



Amorphous carbon coated multiwalled carbon nanotubes@transition metal sulfides composites as high performance anode materials for lithium ion batteries



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ARTICLE INFO

Article history:

Received 12 June 2017

Received in revised form 11 October 2017

Accepted 12 October 2017

Available online 13 October 2017

Keywords:

Transition metal sulfides

Carbon nanotubes

Anodes

Lithium-ion batteries

Electrochemical reaction mechanism

ABSTRACT

Transition metal sulfides as anodes for lithium-ion batteries (LIBs) have attracted much attention because of their large Li⁺ storage capacity. However, the lower electrical conductivity and rapid capacity fading during the charge/discharge process strictly prohibit their practical applications. Here, a new strategy is adopted to accommodate the volume change and enhance the electrical conductivity by anchoring Co_{1-x}S and NiS nanocrystals on amorphous carbon coated multiwalled carbon nanotubes (CNTs). Benefiting from the unique structure, the Co_{1-x}S and NiS anodes present excellent electrochemical performances including remarkable cyclability and outstanding rate property. Furthermore, the electrochemical reaction process of the anodes is investigated by high-resolution transmission electron microscope and X-ray photoelectron spectroscopy technique.

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1. Introduction

Lithium-ion batteries (LIBs) have been applied in energy storage devices due to the advantages such as high energy density and long cycle life [1–5]. However, the commercial graphite anodes with low theoretical capacity (372 mAh g⁻¹) cannot meet the pressing requirements of future electric vehicles and portable electronics [6]. Thus, searching alternative materials to replace the graphite carbon becomes of extreme importance. Transition metal sulfides with high theoretical capacity have been considered as promising alternative anode materials [7–16]. Unfortunately, the practical application of these metal sulfides is still prohibited by large volume change during lithium ion insertion and extraction process [17–19]. In addition, the electrical conductivity of these metal sulfides is comparatively lower, which leads to the poor rate capability [20,21]. To solve these issues, enhancing their electrical conductivity and structure stability during cycling becomes crucial strategies. Therefore, different size and morphologies of metals sulfides such as nanorods [22–24], nanowires [25], nanobelts [26], nanosheets [27,28], and hierarchical structures [29–32] have been prepared to buffer the volume variation and reduce the lithium ion migration distance. Constructing nanocrystals with conductive

additives is another procedure to enhance the lithium storage and cycling performance, which not only accommodates the volume change, but also increases the electrical conductivity of electrode during cycling [33–40]. Among these conductive substrates, multiwalled carbon nanotubes (CNTs) have been attracted much attention due to its superior electrical conductivity and good chemical stability. Therefore, the combination of CNTs and metals sulfides is considered to be an effective method to improve the performance of the nanocomposites.

Among these metal sulfides for Li ion storage, NiS_x and CoS_x have attracted great attention. In order to improve their performances, NiS hierarchical hollow spheres [41], CoS₂ hollow spheres [42], rose-like Co₉S₈ [43], and yolk-shell Co₉S₈ microspheres [44] have been fabricated and evaluated as anodes to show their potential in LIBs. In addition, hybridizing nanostructured NiS_x and CoS_x with carbon can prevent the aggregation and pulverization of the electrodes and enhance the electrical conductivity, which further improves their electrochemical properties. For instance, β-NiS nanoparticles embedded in porous carbon matrices deliver a specific capacity of 300 mAh g⁻¹ after 100 cycles at 60 mA g⁻¹ [45]. NiS nanorod-assembled nanoflowers grown on graphene exhibit a reversible capacity of 887 mA h g⁻¹ after 60 cycles at 59 mA g⁻¹ [46]. Graphene-wrapped CoS nanoparticles display the reversible capacity of 749 mA h g⁻¹ at 62.5 mA g⁻¹ [37]. CoS/CNTs nanocomposites are prepared by an effective solvothermal method, which deliver the capacity of 780 mA h g⁻¹ after 50 cycles at the

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current density of 100 mA g^{-1} [47]. The reversible capacity is promoted to 950 mAh g^{-1} after 150 cycles at 200 mA g^{-1} by $\text{CoS}_x/\text{graphene}$ nanocomposites [48]. The capacity of $\text{MWCNT@C@Co}_9\text{S}_8$ is pushed up to 662 mAh g^{-1} after 120 cycles even at high rate of 1 A g^{-1} [40]. Although some studies have been focused on the synthesis of transition metal sulfides/carbon hybrids for improving the electrochemical properties, the construction of nanostructured metal sulfides on conductive substrate is still appealing.

Here in this work, Co_{1-x}S nanoparticles and NiS nanosheets anchored on amorphous carbon coated CNTs (denoted as $\text{CNTs@C@Co}_{1-x}\text{S}$ and CNTs@C@NiS , respectively) have been synthesized through a hydrothermal/solvothermal process accompanied by a high-temperature calcination treatment using amorphous carbon coated CNTs (CNTs@C) as template. Due to the unique structure, the $\text{CNTs@C@Co}_{1-x}\text{S}$ and CNTs@C@NiS nanocomposites display high reversible capacity, excellent cycling stability and rate capacity when evaluated as anode materials in LIBs. Furthermore, the electrochemical reaction mechanism is investigated by *ex situ* HRTEM and XPS analysis.

2. Experimental section

2.1. Synthesis of CNTs@C

All reagents used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd. The multiwalled carbon nanotubes were provided by Shenzhen Nanotech Port Co., Ltd. In the typical synthesis, 50 mg of CNTs and 0.15 g of glucose were dispersed in 15 mL of distilled water. Then, the mixed solution was sealed into a 25 mL of Teflon-lined autoclave and heated at 180°C for 6 h. The products were collected and washed with distilled water and 95% ethanol for several times.

2.2. Synthesis of $\text{CNTs@C@Co}_{1-x}\text{S}$ and CNTs@C@NiS

The CNTs@C@NiS was prepared via a solvothermal process using CNTs@C as template. 50 mg of the pretreated CNTs@C , 0.236 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.3 g of thiourea and 0.2 g glucose were dissolved into 10 mL of distilled water and constantly stirred for 10 min. Then, 10 mL of ethylene glycol was added into above solution and ultrasonically treated for 30 min. Subsequently, the mixture was sealed and held at 180°C for 12 h. The $\text{CNTs@C@Co}_{1-x}\text{S}$ was synthesized by a hydrothermal method. 50 mg of CNTs@C , 0.252 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.4 g of thioacetamide combined with 0.2 g of glucose were ultrasonically dispersed in 20 mL of distilled water for 30 min. The suspension was transferred into Teflon-lined autoclave (80% degree of filling) and then heated at 180°C for 12 h. The obtained $\text{CNTs@C@Co}_{1-x}\text{S}$ and CNTs@C@NiS were collected,

washed with distilled water and ethanol for several times and dried under vacuum at 80°C for 12 h. After that, the dried products were sintered at 400°C for 4 h with the protection of argon. For comparison, the $\text{CNTs@Co}_{1-x}\text{S}$ and CNTs@NiS were fabricated by using pure CNTs as template instead of CNTs@C without changing other reaction conditions.

2.3. Materials Characterization

Powder X-ray diffraction (XRD) pattern of the samples was obtained by Rigaku D/Max-2550 pc X-ray diffractometer in the 2θ range of 10° – 80° . The morphology and structure features of the samples were detected on FEI Quanta 200F field-emission scanning electron microscope and Tecnai G2 S-Twin transmission electron microscope. A PHI-5702 multifunctional X-ray photoelectron spectrometer was applied to analyze the chemical state and composition of the samples. The exact composition of the products was characterized by a NexION 300 inductively coupled plasma (ICP, USA). The content of the Co_{1-x}S and NiS was characterized by thermal gravimetric analysis (TGA, Mettler, TGA/DSC 1/1600HT) with a heating rate of $10^\circ\text{C min}^{-1}$ in flowing air atmosphere.

2.4. Electrochemical Measurements

To prepare the working electrode, the obtained sample (active materials), carbon black, and polyvinylidene fluoride (PVDF) with the weight ratio of 80:10:10 were mixed in N-methyl-2-pyrrolidinone (NMP) and constantly stirred for 8 h to form homogenous slurry. The slurry was spread onto copper foil and dried at 120°C for 12 h. The mass of active material for each electrode was $\sim 1 \text{ mg}$. The CR2025 coin cells were assembled in argon-filled glovebox, in which lithium metal foil was applied as the counter and reference electrode, Celgard 2400 membrane was used as the separator. The electrolyte was composed of 1 mol L^{-1} of LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) with the volume ratio of 1:1. Charge/discharge measurements were evaluated on a NEWARE BTS-3008 (Neware Co., Ltd, China) between 0.01 V and 3.0 V. Cyclic voltammetry (CV) measurements were tested on CHI660E electrochemical workstation at a scan rate of 0.2 mV s^{-1} in the potential range of 0.01–3.0 V. Electrochemical impedance spectra (EIS) were performed on the same electrochemical workstation between the frequency range of 10 kHz to 0.1 Hz.

3. Results and discussion

Fig. 1a shows the XRD pattern of the $\text{CNTs@C@Co}_{1-x}\text{S}$ after hydrothermal treatment at 180°C . The diffraction peaks at 25.9° and 42.7° are ascribed to the (002) and (100) planes of carbon

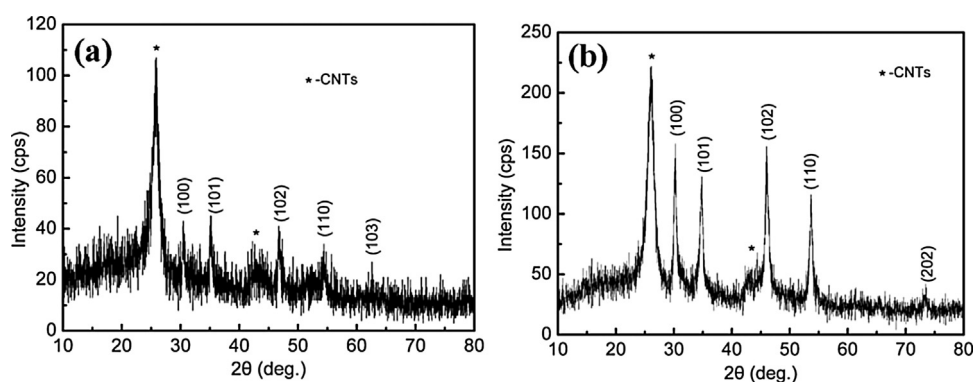


Fig. 1. XRD patterns of the synthesized (a) $\text{CNTs@C@Co}_{1-x}\text{S}$, and (b) CNTs@C@NiS .

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