Electrochimica Acta 173 (2015) 458–464

Contents lists available at ScienceDirect

Electrochimica Acta

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

Carbon coated flower like Bi_2S_3 grown on nickel foam as binder-free electrodes for electrochemical hydrogen and Li-ion storage capacities

Rencheng Jin [a,*], Guihua Li [a], Zhengjiang Zhang [a], Li-Xia Yang [a], Gang Chen [b,*]

[a] School of Chemistry & Materials Science, Ludong University, Yantai 264025, PR China
[b] Department of Chemistry, Harbin Institute of Technology, Harbin 150001, PR China

ARTICLE INFO

Article history:
Received 6 March 2015
Received in revised form 14 April 2015
Accepted 5 May 2015
Available online 19 May 2015

Key words:
Bismuth sulfide
electrochemical hydrogen storage
lithium-ion batteries
binder free
porous structure

ABSTRACT

Carbon coated flower like Bi_2S_3 on nickel foam are simply fabricated by a solvothermal synthesis method accompanying with glucose as a precursor of subsequent carbonization. The architectures are directly used as electrodes for electrochemical hydrogen and Li-ion storage. Such architectures display high electrochemical hydrogen storage and the discharging capacity of 165 mAh g^{-1} is obtained. When used as anode material, the binder free Bi_2S_3@C/Ni electrode delivers superior cycling stability and rate capability. Discharge capacity reaches as high as 698 mAh g^{-1} after 50 cycles at a current density of 100 mA g^{-1}. Even at 1000 mA g^{-1}, the capacity still remains at 510 mAh g^{-1} after 40 cycles. The superior performance can be ascribed to the unique electrode. The porous electrode gives more reaction sites and accommodates volume change during cycling; while the carbon shell improves electronic conductivity and suppresses particle aggregation.

1. Introduction

Recently, transition metal chalcogenides such as CoS,[1–4] Ni_3S_4,[5] MoS_2,[6] Bi_2S_3,[7] SnS[8–10] and ZnS[11] have attracted much attention due to their excellent magnetic,[3] optical,[4,9] electrochemical[1,2,5–7,10] and catalytic properties,[11] which can be applied as supercapacitors, lithium-ion batteries, and dye-sensitized solar cells, et al. Among these metal sulfides, Bi_2S_3 has been of particular interest due to its application in thermoelectric devices,[12,13] electrochemical hydrogen storage[7,14] and lithium-ion batteries.[15] However, electrodes based on bismuth sulfide suffered from poor cycle stability and a large volume change during Li-ion or H_2 insertion/extraction.[14,16] To solve these issues, enormous efforts have been made. One effective method is to prepare nanostructured Bi_2S_3, which offers high surface to volume ratio, high surface area, enhanced electron transport, and reduced strain associated with the intercalation process. [15,17] Another approach is focused on the formation of composition between Bi_2S_3 and carbon. For example, carbon-coated Bi_2S_3 nanomeshes with large capacity and stable cyclability have been fabricated.[18] Ni's research group reported that bismuth sulfide-carbon nanotube hybrid exhibited a high reversible capacity and remarkable rate capability.[19,20] These Bi_2S_3/carbon hybrids could enhance electronic conductivity and provide flexible space for suppressing the large volume expansion during cycling. Although different nanostructured Bi_2S_3 and Bi_2S_3/carbon hybrids have been fabricated and the electrochemical properties have been investigated, there is still much room for progress with regard to the development of Bi_2S_3 for energy storage.

For preparing the electrodes, the adhesives and conductive agents are used to make the active materials adhere tightly to current collectors and improve the electrical conductivity of electrodes. However, these two materials have lower or no capacities, decreasing the capacity of the electrodes. Therefore, the fabrication of binder- and conductive agent-free electrodes to enhance the electrochemical property is essential. For instance, Li and co-authors synthesized carbon-wrapped Fe_3O_4 nanoparticles on nickel foam substrates, and presented reversible capacity of 543 mAh g^{-1} at a current density of 10 C after more than 2000 cycles (used as Li-on batteries). [21] Cobalt hydroxide nanorods and nanosheets on nickel foam depicted excellent specific capacitance and high cycling stability.[22,23] However, fabrication of these materials on nickel foam is complicated and high temperature calcination is needed for the formation of carbon layer. In addition, no report has focused on the fabrication of carbon coated Bi_2S_3 nanoparticles on nickel foam.

In the present study, we synthesized carbon coated flower like Bi_2S_3 microcrystals on nickel foam substrates through a facile solvothermal method. The electrochemical measurements showed

* Corresponding authors.
E-mail addresses: jinrc427@126.com (R. Jin), gchen@hit.edu.cn (G. Chen).

http://dx.doi.org/10.1016/j.electacta.2015.05.021

that the obtained materials delivered good electrochemical hydrogen storage and high electrochemical lithium storage performance.

2. Experimental section

2.1. Synthesis of flower like Bi_2S_3/Ni electrode

In the typical procedure, nickel foam was immersed into 1 M HCl and ultrasonically treated for 5 min and then rinsed with distilled water and ethanol. The obtained clean nickel foam substrate was transferred into a Teflon-lined stainless autoclave with the capacity of 25 mL. After that, 6 mL of distilled water and 12 mL of isopropanol containing 0.388 g bismuth nitrate were introduced in the autoclave. Subsquently, 0.5 mL of thioglycollic acid was added. After 10 h growth at 160 °C, the autoclave was cooled down naturally to room temperature. The obtained samples were washed with distilled water and ethanol for three times under ultrasonic treatment. Finally, the products were dried at 80 °C for 12 h.

2.2. Synthesis of flower like Bi_2S_3@C/Ni electrode

The obtained Bi_2S_3/Ni electrode was immersed in 0.1 M 20 mL of glucose and ultrasonically treated for 5 min. Then the obtained solution was transferred into a Teflon-lined stainless autoclave and held in the oven at 190 °C for 5 h. The electrodes were washed with distilled water three times and dried in a vacuum oven 80 °C overnight.

2.3. Characterization

The composition and phase of the products were characterized by X-ray powder diffraction (XRD, Rigaku D/Max-2550pc with Cu Kα radiation). The field emission scanning electron microscopy (FESEM, FEI Quanta 200F) and transmission electron microscopy (TEM, FEI Tecnai G2 S-Twin) were applied to determine the morphology and structure of the samples.

2.4. Electrochemical measurement

2.4.1. Electrochemical hydrogen storage

Electrochemical hydrogen storage was performed on a Land battery system (CT2001A) at room temperature. The used three electrode system consists of $Ni(OH)_2$/NiOOH as the counter electrode, Hg/HgO as a reference electrode, and the obtained sample as working electrode. The electrolyte was 6 M KOH aqueous solution. The Bi_2S_3 electrode was charged for 4 h and then discharged to −0.1 V (versus Hg/HgO) at a current density of 50 mA/g. Cyclic voltammetry (CV) was carried out at a scan rate of 5 mV/s from −1.2 to 0 V (versus Hg/HgO) on a CHI604C electrochemical workstation. For comparasion, the nickel foam of Bi_2S_3/Ni was dissolved in 3 M HCl. The obtained flower like Bi_2S_3 microcrystals combined with polyvinylidene fluoride (PVDF) and acetylene black with the weight ratio 80:10:10 were directly pressed on a sheet of nickel foam.

2.4.2. Li-ion storage property

The Li-ion storage properties were investigated using CR-2025 coin cells. The cells were assembled in a high-purity argon filled glovebox by using flower like Bi_2S_3 microcrystals on nickel foam as the working electrode, the lithium metal as the counter and reference electrodes, and Celgard 2400 as the separator. 1 M $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) with a volume ratio of 1:1:1 was used as the electrolyte. The cells were galvanostatically discharged/charged on a NEWARE battery test system at different current densities between 0.01 and 3.0 V (vs. Li^+/Li). To compare the Li-ion storage properties of the products, the pure flower like Bi_2S_3 microcrystals electrode were prepared using a mixture of active material (flower like Bi_2S_3 microcrystals), acetylene black, and polyvinylidene difluoride (PVDF) at a weight ratio of 80:10:10. Then the mixture was spread on the copper foil substrate. The electrode was prepared by cutting copper foil substrate into circular strips.

3. Results and discussion

In order to confirm the composition of the samples, the nickel foam substrate was removed by dissolving the Bi_2S_3@C/Ni electrode in 3 M HCl. The obtained product was characterized by XRD and the result was presented in Fig. 1. All diffraction peaks match well with the orthorhombic Bi_2S_3 (JCPDS No. 17-0320), and no other peaks from impurities can be detected. In this work, thioglycollic acid can be used as sulfur source. Meanwhile, the thioglycollic acid can coordinate with Bi^{3+} to form the coordination complex, which may alleviate the reaction between Ni and Bi^{3+}. Therefore, less or no NiS generates in the reaction system. Fig. 2a-c demonstrates SEM images of the prepared sample vertically aligned on the surface of the Ni foam at different magnification. It can be seen that the film on Ni foam consists of numerous flower like Bi_2S_3 with the diameter ranging from 1-6 μm. These structures are composed of branched nanosheets with the thickness of ~20 nm. Furthermore, the flower like Bi_2S_3 owns the porous structure, which may provide higher number of electrochemical reaction sites when used as electrode materials. It should point out that the electrode has no apparent change after ultrasonic treatment for 1 h, demonstrating the excellent physical adhesive of carbon coated Bi_2S_3 on the current collector of Ni foam. TEM images shown in Fig. 2d-e confirm that the sample is composed of the flowery microcrystals. And the entire flower is built from cross-linked thin nanosheets, which is in agreement with the SEM observations. A representative HRTEM image at the edge of an individual nanosheet is presented in Fig. 2f. The lattice spacings are clearly visible with a spacing of about 0.786 nm, which is in good agreement with the (101) interplanar distance of Bi_2S_3. More importantly, the single nanosheet is wrapped by a thin layer of carbon (Fig. 2f).

To investigate the electrochemical hydrogen storage property of flower like Bi_2S_3 on nickel foam, a series of electrochemical

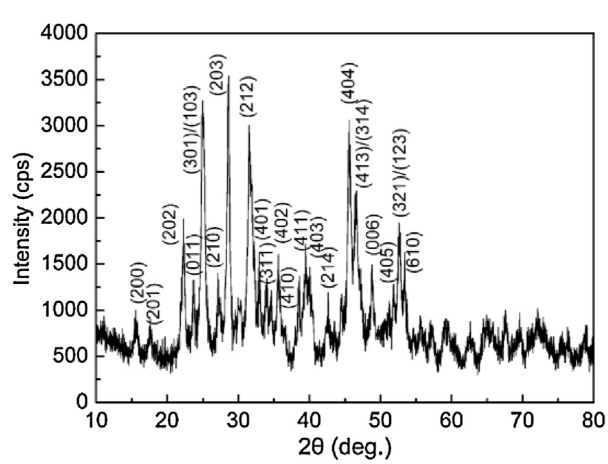

Fig. 1. XRD pattern of the products scraped from Ni foam.