

Preparation of FeS₂ nanotube arrays based on layer-by-layer assembly and their photoelectrochemical properties



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ABSTRACT

Well-aligned one-dimensional iron pyrite FeS₂ nanotube arrays have been fabricated *via* layer-by-layer assembly technique on ZnO nanorod arrays in combination with subsequent sulfurization. The as-prepared products were confirmed to be pure phase pyrite FeS₂ with Fe/S ratio approaching 1/2. Typical nanotube structure was observed for the FeS₂ with average outer diameter of 150 ± 20 nm and wall thickness of 50 ± 5 nm. Comparisons of photoelectrochemical properties between FeS₂ nanotubes and FeS₂ nanoparticles were conducted. Tafel polarization curves and electrochemical impedance spectroscopy indicate that FeS₂ nanotubes possess high corrosion resistance and electrochemical stability. The *J*-*V* curves show that the photocurrent at 1.0 V for FeS₂ nanotubes is more than five times larger than that of FeS₂ nanoparticles, indicating enhanced photoresponse and rapid charge transfer performances of 1-D nanotube structure. The enhanced photoelectrochemical properties mainly benefit from the unique architecture features of nanotube array structure.

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1. Introduction

Iron pyrite FeS₂ is of great promise for applications in solar photovoltaics [1], photoelectrochemical cells [2,3] and Li-ion batteries [4,5] due to unique properties, such as suitable band gap ($E_g = 0.95$ eV), high optical absorption coefficient ($\alpha > 10^5$ cm⁻¹ for $\lambda \leq 700$ nm) [6–8] and adequate minority carrier diffusion length (100–1000 nm) [9]. Compared with other chalcogenide semiconductors, storage abundance and nontoxicity as well as low cost of the component elements (Fe, S) further attract enormous interest in pyrite FeS₂ [10]. Despite these advantages, its applications in energy-based devices has been limited by defect states (sulfur vacancies) and intermediate phases (e.g. FeS and Fe_{1-x}S) [11], which is commonly observed in FeS₂-based systems [12]. Recently, many researchers [13–15] have put their eyes on one-dimensional (1-D) structure design of materials to compensate for performances loss caused by defects.

Though many methods, such as chemical vapor transport [16], hydrothermal/solvothermal method [17], molecular self-assembly [18,19], anodic oxidation [20] and template directed synthesis [21] have been developed for the fabrication of nanotube structure, researches about FeS₂ nanotubes are still very few. To the best of our knowledge, Shi et al. [8] and Li et al. [10] applied sulfurization of precursor and anodic aluminum oxide (AAO) template-directed methods, respectively, to prepare ordered FeS₂ nanotube arrays and study their optical absorption property. Liao et al. [22] obtained macroporous FeS₂ nanotubes *via* solvothermal method and explore its Li-ion battery properties. In addition, there are some similar research about nanotube design for other materials, such as iron sulfide (FeS) [23] and TiO₂/FeS₂ composite [24]. Among these researches, most focus on either the fabrication as well as structure characterization or the light absorption and photoresponse performances of nanotube. Beside these researches, we additionally explored the electrochemical properties (e.g. corrosion resistance and electrochemical stability) of 1-D nanotube and the influence of different structures has on the properties. It lays a foundation for its future applications in electrochemical field.

In this work, we report the use of layer-by-layer (LBL) assembly method, for the first time, to synthesize sulfide, e.g. FeS₂. A detailed schematic diagram was drawn to describe the preparation process.

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Abundant characterization approaches were used to investigate the phase purity and structure of FeS₂ nanotubes. Comparisons of the electrochemical properties and photoresponse performance between FeS₂ nanotubes and FeS₂ nanoparticles were conducted.

2. Experimental

2.1. Synthesis of ZnO nanorods

ZnO nanorod arrays (ZNAs) were prepared via a two-step seeding and solution hydrothermal growth process. The detailed chemical reagents and experimental procedures were described in our previous report [25].

2.2. Synthesis of polyelectrolyte-modified ZnO nanorods

Poly(diallyldimethylammonium chloride) (PDDA; *M_w* < 500,000 Da) and poly(sodium 4-styrenesulfonate) (PSS; *M_w* < 70,000 Da) were purchased from Alfa Aesar Co. Ltd. All the chemicals were analytical grade without further purification. ZNAs were firstly modified by PDDA and PSS in sequence via LBL assembly. Briefly, ZNAs grown on fluorine doped tin oxide (FTO) substrate were put into 50 mL 0.5 M NaCl solution and sonicated for 1 h. Then 50 mg PDDA was added into above solution and stirred for 0.5 h. Subsequently, the excess PDDA was removed by washing repeatedly six times. Similarly, the PSS layers were then coated onto the surface of the PDDA modified ZNAs. Finally, negatively charged PDDA/PSS-modified ZNAs were achieved.

2.3. Synthesis of FeS₂ nanotubes

PDDA/PSS-modified ZNAs were kept still in 50 mL 0.015 M FeCl₃ aqueous solution for 30 min. Then, 10 mL NaBH₄ (2 g/L) aqueous solution was added into the FeCl₃ solution drop by drop. After finishing the dropping process, the intermediate product films were washed with distilled water and ethanol, and dried at 100 °C in air. The obtained intermediate product and sublimed sulfur powder (an amount calculated to produce 80 kPa sulfur pressure at the annealing temperature) were sealed in quartz ampoules, which were filled with pure Ar and evacuated repeatedly five times before sealing. Finally, FeS₂ nanotubes were obtained by annealing the sealed quartz ampoules at 350 °C for 2 h. The calculation equation between the amount of sulfur powder and resulting vapor pressure is shown as follows:

$$PV = nRT \quad (1)$$

where *P* represents the sulfur pressure; *V* is the volume of quartz ampoule; *n* is the molar quantity of sulfur powder; *R* is the gas constant; *T* represents the absolute temperature of sulfurization.

2.4. Characterization of FeS₂ nanotubes

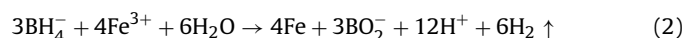
The crystalline phase of the products was determined by an X-ray diffractometer (XRD, Shimadzu XRD-6000) with Cu *K α* radiation. A Renishaw inVia confocal Raman microscope with 532 nm laser excitation was used for the Raman measurements. The ionic characteristics and surface composition were studied by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). The morphologies of the samples were observed by field-emission scanning electron microscopy (FESEM, Hitachi SU-70). High-resolution transmission electron microscopy (HRTEM, FEI-F20) equipped with an energy-dispersive spectrometer (EDS, Oxford INCA) was applied to further investigate the microstructure and composition of the products. Electrochemical experiments were performed in an electrochemical workstation (Parstat 2273, Princeton Applied Research) equipped with a three-electrode system

using FeS₂ film (1 cm × 1 cm) as the working electrode, a platinum foil (1 cm × 1 cm) as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and 0.5 M H₂SO₄ solution as the electrolyte. Open circuit potential (OCP) curves were measured for 600 s and at a scan rate of 0.2 s per point. Tafel polarization curves were measured from 0.1 to 0.8 V at a constant rate of 10 mV/s. Electrochemical impedance spectroscopy (EIS) were performed at the open circuit potential and in the frequency range of 1 × 10⁵ to 0.01 Hz. The amplitude of the sinusoidal excitation signal was 10 mV. The photoresponse measurements were conducted using a xenon lamp with intensity of 500 mW cm⁻² as irradiation source and 0.5 M Na₂SO₄ solution as electrolyte.

3. Results and discussion

3.1. Synthetic scheme

A brief introduction about the fabrication process of FeS₂ nanotubes is depicted as shown in Fig. 1. The specific procedures are described as follows. First step, the negatively charged ZnO nanorods were obtained by absorbing the positively charged PDDA and negatively charged PSS polyelectrolyte in sequence via the LBL assembly. Second step, positively charged metal iron ions (Fe³⁺) were absorbed onto the surface of the negatively charged polyelectrolyte-modified ZnO nanorods due to the strong electrostatic interaction between positive and negative charges. Third step, the adsorbed metal iron ions (Fe³⁺) were reduced to metallic Fe by adding NaBH₄ to the solution drop by drop. The chemical equation is described as follow [26]:



Meanwhile, the H⁺ produced in the above step will dissolve ZnO *in situ*, which prefers to happen along the axis of ZnO nanorod. As a result, Fe nanotubes were obtained by removing out the ZnO nanorod templates completely. Fourth step, the metallic Fe was quickly oxidized into Fe₂O₃ because of oxygen dissolved in the solution from the surrounding ambient air. Fe nanotubes were transformed to Fe₂O₃ nanotubes. Final step, FeS₂ nanotubes were obtained by sulfurization of the obtained Fe₂O₃ nanotubes. Different from carbon nanotube [27] and polycarbonate [28] templates used in LBL assembly for nanotube preparation, ZnO template can be completely removed out *in situ* after LBL assembly and no extra template removal steps such as calcination and solution dissolution are required. To a large extent it can simplify the operation steps and shorten experimental period.

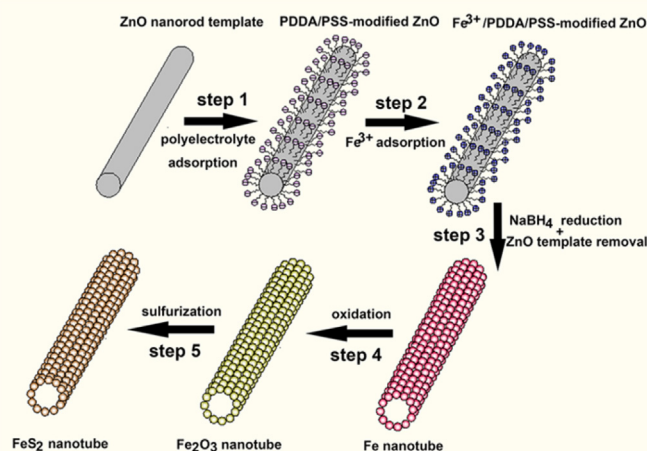


Fig. 1. Schematic diagram for the growth process of FeS₂ nanotubes.

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