Journal of Colloid and Interface Science 533 (2019) 733–741

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

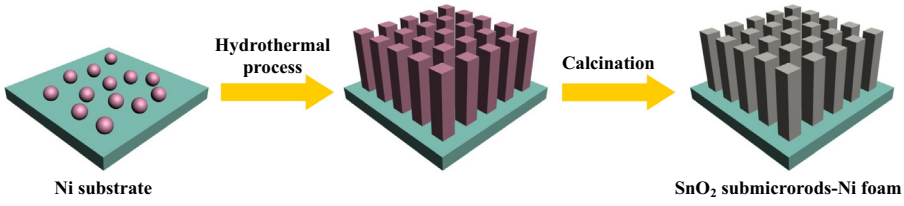
In situ synthesis of tin dioxide submicrorods anchored on nickel foam as an additive-free anode for high performance sodium-ion batteries

Jiamei Wang [a,d], Gang Zhu [c], Xiaojie Liu [b,d], Gang Wang [a,d,*], Hui Wang [b,d], Jintao Bai [a,d,*]

[a] National Key Laboratory of Photoelectric Technology and Functional Materials (Culture Base), National Photoelectric Technology and Functional Materials & Application International Cooperation Base, Institute of Photonics & Photon-Technology, Northwest University, Xi'an 710069, PR China
[b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry (Ministry of Education), College of Chemistry & Materials Science, Northwest University, Xi'an 710069, PR China
[c] School of Chemistry and Chemical Engineering, Xi'an University of Arts and Science, Xi'an 710065, PR China
[d] Shaanxi Joint Lab of Graphene (NWU), Xi'an 710127, PR China

GRAPHICAL ABSTRACT

A hybrid of tin dioxide submicrorods anchored on conductive nickel foam was in-situ synthesized, which exhibited superior electrochemical performance as an additive-free anode for sodium ion batteries.



ARTICLE INFO

Article history:
Received 30 May 2018
Revised 2 September 2018
Accepted 3 September 2018
Available online 4 September 2018

Keywords:
Tin dioxide submicrorods
Nickel foam
Additive-free anode
Sodium-ion batteries

ABSTRACT

A hybrid of tin dioxide submicrorods anchored on conductive nickel foam (SnO_2 submicrorods-Ni foam) is in-situ synthesized via a hydrothermal and a subsequent heat treatment by using stannic chloride and sodium hydroxide as the starting materials. Characterization results indicate that the synthesized SnO_2 submicrorods has a length of ~400 nm and a diameter of ~150 nm anchoring tightly on Ni foam. The electrochemical properties of the material as an additive-free anode for sodium-ion batteries are investigated. And a comparative research of the reversible sodium storage properties between the additive-free electrode of SnO_2 submicrorods-Ni foam and the additive electrode of SnO_2 rod-assembly microspheres is carried out. The results demonstrate that the SnO_2 submicrorods-Ni foam is a highly attractive anode for sodium ion batteries, which could exhibit much better sodium storage properties than the SnO_2 rod-assembly microspheres and other reported SnO_2-based additive electrodes. The excellent sodium storage properties of the SnO_2 submicrorods-Ni foam electrode can be attributed to its structure advantages without additive-assistant, which increase sodium storage active sites, facilitate the electronic/ionic transport and stabilize the total electrode structure during charge-discharge process.

1. Introduction

Energy, as one of the three pillars of modern civilization, has been the power of human development and social progress. However, with the fast depletion of fossil fuels and what has triggered

* Corresponding authors at: National Key Laboratory of Photoelectric Technology and Functional Materials (Culture Base), National Photoelectric Technology and Functional Materials & Application International Cooperation Base, Institute of Photonics & Photon-Technology, Northwest University, Xi'an 710069, PR China.
E-mail addresses: gangwang@nwu.edu.cn (G. Wang), baijt@nwu.edu.cn (J. Bai).

https://doi.org/10.1016/j.jcis.2018.09.006
0021-9797/

serious environmental issues, it is of emergency need to develop renewable energy sources [1]. As we all know, electric energy is the cleanest and most convenient form of energy. Therefore, electric energy storage devices are very necessary to convert other renewable sources into electric energy for improving the energy utilization efficiencies [2]. So far, lithium-ion batteries (LIBs) are the predominant power sources for various portable devices and electric/hybrid vehicles due to the merits of high capacity, long cycle life, no memory effect and environmental benignity [3,4]. However, the sustainable development of LIBs has been hindered seriously by the exploitation and exhaustion of lithium resources in the near future. Currently, by sharing similar energy storage mechanisms with LIBs, sodium-ion batteries (SIBs) have been considered as most promising candidates in energy storage systems due to their advantages including abundant sodium resources, eco-friendly, and similar redox potential to lithium [5–7]. As one of the intercalation-type electrode, graphite has been applied as the common commercialized anode material for LIBs. However, because of sodium ion radius is larger than lithium ion, the graphite capacity is down to 30 mA g^{-1} when used in SIB systems [8,9]. This situation leads to a worldwide search for advanced electrode materials exhibiting excellent specific capacity, long cycle life, and high rate capability for SIBs.

Transition metal oxides with various structures or dimensions have been employed as anode substitute for SIBs due to their high theoretical capacities [6,10-14]. Among the available transition metal oxide anode materials, SnO_2 has attracted special attention because of a variety of advantages, such as low cost and toxicity, abundance, fabrication convenience, low working potential (vs. Na^+/Na), and high theoretical capacity of 667 mAh g^{-1} [15,16]. The sodium storage in SnO_2 relies on the reversible conversion and alloying reactions, which are displayed by the following two chemical equations [16,17]:

$$SnO_2 + 4Na^+ + 4e^- \leftrightarrow Sn + 2Na_2O \quad (1)$$

$$Sn + xNa^+ + xe^- \leftrightarrow Na_xSn\ (x \leq 3.75) \quad (2)$$

Although SnO_2 has shown fascinating prospect in SIB system, the low intrinsic conductivity and large volume change problems hinder the usage of SnO_2 electrodes [18]. And as a result, SIBs fabricated by using SnO_2 anodes usually suffer from fast capacity decay and unsatisfactory cycling properties. To solve the problems of SnO_2 electrodes effectively, different strategies such as designing special structures, reducing size, and forming hybrids with conductive or flexible materials have been developed to realize better specific capacity and longer cycle life [15–24]. Among them, two methods are widely practiced. One way is to design SnO_2 materials with micro or nano structure, which consists of one-dimensional fibers, two-dimensional sheets, and three-dimensional spheres [19–21]. It has been demonstrated that these nanoarchitectures with short diffusion lengths or large exposed surfaces could interact with sodium ions more efficient. Another commonly adopted approach is to make SnO_2-based hybrids by introducing a flexible and stable medium. Particularly, being modified with carbonaceous materials, like graphene, carbon coating layers, carbon nanotubes, carbon nanofibers, porous carbon, and etc [18,22-24]. These modified methods can not only make a contribution to an enhanced electrical conductivity, but also provide a cushion effect against the volume change. However, it should be noteworthy that the materials synthesized by using the above mentioned methods are generally composed of micro or nano particles in a powder state, they need to be mingled with binders and conductive additives and pressed or coating on current collectors during electrode preparation procedures. The electrode fabrication process is complicated, and the exfoliation of sodium storage active materials from the current collectors occurred easily, resulting in the degradation of electrochemical performances.

The in situ synthesis of electroactive materials with well-designed architectures on conductive substrates can be directly processed for the assembly of batteries without the need for extra binders or conductive additives, which will be the orientation that scientists devoted to improve the electrochemical performance for energy storage devices [25–28]. Compared with those electrodes in the physical mixing and pressing approaches, the interfacial contacts and electronic conductivities between the electroactive materials and current collector could be enhanced in the additive-free electrodes. Moreover, owing to the existence of extra free space between neighboring materials, paths for electrolyte penetration and buffers for volume accommodation during charge-discharge processes could be realized on the additive-free electrodes. Considering the advantages of additive-free electrodes, it is suggested that micro/nano-structure metal compounds directly grow on a conductive substrate would be a promising strategy to overcome the drawbacks of these compounds and to enhance the SIB cycling performance and rate capability. Recently, some of metal compounds with specific structures like CuO nets, Cu_3P nanowires, V_2O_5 arrays, TiO_2 nanorods have been successfully grown on different current collectors (copper foil, titanium foil, and carbon cloth) and have shown excellent electrochemical properties when evaluated as additive-free electrodes for SIBs [27,29–31]. However, insufficient attention has been paid to the controlled fabrication of additive-free SnO_2-based electrodes. And there is a need to develop suitable route for the in-situ preparation of SnO_2-current collector type electrodes without additives for high performance SIB systems.

In the present work, the synthesis of SnO_2 submicrorods grown on conductive nickel foam (denoted as SnO_2 submicrorods-Ni foam) through a hydrothermal and a subsequent heat treatment by using stannic chloride and sodium hydroxide as the starting materials was realized. Characterization results indicated that the synthesized SnO_2 submicrorods-Ni foam has a length of ~400 nm and a diameter of ~150 nm anchoring tightly on Ni foam. The electrochemical properties of the material as an additive-free anode for SIBs was investigated and evaluated. And a comparative research of the sodium storage properties between the additive-free electrode of SnO_2 submicrorods-Ni foam and the additive electrode of SnO_2 rod-assembly microspheres has been carried out. The results demonstrated that the SnO_2 submicrorods-Ni foam is a highly attractive anode for SIBs, which could exhibit much better sodium storage properties than the SnO_2 rod-assembly microspheres and other reported SnO_2-based additive electrodes.

2. Experimental

2.1. Synthesis of SnO_2 submicrorods-Ni foam

All the chemical reagents used in this study were of analytical grade and used without any further purification. In a typical synthesis, 0.174 g of $SnCl_4{\cdot}5H_2O$ and 0.534 g of NaOH were dissolved in 30 ml of deionized (DI) water under stirring for 5 min. The pH value of the precursor solution is 12. The solution was transferred in a 50 ml Teflon-lined stainless steel autoclave. And then a piece of Ni foam wafer (16 mm in diameter and 1 mm in thickness) was inserted into the solution. The autoclave was sealed and held at 220 °C for 2 h. After cooling down naturally, the Ni foam sample was washed with DI water and ethanol, and then dried in a vacuum oven at 60 °C for 10 h. The final SnO_2 submicrorods-Ni foam product was obtained via thermal treatment in Ar at 400 °C for 2 h with a heating rate of 2 °C min^{-1}. The synthesis route of the sample is illustrated schematically in Fig. 1. The loading amount of the