylacetonate salts and sulfur powder. The electrochemical performances of the as-obtained composites as electrode materials for lithium storage are investigated in the ether-based electrolytes at the potential window of 1.0–3.0 V. Benefiting from the unique structure, the as-synthesized MS_2 (FeS_2 , CoS_2)@C exhibit extraordinary electrochemical lithium storage performance.

2. Experimental section

2.1. Materials synthesis

All chemicals used in this work are analytical. In a typical synthetic procedure of FeS_2 @C composites, 40 mg of Iron (III) acetylacetonate ($Fe(acac)_3$) and 100 mg of sulfur powder were firstly ground together for 30 min by using a mortar and then put into a quartz tube. Then the temperature was heated from room temperature to 350 °C and maintained this temperature for 2 h in Ar flow with a ramping rate of 1 °C min^{-1} . And the black product was collected after cooled down naturally to room temperature in the Ar-filled environment. The same procedure was employed to synthesize CoS_2 @C except that Cobalt (II) acetylacetonate ($Co(acac)_2$) was used instead of $Fe(acac)_3$.

2.2. Characterization and electrochemical measurements

The phase of the products was characterized by powder X-ray

diffraction (XRD) measurement (Cu $K\alpha$ radiation $\lambda = 0.15418$ nm, Bruker D8 X-ray Diffractometer) at a scan rate of 5 °C min^{-1} . A Hitachi S-4800 field emission scanning electron microscope (SEM) using an accelerating voltage of 10 kV was used to measure the morphologies and microstructures of the products. Transmission electron microscopy (TEM) images, high-angle annular dark-field TEM image and the EDX mapping images were examined on FEI Tecnai G2 S-twin instrument. Thermogravimetric (TG) curve was obtained in Ar atmosphere at a heating rate of 10 °C min^{-1} . Raman spectra were characterized on a Jobin Yvon Labor Raman using 438 nm laser as excitation source. X-ray photoelectron spectroscopy (XPS) spectra were carried out on an ESCALABMKLL XPS spectrometer using Al $K\alpha$ source.

The electrochemical tests of the as-obtained materials were examined by using CR 2025 coin-type half cells assembled in an Ar-filled glove box with the oxygen and moisture controlled below 1 ppm. The slurry was prepared by mixing the as-prepared products with carbon black and poly(vinylidene difluoride) in a weight ratio of 70:20:10 using N-methyl-2-pyrrolidone (NMP) as solvent, and then pasted onto a pure copper foil and dried at 80 °C for 12 h in vacuum. The electrolyte was 1 M $LiN(CF_3SO_2)_2$ (LiTFSI) in 1,3-dioxolane/dimethoxymethane (1:1 in volume). Galvanostatic charge-discharge tests were measured on the LAND CT2001A multi-channel battery tester. The active material loadings were about 1.0 $mg\ cm^{-2}$ with a diameter of 14 mm, and the specific capacity ($mAh\ g^{-1}$) of electrodes was calculated based on the total mass of active materials (both MS_2 and carbon). Cyclic voltammetry (CV) measurements were carried out on a BioLogic VMP3 electrochemical workstation. All the tests were measured at ambient temperature.

3. Results and discussion

The MS_2 @C ($M = Fe, Co$) composites were obtained by thermolysis of the $Fe(acac)_3$ or $Co(acac)_2$ with S powders at 350 °C in Ar atmosphere. The heat-treated temperature of 350 °C is chosen according to TGA curves of the physical mixture of $Fe(acac)_3$ and $Co(acac)_2$ with S powders ($w/w = 40:100$) (Fig. S1a and S1b, Supporting Information). During the annealing process, the organic parts of the precursors are thermally polymerized firstly to form cross-linked organics and then pyrolyzed to produce the oxygen-rich carbon layer, and metallic ions react with S to generate MS_2 nanoparticles. It should be emphasized that the formation of amorphous carbon and MS_2 nanoparticles is taken place simultaneously. Therefore, MS_2 nanoparticles are well wrapped by carbon layers. The crystal structure and phase compositions of the sample

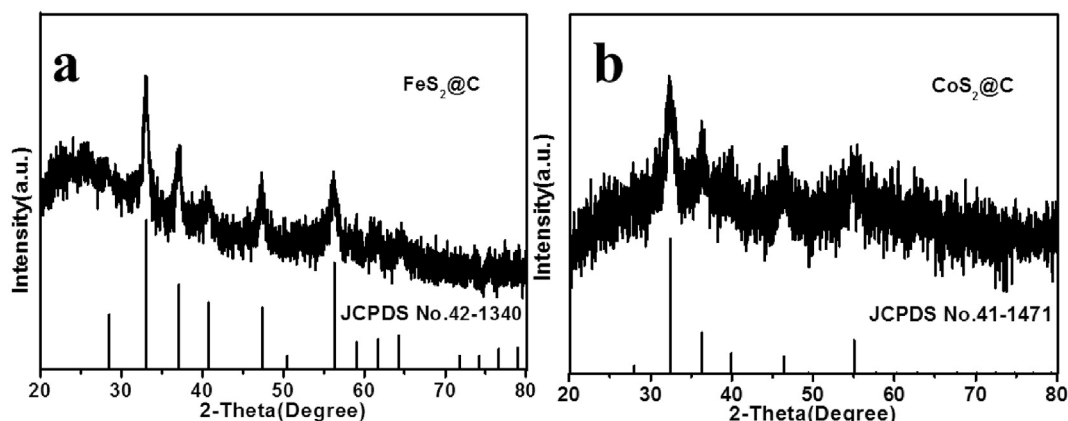


Fig. 1. XRD patterns of (a) FeS_2 @C and (b) CoS_2 @C.

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