



Construction of cobalt sulfide/nickel core-branch arrays and their application as advanced electrodes for electrochemical energy storage



Minghua Chen^{a,*}, Jiawei Zhang^a, Xinhui Xia^b, Meili Qi^a, Jinghua Yin^a, Qingguo Chen^{a,*}

^a Key Laboratory of Engineering Dielectric and Applications (Ministry of Education), School of Applied Science, Harbin University of Science and Technology, Harbin 150080, PR China

^b State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, and School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

Design/fabrication of advanced electrodes with tailored functionality is critical for the development of advanced electrochemical devices. Herein, we report a powerful strategy for construction of high-quality cobalt sulfide (CoS)/Ni core-branch arrays via combined methods of hydrothermal and electro-deposition. Electrodeposited thin porous Ni branch is successfully decorated on the CoS nanowires arrays with the help of hydrothermal ZnO nanorods template. Enhanced mechanical stability and improved ion/electron transfer characteristics are achieved in this composite system. As compared to the pure CoS nanowires arrays, the CoS/Ni core-branch arrays show enhanced electrochemical performance with lower polarization, better high-rate capability and superior cycling life. A high capacity of 605 mAh g⁻¹ at 2C and 371 mAh g⁻¹ at 6C is obtained in the composite core-branch system, respectively. Our developed electrode design protocol can be applicable for fabrication of other advanced metal sulfides electrodes for applications in solar cells, batteries and supercapacitors.

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1. Introduction

Currently, lithium ion batteries (LIBs) are the dominant power source in the portable electronics market because of their fascinating characteristics of high voltage, large energy density and good wide-temperature performance [1,2]. It is well known that the electrochemical performance of LIBs is mainly dependent on electrode materials, which are the key parts and determine the final performance of LIBs [3–5]. Therefore, design/fabrication of advanced electrode materials with tailored functionality or structure is always the research focus of LIBs [6].

In parallel with the advancement of cathode materials, there is also a great progress in the development of anode materials. Except for the commercial graphite, lots of high-capacity anodes (such as silicon [7–9], Sn and alloys [10,11], transition metal oxides [12,13], metal carbides [14], metal sulfides [15,16]) emerge and show much higher capacities than that of graphite. Typically, metal sulfides are entering into people's perspective due to their excellent reactivity and high capacity [17,18]. Cobalt sulfide (CoS) is considered to be one of the most promising candidates [19], but still not widely

investigated. Different from anodes with intercalation reactions (e.g., graphite), anodes (metal sulfides) by conversion reactions usually suffer from two main issues [20]. One is poor mechanical stability leading to inferior cycling life, the other is low electrical conductivity and slow ion diffusion resulting in compromised high-rate performance [21,22]. In a nutshell, smart design/fabrication and conductivity modification are highly desirable to overcome the above problems to achieve high performance.

To date, nanoporous conductive design/fabrication of arrays electrode is becoming one of most effective strategies to enhance the electrochemical performances. Xia et al. [23–25] have demonstrated that conductive core-branch nanoarrays (e.g., nanowires [23], nanotubes [26], nanoflakes [27]) could effectively solve the above problems and improved performances have been proven in these composite core-branch arrays. The nanoporous conductive core-branch arrays usually possess the following merits. 1) Good electrical contact by direct growth on the current collectors. The active nanoarrays directly grown on the current collectors can avoid the electrode fabrication process for powder materials, and eliminate some unnecessary interfaces without using polymers and additives. Additionally, nanoarrays have their own contact with the current collector and ensure full participation in the electrochemical reactions leading to higher utilization

* Corresponding authors. Tel.: +86 451 86390778; Fax: +86 451 86390779.
E-mail addresses: chenminghua@126.com (M. Chen), qgchen@263.net (Q. Chen).

of active materials [28]. 2) Highly porous network and fast diffusion of ions. There are lots of nanospace between nanoarrays facilitating fast transfer of ions and sufficient contact between active materials and electrolyte [29]. 3) High electrical conductivity. In the composite core-branch arrays, the active materials are usually decorated on the conductive core or coated by conductive branch. This can further improve the electrical conductivity providing fast electron transfer path to accelerate reaction kinetics [22]. 4) Enhanced mechanical stability. Nanoarrays with protective conductive shell possess good strain accommodation to keep electrode stable resulting in better cycling stability [30].

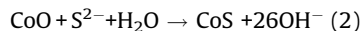
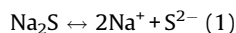
Up to now, CoS nanostructures (nanoparticles [19], and nanoflowers [31]), CoS/carbon polyhedra/CNTs [18], and CoS/reduced graphene oxides [32], have been reported and investigated as anodes of LIBs, but there are no reports on CoS based core-branch arrays and their application for electrochemical energy storage. In this work, we report a powerful strategy for construction of CoS/Ni core-branch arrays with the help of hydrothermal (HS) ZnO nanorods sacrificial template. Self-supported CoS nanowire arrays are uniformly decorated by a thin porous Ni branch deposited by an electro-deposition (ED) approach. The obtained CoS/Ni core-branch arrays have properties of enhanced mechanical stability and improved ion/electron transfer characteristics. The as-fabricated CoS/Ni core-branch arrays are characterized as anodes of LIBs and demonstrated with greatly enhanced capacity, lower polarization and cycling life as compared to the pure CoS nanowires. The developed electrode design protocol and surface modification method can provide reference for fabrication of other advanced metal sulfides composite arrays for applications in electrochemical energy storage.

2. Experimental

2.1. Preparation of CoS nanowires arrays

The CoS/Ni core-branch arrays were fabricated by a hydrothermal-ion exchange method as follows. In a typical synthesis, the reaction solution was prepared by dissolving 0.6 g $\text{Co}(\text{NO}_3)_2$, 0.15 g NH_4F and 0.6 g of urea ($\text{CO}(\text{NH}_2)_2$) in 70 mL of DI water. Clean nickel foam was used as the substrate. The solution was transferred into Teflon-lined stainless steel autoclave liners and kept at 120°C for 6 h. Then the samples were rinsed with DI water and followed by annealing at 450°C for 2 h in argon to form precursor CoO nanowires. After that, the samples underwent an ion exchange process by placing into an autoclave with 80 mL solution of 0.1 M sodium sulfide and kept at 90°C for 9 h to form the CoS nanowire

arrays. The ion exchange reactions are simply expressed as follows [33].



The solubility product constant (K_{sp}) of materials plays an important role in the ion exchange conversion from CoO to CoS. The K_{sp} values for CoO and CoS are about 2.9×10^{-18} and 3×10^{-26} , respectively. It is known that materials with lower K_{sp} values are thermodynamically more stable than those with higher K_{sp} values, and the latter will convert into the former in the specific solution (with the same cations or anions). In our case, the K_{sp} value of CoS is much lower than that of CoO, so the former could be formed by the ion exchange reaction in a solution with S^{2-} anions.

2.2. Preparation of CoS/Ni core-branch arrays

The CoS nanowires arrays were then used as the backbone for the growth of thin porous Ni branch by a combined method of hydrothermal (HS)+electro-deposition (ED). The CoS nanowires were first coated with a 10 nm ZnO seed layer by atomic layer deposition with Diethyl zinc (ALD Beneq TFS 200, DEZ, 99.99%, Sigma Aldrich) and H_2O as the Zn and O precursors, respectively. Afterwards, the samples were coated by hydrothermal ZnO nanorods as follows. The above samples were transferred into autoclave liners containing 80 mL solution of 0.29 g $\text{Zn}(\text{NO}_3)_2$ and 0.15 g hexamethylenetetramine and maintained at 90°C for 3.5 h to obtain CoS/ZnO core-branch arrays. Then, the samples were coated by a thin Ni layer by a facile electro-deposition method, which was conducted in a three-electrode cell, the above CoS/ZnO core-branch arrays as the working electrode, saturated calomel electrode (SCE) as the reference electrode and a Pt foil as the counter-electrode. The electrolyte was composed of 0.02 M NiSO_4 + 0.04 M NH_4Cl . The electro-deposition of Ni was performed at a cathodic current density of 0.5 mA cm^{-2} for 10 min. Finally, the ZnO nanorods template was etched by immersing samples into 1 M KOH for 10 min to obtain CoS/Ni core-branch arrays. The load weight of CoS and Ni is about 2.2 mg cm^{-2} and 0.2 mg cm^{-2} , respectively.

2.3. Morphology and structure characterizations

The samples were characterized by field emission scanning electron microscopy (FESEM, FEI SIRION), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F), X-ray

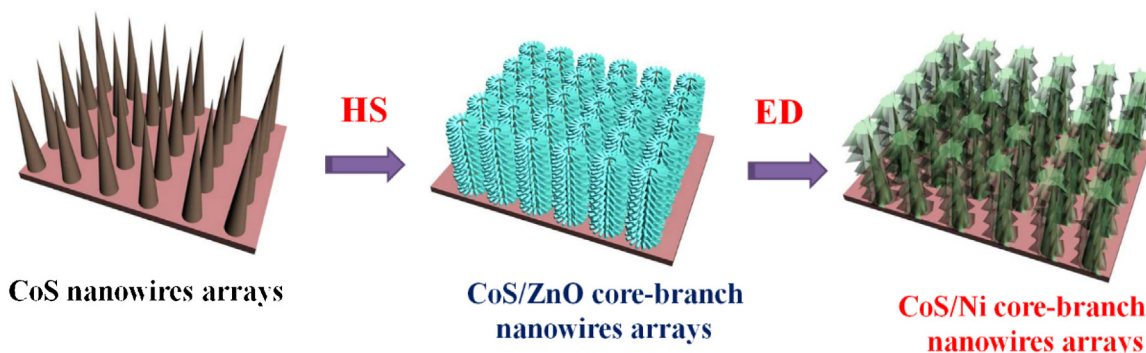


Fig. 1. Schematics of synthesis of CoS/Ni core-branch arrays.

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