Research Article

One-Dimensional Sb$_2$Se$_3$ Nanorods Synthesized through a Simple Polyol Process for High-Performance Lithium-Ion Batteries

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The good crystalline Sb$_2$Se$_3$ nanorods have been successfully synthesized through a simple polyol process. The detailed morphological and structural characterizations reveal that nanorods are composed of Sb$_2$Se$_3$ single crystals oriented along the [120] orientation; the tiny Sb$_2$Se$_3$ nanorods are found to display a higher crystallinity with respect to thick Sb$_2$Se$_3$ nanorods. The nanorods have been applied as anode materials for lithium-ion batteries, with tiny Sb$_2$Se$_3$ nanorod anodes delivering the relatively high discharge capacity of 702 mAh g$^{-1}$ at 0.1 C and could maintain the capacity of 230 mAh g$^{-1}$ after 100 cycles. A more stable cycling performance is also demonstrated on tiny Sb$_2$Se$_3$ nanorods, which is ascribed to their more pronounced one-dimensional nanostructure.

1. Introduction

With the increase of the world energy demand and the decrease of resources, Li-ion batteries (LIBs) are one of the most important electrical energy storage devices and are widely used in various portable electronic devices due to its relatively high energy density [1–7]. Nowadays, the low-cost graphite material is the most popular anode material used in commercial LIBs [8, 9]. However, graphite anodes possess a low theoretical specific capacity (372 mAh g$^{-1}$), which could hardly meet the requirements for high capacity and safety in practical energy storage application such as power stations. To improve the specific capacity of anode materials for LIBs, fabricating and testing new anode materials have become the focus of a multitude of scientific researches, such as metal oxides and metal sulfides. Among them, metal chalcogenides have emerged as promising anode materials for LIBs. In particular, researchers have fabricated antimony-based chalcogenide materials such as Sb$_2$O$_3$ nanomaterials and Sb$_2$Se$_3$ thin films, which could sensibly increase capacity and cycle performance with respect to graphite electrodes [10]. In the last few years, the Sb$_2$Se$_3$ nanostructured materials have been synthesized by other various techniques such as solvothermal process [11]. Recently, Kwon et al. prepared one-dimensional Sb$_2$Se$_3$ by evaporating a stacked elemental layer (Sb/Sb–Se/Se) deposition and then an additional annealing treatment process removed excess Se elements [12]. Ma et al. adopted a template-free solvothermal route to obtain the large-scale single-crystalline Sb$_2$Se$_3$ nanowires [13]. Xue and Fu have researched Sb$_2$O$_3$ nanomaterials, which have the high reversible capacity of about 794 mAh g$^{-1}$ and a relatively large irreversible capacity loss (234 mAh g$^{-1}$). Besides, Xue and Fu have also reported on a large reversible discharge capacity in Sb$_2$Se$_3$ thin films deposited by pulsed laser deposition for Li-ion batteries cycled between 0.3 and 2.5 V. The capacity was found in the range between 530.5 and 660.7 mAh g$^{-1}$ during the first 100 cycles. This indicates that the Sb$_2$Se$_3$
anode material has high reversible capacity in Li-ion batteries [14]. However, the loading charge in Sb2Se3 thin films is very low and its alloying combination reaction is associated with a drastic volume expansion upon lithiation, thus usually resulting in the active material pulverization and falling out from the collector, finally leading to the marked decrease of the long-term cycle performance. In addition, the pulsed laser deposition method is not compatible with low-cost fabrication. It is commonly agreed now that by using nanostructured electrode materials having particular dimension-related effects and large specific surface area can greatly relieve the volume expansion following the Li-alloying reaction. Therefore, the Sb2Se3 nanostructured composite material has been investigated showing excellent electrochemical properties in this paper, such as long cycle stability, good initial coulombic efficiency, and high energy density. In order to investigate the improved electrochemical properties of Sb2Se3 nanostructured materials, we report on a new low-cost fabrication method to dissolve the Se powder based on the mixed solvents of monoethanolamine and thioglycolic acid at room temperature in air for the first time [15].

2. Experimental

As shown in Scheme 1, 1 mmol antimony trichloride (SbCl3, 99.9%, Aladdin) was dissolved in 20 mL triethylene glycol (TEG, 99%, Aladdin) with magnetic stirring at room temperature for 2 h to get a clear cationic solution. 3 mmol Se powder was immediately dissolved in 2.7 mL monoethanolamine (MEA, 99%, Aladdin) and 0.3 mL thioglycolic acid (TGA, 80%, Aladdin) after stirring at room temperature to get a brownish red Se precursor solution. 80 mL TEG with 0.2 g PVP in a three-necked flask was installed in a heating mantle through magnetic stirring and attached to a Schlenk line. The three-necked flask was degassing and flowing nitrogen alternately for three times at room temperature. Then, the Se precursor solution was injected into the flask and stirred for 30 min under nitrogen flow. Then, the three-necked flask was heated to 210°C. Meanwhile, 10 mL cationic solution was swiftly injected into the flask and kept for 20 min at the same temperature. Afterward, the reaction solution was cooled to room temperature and precipitated by high-speed centrifugation. The precipitation was washed ultrasonically with excess amounts of absolute ethanol (CH3CH2OH, 99.7%, Aladdin) followed by centrifugation for 4 times in order to purify the thick Sb2Se3 nanorods. In addition, we found that it is possible to control the size of nanorods by adjusting the heating temperature of the three-necked flask. The three-necked flask with a mixture of Se precursor solution and cationic solution was heated at 180°C for 20 min and then proceed on to the next steps, such as nature cooling, centrifugation, and washing. We eventually obtained the tiny Sb2Se3 nanorods. The purified products were used for further characterization. The chemical equations associated with the preparation of Sb2Se3 are as follows:

$$2SbCl_3 + 3H_2O \rightarrow Sb_2O_3 + 6HCl$$
$$2Sb_2O_3 + 6Se \rightarrow 2Sb_2Se_3 + 3O_2$$  \hspace{1cm} (1)

The crystal structural characterizations were carried out by X-ray diffraction (XRD, D8 Advance, Bruker) using Cu Ka radiation ($\lambda = 0.1542$ nm). The surface morphologies and microstructure were characterized by scanning electron microscopy (SEM, JSM-6700F, JOEL) and transmission electron microscopy (TEM, JEM-2100F, JOEL), respectively.

The electrochemical performance was investigated using coin-type cells (CR2025), in which the Sb2Se3 nanorods were used as a working electrode and lithium foil was used as the counter and reference electrode. The electrolyte was 1 mol dm$^{-3}$ LiPF$_6$ dissolved in a mixture of ethylene carbonate/diethyl carbonate/dimethyl carbonate (EC/DEC/DMC) with a volume ratio of 1 : 1 : 1, and the separator was microporous polypropylene film. The Sb2Se3 electrode was prepared by mixing 80 wt% of as-prepared dispersed Sb2Se3 nanorods, 10 wt% polyvinylidene fluoride (PVDF, Kynar,
peaks with the orthorhombic phase of Sb$_2$Se$_3$ with space
compositions and the valence states of elements in the Sb$_2$Se$_3$ nano-
existence of the pure Sb$_2$Se$_3$ phase [16].
peaks at around 3d$_{3/2}$ (537.87 eV) and 3d$_{5/2}$ (528.47 eV),
rods. Figure 3(a) reveals two obvious high intensity Sb
argon-(99.9995%, purity)
hydrogen (99.9995%, purity) in a cut-off potential window
from 0.01 to 3.0 V vs. Li$^+$/Li at different current densities.

3. Results and Discussion

Figure 1 shows the XRD patterns of the tiny Sb$_2$Se$_3$ and thick
Sb$_2$Se$_3$ nanorods. We could clearly index all the diffraction
peaks with the orthorhombic phase of Sb$_2$Se$_3$ with space
group of Pbnm (62), in good agreement with the standard
JCPDS card no. 15-0861. Interestingly, no impurity phases
are found in the diffraction pattern. Compared with the thick
Sb$_2$Se$_3$, the tiny Sb$_2$Se$_3$ nanorods exhibit the stronger diffrac-
tions (110) and (040), which indicates the enhanced crystall-
linity of the tiny Sb$_2$Se$_3$ nanorods.

Raman spectroscopy is used to further analyze the
structure of the crystalline thick Sb$_2$Se$_3$ and tiny Sb$_2$Se$_3$
nanorods. Both of the spectrum in Figure 2 are detected
at 83, 118, 189, 252, 356, 373, and 450 cm$^{-1}$, respectively,
implying that the existence of the pure Sb$_2$Se$_3$ phase [16].
Compared with the thick Sb$_2$Se$_3$ nanorods, the greater
peak intensity with the tiny Sb$_2$Se$_3$ nanorods indicates the
enhancement of crystallinity.

XPS data are carried out to verify the chemical com-
ponents and the valence states of elements in the Sb$_2$Se$_3$
nanorods. Figure 3(a) reveals two obvious high intensity Sb
peaks at around 3d$_{3/2}$ (537.87 eV) and 3d$_{5/2}$ (528.47 eV),
which are ascribed to the charge state of Sb$^{3+}$ [17]. In addi-
tion, the other two relative weak Sb peak at around 3d$_{3/2}$
(539.15 eV) and 3d$_{5/2}$ (529.78 eV), implying the oxidation
of the surfaces for Sb$_2$Se$_3$ nanorods although Sb$_2$O$_3$ is not
detected by XRD and Raman results [18]. The XPS data for
the valence state of Se$^{2-}$ is split into 3d$_{3/2}$ (53.81 eV) and
3d$_{5/2}$ (53.01 eV) in Figure 3(b) [17]. Both of the thick Sb$_2$Se$_3$
and tiny Sb$_2$Se$_3$ nanorods with Sb$^{3+}$ and Se$^{2-}$ states prove the
purity of Sb$_2$Se$_3$ phase.

High-resolution transmission and scanning electronic
microscopy (HR-TEM and SEM) images from the thick
Sb$_2$Se$_3$ and tiny Sb$_2$Se$_3$ nanorods are shown in Figures 4
and 5, respectively. The images show the diameter distribu-
tion histograms of the Sb$_2$Se$_3$ nanorods obtained from SEM
data. As shown in Figures 4(a)–4(c), the arrangement of thick
Sb$_2$Se$_3$ nanorods is relatively disordered and the average
diameter of nanorods has already exceeded the value of
90 nm. However, the other Sb$_2$Se$_3$ nanorods are well-
dispersed, tiny, and smooth with an average diameter
ranging from 6 to 8 nm in Figures 5(a)–5(c). The analysis
on HR-TEM images provides further insights on the Sb$_2$Se$_3$
nanostructure: both Figures 4(d) and 5(d) show the
presence of lattice fringes with a plane spacing of 0.525 nm,
corresponding to the (120) lattice plane of single-crystal
Sb$_2$Se$_3$ nanorods. The result also indicates that the preferen-
tial growth direction of Sb$_2$Se$_3$ nanorods is along the [120]
crystal orientation. Consistent with the XRD, Raman, XPS,
SEM, and TEM results, the tiny Sb$_2$Se$_3$ nanorods deliver a
well-crystallized form. The EDS mapping of the tiny Sb$_2$Se$_3$
nanorods shown in Figure 6 indicates a uniform distribution
of Sb and Se throughout the tiny Sb$_2$Se$_3$ nanorods.

The electrochemical performance of thick Sb$_2$Se$_3$ and
tiny Sb$_2$Se$_3$ nanorod electrodes was investigated in a LIB cell
assembly with lithium metal acting as the counter and refer-
ence electrode. Figures 7(a) and 7(b) showed the galvanosta-
ic charge and discharge behavior obtained for the tiny Sb$_2$Se$_3$
nanorods, and the thick Sb$_2$Se$_3$ nanorods as working elec-
trode were measured at a current density of 0.1 C between
0.01 and 3 V. As can be seen from Figure 7(a), all the dis-
charge curves at the initial three cycles have two prolonged
plateaus at about 1.5 V and 0.9 V, corresponding to the two-step reaction of reduction. The upper plateau at about 1.5 V is associated to the lithiation process of Sb$_2$Se$_3$ directly to Sb and Li$_2$Se [19]. And the other plateau at about 0.9 V is attributed to the alloying reaction of metallic Sb to Li$_3$Sb [20]. These results confirm the global reactions (2) and (3) based on the simple equations, which suggests that a lithium insertion could take place [21–23].

\[
\text{Sb}_2\text{Se}_3 + 6\text{Li}^+ + 6\text{e}^- \rightarrow 2\text{Sb} + 3\text{Li}_2\text{Se} \quad (2)
\]

\[
6\text{Li}^+ + 2\text{Sb} + 6\text{e}^- \rightarrow 2\text{Li}_3\text{Sb} \quad (3)
\]
Besides, the plateaus in the charge curves are ascribed to the multistep oxidative transformation of Li$_3$Sb associated with the formation of Sb$_2$Se$_3$ [24]. The discharge capacities of thick Sb$_2$Se$_3$ nanorod electrode during the first three cycles are 634 mAh g$^{-1}$, 318 mAh g$^{-1}$, and 280 mAh g$^{-1}$, shown in Figure 7(b). However, the initial discharge and charge capacities of tiny Sb$_2$Se$_3$ nanorod electrode are around 702 mAh g$^{-1}$ and 475 mAh g$^{-1}$, respectively, and the initial coulombic efficiency of the LIB is 67.7%. The irreversible capacity may be attributed to the irreversible electrolyte decomposition and the inevitable formation of the SEI film on the electrode surface [25]. What is more, the well-defined voltage plateaus and potential positions remained almost unchanged during the subsequent cycles. This phenomenon suggests a good cycling stability of the tiny Sb$_2$Se$_3$ nanorod electrode in LIBs.

The cycling performance and coulombic efficiency of the tiny Sb$_2$Se$_3$ and the thick Sb$_2$Se$_3$ nanorod electrodes are compared in Figure 8. Indeed, the thick Sb$_2$Se$_3$ nanorod electrode only shows a discharge capacity of 48 mAh g$^{-1}$ after 50 cycles at 0.1 C. However, a reversible capacity of the tiny Sb$_2$Se$_3$ nanorods is still 230 mAh g$^{-1}$, indicating a much higher capacity retention after 100 cycles at 0.1 C. In addition, the coulombic efficiency increases significantly during the first five cycles and stabilizes around 99% in the subsequent cycles. Compared with the tiny Sb$_2$Se$_3$ nanorod electrodes,
the thick Sb$_2$Se$_3$ nanorod electrodes exhibit faster capacity fading and minimum reversible capacity because of the presence of different Sb$_2$Se$_3$ nanorod diameters. We can attribute the improved cycle stability to the pure one-dimensional Sb$_2$Se$_3$ nanostructure, which cannot only increase the contact area between the active materials and the electrolyte improving the utilization of Sb$_2$Se$_3$ nanorods but also decrease diffusion length of lithium ions. In addition, the one-dimensional nanostructure could relieve the intrinsic stress in Sb-based electrode materials, then slow the electrode pulverization upon cycling and enhance the capacity and cycling stability [26].

Figure 7 exhibits the rate performances of tiny Sb$_2$Se$_3$ nanorods and thick Sb$_2$Se$_3$ nanorods. As shown in Figure 7(a), after the first cycle at 0.1 C, the tiny Sb$_2$Se$_3$ nanorods have an average discharge capacity of 438 mAh g$^{-1}$ at 0.1 C. With the increasing current rate, the capacity drops to 120 mAh g$^{-1}$ at 1 C. More importantly, the tiny Sb$_2$Se$_3$ nanorods exhibit faster capacity fading and minimum reversible capacity because of the presence of different Sb$_2$Se$_3$ nanorod diameters. We can attribute the improved cycle stability to the pure one-dimensional Sb$_2$Se$_3$ nanostructure, which cannot only increase the contact area between the active materials and the electrolyte improving the utilization of Sb$_2$Se$_3$ nanorods but also decrease diffusion length of lithium ions. In addition, the one-dimensional nanostructure could relieve the intrinsic stress in Sb-based electrode materials, then slow the electrode pulverization upon cycling and enhance the capacity and cycling stability [26].

Figure 9 exhibits the rate performances of tiny Sb$_2$Se$_3$ nanorods and thick Sb$_2$Se$_3$ nanorods. As shown in Figure 9(a), after the first cycle at 0.1 C, the tiny Sb$_2$Se$_3$ nanorods have an average discharge capacity of 438 mAh g$^{-1}$ at 0.1 C. With the increasing current rate, the capacity drops to 120 mAh g$^{-1}$ at 1 C. More importantly, the tiny Sb$_2$Se$_3$ nanorods exhibit faster capacity fading and minimum reversible capacity because of the presence of different Sb$_2$Se$_3$ nanorod diameters. We can attribute the improved cycle stability to the pure one-dimensional Sb$_2$Se$_3$ nanostructure, which cannot only increase the contact area between the active materials and the electrolyte improving the utilization of Sb$_2$Se$_3$ nanorods but also decrease diffusion length of lithium ions. In addition, the one-dimensional nanostructure could relieve the intrinsic stress in Sb-based electrode materials, then slow the electrode pulverization upon cycling and enhance the capacity and cycling stability [26].

**Figure 7**: Galvanostatic charge and discharge profiles of (a) tiny Sb$_2$Se$_3$ nanorods and (b) thick Sb$_2$Se$_3$ nanorods as working electrodes in LIBs.

**Figure 8**: Cycling performance and corresponding coulombic efficiency of the thick Sb$_2$Se$_3$ nanorods (green) and tiny Sb$_2$Se$_3$ nanorods (blue) as working electrodes in LIBs.

**Figure 9**: Rate performances of (a) tiny Sb$_2$Se$_3$ nanorods and (b) thick Sb$_2$Se$_3$ nanorods.
nanorods can regain the reversible capacity of 304 mAh g$^{-1}$, when the current rate returns back to 0.1 C. The thick Sb$_2$Se$_3$ nanorods present reversible capacities of 283, 140, 79, and 37 mAh g$^{-1}$ at current rates of 0.1, 0.2, 0.5, and 1 C, respectively. Hence, the tiny Sb$_2$Se$_3$ nanorods deliver a relative excellent rate performance.

Figure 10 shows the CV curves of (a) the tiny Sb$_2$Se$_3$ nanorods and (b) the thick Sb$_2$Se$_3$ nanorods.

Figure 10: CV curves of (a) the tiny Sb$_2$Se$_3$ nanorods and (b) the thick Sb$_2$Se$_3$ nanorods.

Electrochemical impedance spectroscopy (EIS) plots of the tiny Sb$_2$Se$_3$ and the thick Sb$_2$Se$_3$ nanorod electrodes are at different depths of discharge (DODs). In Figure 11, D1, D2, and D3 represent relevant curves obtained at DODs of 0 mAh g$^{-1}$, 200 mAh g$^{-1}$, and full discharge in this study. Both of the Nyquist plots deliver a semicircle corresponding to the charge transfer resistance ($R_{ct}$) in the high-to-medium frequency and an inclined line of the Warburg impedance in the low frequency. The equivalent circuit of the discharge behavior for samples is shown in Figure 12. $R_1$ represents the Ohmic resistance, and $R_{ct}$ and $R_2$ represent the charge transfer resistance and the resistance of the surface layer of Sb$_2$Se$_3$ in contact with the electrolyte, respectively. CPE$_{ct}$ and CPE$_2$ are the double-layer capacitances, and ZW
is the Warburg impedance. With the increase in DOD, the diameter of the semicircle becomes increasingly larger, indicating higher charge transfer resistance. Compared with the thick Sb$_2$Se$_3$ nanorods, the tiny Sb$_2$Se$_3$ nanorods all displayed lower charge transfer resistance throughout the whole discharge process, as indicated by their semicircles, which may contribute to the increase in the discharge capacity [27].

To further understand the mechanism of Li cycling, the electrode after 50 cycles was investigated by SEM images. As shown in Figure 13, both of the Sb$_2$Se$_3$ nanorod morphologies change after cycling, and a partial agglomeration of the active material was observed. Such change can negatively affect the battery performance due to separation of active substance from the conducting agent. The morphology and structure of the one-dimensional tiny Sb$_2$Se$_3$ nanorod structure were retained after cycling and indicate its structural stability upon electrochemical cycling in Figure 13(a). However, the thick Sb$_2$Se$_3$ nanorods are almost invisible in Figure 13(b). It is clear that the tiny Sb$_2$Se$_3$ nanorods deliver a favorable electrochemical performance with high reversible capacity and good cycling stability in LIBs.

4. Conclusions

In this study, a new and facile polyol process is reported preparing Sb$_2$Se$_3$ nanorods, with controlled sizes, applied as working electrode material for LIBs. Compared with the thick Sb$_2$Se$_3$ nanorods, the tiny Sb$_2$Se$_3$ nanorods demonstrate a favorable electrochemical performance with high reversible capacity and good cycling stability in LIBs. The high reversible capability of the Sb$_2$Se$_3$ nanorods is 230 mAh g$^{-1}$ after 100 cycles at 0.1 C. This study provides insights and indications on how to develop Sb$_2$Se$_3$-based electrode materials for conversion alloying reactions for high-performance batteries.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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Figure 13: SEM images of (a) the tiny Sb$_2$Se$_3$ nanorods and (b) the thick Sb$_2$Se$_3$ nanorods after 50 charge/discharge cycles.
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