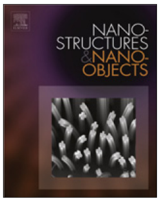
Nano-Structures & Nano-Objects ▮ (▮▮▮▮) ▮▮▮–▮▮▮

Contents lists available at ScienceDirect

Nano-Structures & Nano-Objects

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



# Graphene scrolls coated $Sb_2S_3$ nanowires as anodes for sodium and lithium ion batteries

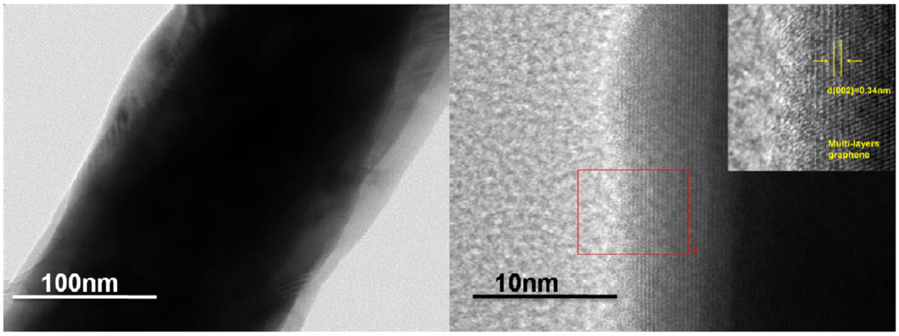
Yuting Wu, Ping Nie, Hui Dou, Jiangmin Jiang, Yaoyao Zhu, Xiaogang Zhang [*]

*Jiangsu Key Laboratory of Materials and Technology for Energy Conversion, College of Material Science and Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China*

## HIGHLIGHTS

- $Sb_2S_3$ nanowires templated graphene scrolls synthesized though two-step wet chemical processes.
- Superior electrochemical properties for sodium ion and lithium ion batteries.
- 1 M $NaClO_4$ in EC/DMC promotes the electrochemical performance of $Sb_2S_3$ anode.

## GRAPHICAL ABSTRACT



$Sb_2S_3$ nanowires templated graphene scrolls exhibit high-rate capability and superior cycling stability when used as anode materials for Li-ion and Na-ion batteries.

## ARTICLE INFO

*Article history:*
Received 2 August 2017
Received in revised form 28 September 2017
Accepted 28 September 2017

*Keywords:*
$Sb_2S_3$nanowires
Graphene scrolls
Electrolyte
Lithium-ion batteries
Sodium-ion batteries

## ABSTRACT

One-dimensional stibnite ($Sb_2S_3$) nanowires templated graphene scrolls (SbGSs) synthesized through two-step wet chemical processes have been applied as anode materials for lithium-ion and sodium-ion batteries (LIB, NIB), where they delivered high reversible capacity of 690 mAh $g^{-1}$ and 680 mAh $g^{-1}$ at a current density of 50 mA $g^{-1}$ without any capacity fading after 50 cycles both in LIB and NIB. Increased current density up to 2000 mA $g^{-1}$, discharge capacity of 457.6 mAh $g^{-1}$ in LIB and 444.8 mAh $g^{-1}$ in NIB can be obtained, indicating that NIB performance is rival to LIB. Further study on optimizing electrolyte manifested that 1 M $NaClO_4$ in ethylene carbonate/dimethyl carbonate (EC/DMC) promoted the electrochemical performance of NIB.

## 1. Introduction

Rechargeable Li-ion batteries (LIB) have become successful and sophisticated energy storage devices since its first commercialization, graphite // $LiCoO_2$ cell, by Sony in 1991 [1–4]. Recently, Tesla motors have been acknowledged by its pioneering work in electric vehicles (EV). LIBs with electric motors are now used as an alternative power source for combustion engines with a fuel tank, which could reduce the energy dependence on fossil fuels for a transportation system in the future [5–8]. Apart from EV, an energy storage system for smart grid is necessary to utilize renewable energy with high efficiency and for peak shift operation. Although LIBs potentially provide a solution to meet these tough challenges to realize sustainable energy development emerging market for electrochemical energy storage (EES), we must reconsider the availability of lithium sources and their uneven distribution, which certainly prove obstacles to LIBs. As a substitution

---

[*] Corresponding author.
*E-mail addresses:* azhangxg@nuaa.edu.cn, azhangxg@163.com (X. Zhang).

https://doi.org/10.1016/j.nanoso.2017.09.015
2352-507X/

Please cite this article in press as: Y. Wu, et al., Graphene scrolls coated $Sb_2S_3$ nanowires as anodes for sodium and lithium ion batteries, Nano-Structures & Nano-Objects (2017), https://doi.org/10.1016/j.nanoso.2017.09.015.

for LIBs, sodium-ion batteries (NIBs) hold much promise due to abundance of sodium as well as its electrochemical resemble to lithium [9–15].

In spite of a significant progress in positive electrode for NIBs, [16–19] identifying a high-performance negative electrode remains a key challenge [20–22]. Problematic issues of current anode materials can be concluded to a low specific capacity as well as a poor cycling performance [23–26]. In contrast, various sodium alloys can potentially enable the design of high-performance anodes for NIBs due to their high specific capacity for Na-ion. A number of recent researchers have established alloying reaction with Na under electrochemical setting in group-14 and group-15 elements, including metals (Sn, Pb, Bi), metalloids (Ge, As, Sb), and polyatomic non-metal (P), are known to form binary compounds with Na [27–32]. Among the anode candidates, stibnite $Sb_2S_3$ is one of the most promising due to its high theoretical capacity and relatively low reaction potential. Complete sodiation of $Sb_2S_3$ can accommodate about 12 moles of electron and $Na^+$ ion storage per mole. The theoretical capacity is 946 mAh $g^{-1}$. Ovadia et al. [33] has initially reported nanocrystal stibnite ($Sb_2S_3$) onto reduced graphene oxide (rGO) as NIB anode materials. About 9.2 moles of Na (730 mAh $g^{-1}$) can be reversibly inserted and removed from the material at a rate of 50 mA $g^{-1}$. Even when current density increased to 3000 mA $g^{-1}$, >70% of the capacity (520 mAh $g^{-1}$) can still be obtained. In our previous work [34], we have reported flower-like $Sb_2S_3$ performs excellent cycle performance and superior rate capability as anode materials for NIBs. It maintains a capacity of 641.7 mAh $g^{-1}$ at 200 mA $g^{-1}$ after 100 cycles and a capacity of 553.1 mAh $g^{-1}$ can be obtained up to 2000 mA $g^{-1}$. Current researches are mostly focused on controlling the unfavourable volume changes of the electrodes during cycling and to suppress the decrease of activity of anode masteries [35,36]. Optimization of material compositions and structure, further study of interphase of the electrode materials, coupled with studies on different electrolyte will lead to further improvement of the electrochemical performance as shown in this paper.

Herein, we develop a strategy to synthesize one-dimensional $Sb_2S_3$ nanowire templated graphene scrolls (SbGSs) through two-step wet chemical process. GSs provide open structure at both ends and interlayer galleries, enable wrapping nanowires in the scrolls according to the calculation that nanowires can lead to self-assembly of planar graphene sheets on it [27,37–41]. $Sb_2S_3$ nanowire scrolled within graphene scrolls can enhance electrical transport and buffer the large stress from volume change in the sodiation/desodiation processes [38]. The composite material performed extremely well as the anode for LIBs and NIBs. When served as an anode in LIBs, it provided a capacity of 690 mAh $g^{-1}$ at 50 mA $g^{-1}$ and maintained at 671.9 mAh $g^{-1}$ after 50 cycles with neglectful capacity decay. We also use it as an anode for NIBs, which exhibited a capacity of 680 mAh $g^{-1}$ at current density of 50 mA $g^{-1}$ without any capacity fading after 50 cycles, and a remaining capacity of 620 mAh $g^{-1}$ even after 200 cycles. The material retained its discharge capacity at higher current rates. When setting the current at 2000 mA $g^{-1}$, a discharge capacity of 600 mAh $g^{-1}$ can be obtained. It showed an excellent cycling stability and high-rate capability for anode materials. Selecting a better electrolyte is essential to enhance the electrochemical properties of NIBs, we have done further research on the effect of various electrolytes on SGSs' electrochemical performance.

## 2. Experiment

### 2.1. Materials and methods

GO was synthesized through a modified Hummer method. The $Sb_2S_3$ nanowire was prepared by a solvothermal method. One mmol $SbCl_3$ and 6 mmol $Na_2S$ was dissolved in 20 mL ethylene glycol (EG) solution separately, $SbCl_3$-EG solution was slowly added into $Na_2S$-EG solution under vigorous stirring. The mixture was transferred to a 50 mL stainless steel Teflon-lined autoclave, followed by being sealed and heated inside a conventional oven at 200 °C for 10 h. After cooled to room temperature naturally, brown precipitate was collected by centrifugation and then washed thoroughly with anhydrous ethanol and deionized water. The collected precipitate was dried in vacuum at 80 °C overnight for later use. $Sb_2S_3$ nanowires templated graphene scrolls were prepared by a hydrothermal method. Typically, the aqueous mixture was produced by dispersing the 0.06 g $Sb_2S_3$ nanowires in 30 mL deionized water with 0.03 g of aqueous GO dispersion (0.6 mg/mL). The mixture was transferred to a 50 mL stainless steel Teflon-lined autoclave and heated at 160 °C for 24 h, followed by washing and drying as before.

### 2.2. Material characterization

The morphology and structure of SbGSs were characterized by field-emission scanning electron microscopy (FESEM, LEO 1430VP, Germany). Transmission electron microscopy (TEM) images were recorded using HRTEM/EDS (JEOL JEM-2010). The composition of the samples was analysed using an energy dispersive X-ray spectrometer (EDX) attached to the SEM instrument. The powder X-ray diffraction (XRD) pattern was collected on a Bruker D8 Advance diffractometer equipped with Cu K$\alpha$ radiation over the 2$\theta$ range of 10–70°.

### 2.3. Electrochemical measurement

For electrochemical studies, the working electrode was fabricated by mixing 60 wt% SbGSs, 20 wt% of acetylene black and 20 wt% of carboxymethyl cellulose (CMC) sodium salt binder in a minimal amount of water. This slurry was pasted on clean Cu foil and then dried at 80 °C in vacuum. In an Ar-filled glove box, CR2032 coin cells were assembled with Na foil as the counter electrode, glass microfibre filters (GF/D Whatman) served as the separator. 1M $NaClO_4$ in propylene carbonate (PC), and 1M $NaClO_4$ in ethylene carbonate/dimethyl carbonate (DMC) 1:1(v/v) Merck) were used as the electrolyte for NIB. 5 wt% fluorinated ethylene carbonate (FEC) was added in the electrolyte. CR2016 coin cells for lithium-ion batteries were fabricated using the same procedure for Na batteries. CR2016 coin cell was assembled with lithium metal as the counter electrode, the separator was polypropylene (PP) film. $LiPF_6$ (1 mol $L^{-1}$) in a mixture of ethylene carbonate and dimethyl carbonate (DMC) (1:1, by volume) contained 2% (V) fluoroethylene carbonate (FEC) as an electrolyte solution. Galvanostatic charge/discharge cycles were performed on a LAND 2001A Battery Tester between 0.01–2.00 V at various current densities. Cyclic voltammetry measurements were carried out on an electrochemical workstation (CHI750D) in the potential range of 0.01–2.00 V *vs.* $Na^+$/Na and 0.01–2.75 V *vs.* $Li^+$/Li.

## 3. Results and discussion

The formation of crystalline $Sb_2S_3$ was confirmed by X-ray diffraction (XRD) analysis. Fig. 1 gives the XRD pattern of the as prepared SbGSs. $Sb_2S_3$ is an anisotropic material, easy to construct various microstructures. If we control the reaction condition to induce $Sb_2S_3$ grown along the [001] direction, it will form wire-like morphology. We can match the obtained diffraction peaks to the orthorhombic $Sb_2S_3$ phase [42,43], and no obvious peaks of other crystalline phase were detected.

The morphology of the as-prepared $Sb_2S_3$ nanowires and SbGSs composite characterized by SEM and TEM is presented in

Please cite this article in press as: Y. Wu, et al., Graphene scrolls coated $Sb_2S_3$ nanowires as anodes for sodium and lithium ion batteries, Nano-Structures & Nano-Objects (2017), https://doi.org/10.1016/j.nanoso.2017.09.015.