Preparation and Li-storage properties of SnSb/graphene hybrid nanostructure by a facile one-step solvothermal route

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A SnSb nanocrystal/graphene hybrid nanocomposite was synthesized by a facile one-step solvothermal route using graphite oxide, SnCl$_2$.2H$_2$O and SbCl$_3$ as the starting materials, absolute ethanol as the solvent, and NaBH$_4$ as the reductant. The formation of SnSb alloy and the reduction of the graphene oxide occur simultaneously. SnSb nanoparticles with a size of 30–40 nm were uniformly anchored and confined by the graphene sheets, forming a unique SnSb/graphene hybrid nanostructure. The electrostatic attraction between the positively charged ions (Sn$^{2+}$ and Sb$^{3+}$) and the negatively charged graphene oxide plays an important role in the uniform distribution of the SnSb particles on the graphene sheets. The electrochemical Li-storage properties of the nanocomposite were investigated as a potential high-capacity anode material for Li-ion batteries. The results show that the nanocomposite exhibits an obvious enhanced Li-storage performance compared with bare SnSb. The improvement of the electrochemical performance could be attributed to the formation of two-dimensional conductive networks, homogeneous dispersion and confinement of SnSb nanoparticles and the enhanced wetting of active material with the electrolyte for increased specific surface area by the introduction of graphene into SnSb nanoparticles. Li-ion chemical diffusion coefficient and ac impedance were measured to understand the underlying mechanism for the improved electrochemical performance.

Keywords: tin–antimony nanocrystal; graphene; hybrid nanostructure; lithium storage properties

1. Introduction

In recent years, much interest has been focused on non-carbonaceous anode materials with high specific capacity to replace the currently used carbon-based anodes in commercial Li-ion batteries. In these materials, metallic Sn has received special interest because it yields a high capacity and offers an appropriate Li-storage voltage. However, the Sn anode undergoes rapid capacity fading upon cycling due to large volume changes. Although the introduction of a Li-inert element to form Sn alloys [1–6] can alleviate the volume change to some extent, it will decrease the overall capacity or even make the alloy electrochemically inert [7]. An alternative strategy is to form Sn alloys with another Li-active element. Among them, the SnSb intermetallic compound and its derivatives have attracted particular

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attention because they not only show high electrochemical activity but also show relieved volume changes due to the stepwise lithiation mechanism [8,9].

Much effort has been made to further improve the electrochemical performance of this material. One method is to use nanosized Sn–Sb alloys to reduce the absolute volume changes [10,11]. Nevertheless, nanoparticles are prone to aggregate upon repeated cycling. An effective measure to overcome this problem is to load the nanoparticles onto carbon-based matrices, such as carbon nanotubes [12,13], mesophase carbon microbeads [14], hard carbon spherules [15], carbon [16] and amorphous carbon [17]. Compared with the above carbon materials, graphene, a flat monolayer of carbon atoms arranged in a tightly packed honeycomb network [18], is more attractive due to its appealing properties such as superior electrical conductivity [19], extremely large specific surface area [20], high mechanical strength [21] and high chemical and thermal stability [22]. Recent research on some Sn-based metals [23,24], oxides [25–29] and alloys [30,31] demonstrated that the electrochemical performance of these materials can be significantly improved by loading them onto graphene sheets. The flexible graphene not only accommodates the volume changes and suppresses the aggregation of the nanoparticles, but also provides conductive channels and contributes to the overall capacity.

To date, however, most of the work on the graphene-based composites centers on metals or oxides with alloys rarely reported. Herein, we report a facile preparation of a SnSb/graphene hybrid nanostructure by an in situ one-step solvothermal route. In this work, the nanocomposite was systematically characterized and the formation mechanism is discussed. Electrochemical tests showed that the nanocomposite demonstrates improved cycling stability and rate capability compared with bare SnSb nanoparticles indicating potential application in Li-ion batteries. The underlying mechanism for the improvement in electrochemical properties was also investigated by measurements of Li-ion chemical diffusion coefficients and ac impedance plots.

2. Experimental section

2.1. Preparation of SnSb/graphene nanocomposite

Graphite oxide (48 mg), which was prepared by a modified Hummer’s method [32], was dispersed in 60 mL of absolute ethanol by ultrasonication for 3 h. Then, 2 mmol of SnCl₂.2H₂O and 2 mmol of SbCl₃ were added to the above dispersion with ultrasonication for another 0.5 h, followed by adding 20 mL of 1.5M NaBH₄ ethanol solution slowly to reduce Sn²⁺ and Sb³⁺. The mixture was transferred to a Teflon-lined stainless steel autoclave and maintained at 180°C for 24 h. The resulting product was separated by centrifugation, washed with deionized water and dried at 30°C under vacuum overnight. Bare SnSb was prepared using a similar process without adding graphite oxide. Graphene was also prepared by a similar procedure. A simple SnSb/graphene mixture was also prepared by grinding bare SnSb and graphene at a weight ratio of 93.6:6.4.

2.2. Materials characterization

The crystalline structure of the obtained products was characterized by X-ray diffraction (XRD) on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu Kα radiation (λ = 0.154 nm). The morphologies of the products were characterized by field emission scanning electron microscopy (FE-SEM, FEI-sirion), transmission electron microscopy (TEM, JEM 2100F) and high-resolution TEM (HRTEM). Raman spectra were collected
on a Jobin-Yvon Labor Raman HR-800 Raman system by exciting a 514.5 nm Ar-ion laser. X-ray photoelectron spectroscopy (XPS) measurements were performed on a KRATOS AXIS ULTRA-DLD spectrometer with a monochromatic Al K$_\alpha$ radiation ($h\nu = 1486.6$ eV). The carbon content was measured on a Flash EA 1112 tester.

2.3. Electrochemical measurements

The electrochemical performance of the as-synthesized materials (SnSb/graphene, bare SnSb and graphene) was evaluated using CR2025-type coin cells. The electrode slurry was made by mixing 75 wt % active material, 15 wt % acetylene black and 10 wt % polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP) with magnetic stirring for 2 h. The slurry was then pasted onto Ni foam to make the working electrodes. After drying at 100°C under vacuum for 8 h, the electrodes (the loading of the active material was about 5 mg) were assembled into half cells in an argon-filled glove box using metallic Li foil as the counter electrode, 1M LiPF$_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) as the electrolyte and polypropylene microporous film (Celgard 2300) as the separator. The cells were galvanostatically charged-discharged on a LHS-B-5V5mA8D battery cycler (Wuhan, China) in the voltage range of 0.05–1.5 V (vs. Li/Li$^+$) at various current densities. Cyclic voltammetry (CV) measurements were performed on an Arbin BT2000 system between 0.05 and 1.5 V at various scan rates. Electrochemical impedance spectroscopy (EIS) measurements were carried out on a CHI660C electrochemistry workstation. The impedance plots were recorded by applying an ac signal of 5 mV amplitude over the frequency range from $10^2$ Hz to 10 mHz at de-lithiation state. All the electrochemical measurements were conducted at 25°C.

3. Results and discussion

Figure 1a shows the XRD patterns of the SnSb/graphene composite and bare SnSb. For comparison, a simple mixture of bare SnSb and graphene was also prepared based on the carbon content analysis of the in situ prepared product (6.4 wt %). All the diffraction peaks can be indexed to hexagonal SnSb (space group $R\overline{3}m$, JCPDS No. 33-0118) for both SnSb/graphene and bare SnSb. For the simple mixture, besides the SnSb peaks, a small peak appears at 25° ($2\theta$) (indicated by the arrow in Figure 1a), which is related to the (002) peak of graphene. This suggests that during the in situ preparation of SnSb/graphene composite, the restacking of the reduced graphene oxide is restrained by uniformly loading SnSb particles in between the graphene sheets. The electrostatic attraction between the positively charged ions (Sn$^{2+}$ and Sb$^{3+}$) and the negatively charged graphene oxide sheets [33] plays a crucial role in the attachment of the SnSb particles on the graphene sheets. Energy dispersive X-ray (EDX) analysis shows that the Sn/Sb molar ratio in the product is 48.4:51.6, close to the value in the starting materials.

Figure 1b shows the Raman spectra of graphite oxide, SnSb/graphene and bare SnSb. Two bands at 1350 and 1580 cm$^{-1}$ appear in the Raman spectra of SnSb/graphene, corresponding to the disordered (D) band and graphitic (G) band of carbon materials. Compared with graphite oxide, the composite exhibits an increased D/G intensity ratio, caused by a reduction of the average size of the $sp^2$ domains and an increased number of these small sized domains, suggesting the conversion from graphite oxide to graphene [34]. The small peaks at 200–600 cm$^{-1}$ are related to the Raman active modes of Sb$_2$O$_3$ [35]. Sb$_2$O$_3$ was also observed on the surface of nanosized SnSb in a previous report [10].
Figure 1. (a) XRD patterns of bare SnSb, SnSb/graphene and simple SnSb/graphene mixture. (b) Raman spectra of graphite oxide, SnSb/graphene and bare SnSb. (c) C 1s XPS spectra of graphite oxide and SnSb/graphene. (d) SEM images of SnSb/graphene.

XPS measurements were performed to check the degree of reduction of graphene oxide. Figure 1c shows the C 1s XPS spectra of graphite oxide and SnSb/graphene. The XPS spectra can be deconvoluted into four peaks, corresponding to carbon atoms in different functional groups: sp² carbon (C–C, 284.8 eV), carbon in C–O bonds (286.2 eV), carbonyl carbon (C=O, 287.6 eV) and carboxylate carbon (O–C=O, 289.1 eV) [34,36]. For graphite oxide, the high intensity of the non-sp² carbon reveals a considerable oxidation of graphite. For SnSb/graphene, the peak intensity of the non-sp² carbon shows a remarkable reduction with obvious increased peak intensity of sp² carbon, indicative of a sufficient de-oxygenation during the solvothermal reaction. The XRS results confirm the reduction of graphene oxide to graphene.

Figure 1d shows a typical SEM image of the SnSb/graphene composite. Note that the composite exhibits quasi-two-dimensional thin-flake morphology. Through the transparent graphene, we can see the uniformly dispersed SnSb nanoparticles that were confined by the graphene sheets. Without the confinement of the graphene, the SnSb nanoparticles tend to aggregate, as indicated by the black arrows in Figure 1d. We can also observe wrinkles on the graphene sheets. The presence of these wrinkles strongly signifies the firm contact between the SnSb particles and graphene sheets.

The morphologies of the SnSb/graphene composite were further characterized by TEM. Figure 2a displays typical TEM images of a thin graphene flake with folded edges (indicated by the black arrows), from which it can be inferred that the flake is very thin,
Figure 2. (a,b) Low-magnification TEM images, (c) high-magnification TEM images and (d) HRTEM images of SnSb/graphene.

constructed possibly by single- or few-layer graphene. Figure 2b shows typical TEM images of SnSb/graphene consisting of two partly overlapped graphene flakes (indicated by arrows A and B, respectively). The transparent nature and the wrinkles of flake B also suggest that the graphene flake is rather thin. Note that the SnSb nanoparticles are homogeneously loaded onto the graphene sheets. More importantly, the nanoparticles are confined by the graphene sheets, evident from the color contrast of the SnSb particles between flake A and flake B, agreeing well with the SEM observation. It should be noted that nearly all the SnSb nanoparticles are attached onto the graphene sheets even though the graphene content (6.4 wt %) is low. Note that compared with the sample studied by Seng et al. [31], the SnSb nanoparticles in our sample show a narrower size distribution and a more uniform dispersion by the graphene sheets. The solvothermal treatment in ethanol is possibly responsible for the optimized microstructure of the sample. In addition, the graphene sheets can be completely separated by the loaded SnSb nanoparticles due to the low graphene/SnSb weight ratio (6.4:93.6), which also contributes to the optimized microstructure.

Figure 2c shows high-magnification images of the SnSb/graphene composite. Note that the SnSb particles take on a quasi-spherical shape with an average particle size of around 30–40 nm. It should be emphasized that the SnSb nanoparticles can be firmly attached on the graphene sheets even though they have undergone a strong ultrasonication treatment (for SEM and TEM observation), attributed to the confinement effect of the graphene sheets. Figure 2d shows the lattice-resolved HRTEM images of an individual SnSb particle surrounded by the graphene. The fringe spacing is measured to be 0.31 nm, corresponding to the interplanar spacing of (101) plane of SnSb. Compared with previous studies [30,31],
the sample in our work was more systematically characterized by XRD, Raman, SEM, TEM and HRTEM methods. The formation of the SnSb/graphene hybrid nanostructure is undoubtedly confirmed by these characterizations.

For comparison, the morphologies of graphene and bare SnSb were also observed by TEM to check the interaction between SnSb and graphene during the solvothermal process. It is clear that without the loading of the SnSb nanoparticles, the graphene tends to aggregate (Figure 3a). On the other hand, without the graphene sheets, the SnSb nanoparticles also aggregate, as shown in Figure 3b. Based on the above results, a formation mechanism of the hybrid nanostructure is proposed, as schematically illustrated in Figure 4.

The electrochemical properties of the SnSb/graphene composite were investigated by galvanostatic cycling and CV tests. The first discharge (Li absorption) and charge (Li extraction) capacities of the composite were 1111 and 721 mA h g\(^{-1}\), respectively, at 50 mA g\(^{-1}\) (Figure 5a). The irreversible capacity is related mainly to the decomposition of the electrolyte and the formation of solid electrolyte interface (SEI) layer [10]. Another source of the irreversible capacity is from the reaction of surface oxide Sb\(_2\)O\(_3\) with Li by forming Li\(_2\)O [10]. After the first cycle, both the charge and discharge curves

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**Figure 3.** TEM images of (a) graphene and (b) bare SnSb.

**Figure 4.** Schematic illustration of the formation mechanism of the SnSb/graphene hybrid nanostructure.
Figure 5. Electrochemical properties of the solvothermal products. (a) Charge–discharge curves (50 mA g$^{-1}$) and (b) CV plots (0.1 mV s$^{-1}$) of SnSb/graphene. (c) Comparison of cycling stability among SnSb/graphene, bare SnSb and graphene (50 mA g$^{-1}$). (d) Comparison of rate capability between SnSb/graphene and bare SnSb.

almost overlap, suggesting a high electrochemical reversibility. Figure 5b displays the CV plots of the composite. Two pairs of currents peaks can be observed, corresponding to the two successive potential plateaus at around 0.6 and 1.1 V, respectively. The first pair (A, A') of peaks corresponds to the Li-absorption/extraction of Sn [10,13], whereas the second pair (B, B') of peaks is related to the Li-absorption/extraction of Sb. Again, a high electrochemical reversibility of the composite can also be reflected by the nearly overlapped plots after the first cycle.

Figure 5c compares the cycling stability between bare SnSb and SnSb/graphene at 50 mA g$^{-1}$. Both the samples show a slow capacity fade in the initial cycle due to the small absolute volume changes for nanomaterials since the small size particles are difficult to pulverize, unlike large size particles. After that, SnSb/graphene demonstrates an obviously slow capacity fade rate compared to bare SnSb. After 30 cycles, a charge capacity of 530 mA h g$^{-1}$ can be retained for SnSb/graphene, almost doubling that for bare SnSb. The enhanced cycling stability is attributed to the buffering effect of graphene that alleviates the large volume changes and the confinement effect of graphene that restrains the aggregation of the SnSb nanoparticles. It should be stressed that the long-term cycling stability of the SnSb/graphene composite is not satisfactory yet owing to the intrinsic large volume changes of the SnSb during Li-absorption/extraction. Note that the graphene shows good capacity retention with a low capacity.

Figure 5d compares the rate capability between bare SnSb and SnSb/graphene. Clearly, the nanocomposite shows a better rate capability than bare SnSb. This suggests that the
improved rate capability comes mainly from three factors: first, the highly conductive graphene offers a two-dimensional (2D) conductive channel for the SnSb nanoparticles; second, small-sized, well-dispersed nanoparticles are favorable for rapider Li-ion diffusion; third, the SnSb/graphene hybrid nanostructure facilitates the better wetting of the active material by the electrolyte, leading to the faster Li-ion transport across the electrode/electrolyte interface. It should be noted that the sample studied by Seng et al. [31] exhibited a better electrochemical performance than our sample either in cycling stability or in rate capability, probably due to the higher graphene content (70%) in their sample than that (6.4%) in our sample. This therefore suggests that the electrochemical performance of our sample can be further improved by introducing more graphene into the composite.

To understand the underlying mechanism for the effect of graphene on the electrochemical properties of SnSb, the Li-ion chemical diffusion coefficients, $\tilde{D}_{Li}$, were measured by the CV method. Figure 6 shows the CV plots at various scan rates between 0.05 and 1.5 V. The insets give the peak current ($I_p$) as a function of square root of the scan rate ($v^{1/2}$) and the corresponding linear fitting. For both A and B peaks, $I_p$ exhibits a linear relationship with $v^{1/2}$, which is expected for a diffusion-controlled process. The chemical diffusion coefficients can be calculated with the following equation [37]:

$$I_p = 0.4463n^{3/2}F^{3/2}C_{Li}SR^{-1/2}T^{-1/2}\tilde{D}_{Li}^{1/2}v^{1/2}, \quad (1)$$

where $n$, $F$, $C_{Li}$, $S$, $R$ and $T$ represent the charge transfer number, the Faraday constant, the Li-ion concentration (mol cm$^{-3}$), the surface area of the electrode (cm$^2$), the gas constant and the absolute temperature (K), respectively. For bare SnSb, the $\tilde{D}_{Li}$ values in Sn and Sb are $1.8 \times 10^{-11}$ and $1.1 \times 10^{-11}$ cm$^2$ s$^{-1}$, respectively, whereas for the composite, these values are increased to $4.8 \times 10^{-11}$ and $2.5 \times 10^{-11}$ cm$^2$ s$^{-1}$, respectively. The restrained aggregation of the nanoparticles by graphene leads to more rapid Li-ion diffusion, which is one of the reasons for the improved rate capability of the composite.

To further explain the different electrochemical behaviors between bare SnSb and SnSb/graphene, ac impedance plots were recorded after the cells had been cycled for 30 times, as shown in Figure 7. The Nyquist plots show a depressed semicircle in the high-to-middle frequency region and a slopping line in the low frequency region. The depressed semicircle is actually composed of two partially overlapped semicircles at high

Figure 6. CV plots of (a) bare SnSb and (b) SnSb/graphene at various scan rates. The insets show $I_p$ as a function of $v^{1/2}$ and the corresponding linear fitting.
Figure 7. Impedance plots (symbols) and fitting results (solid line) of the electrodes after 30 cycles. The inset shows the equivalent circuit.

and middle frequency. The Nyquist plots are fitted by an equivalent circuit shown in the inset of Figure 7. In the equivalent circuit, the symbol $R_s$ denotes the electrolyte resistance, corresponding to the intercept of high-frequency semicircle at $Z_{re}$ axis. The $R_{SEI}$ and $CPE_1$ elements, corresponding to the high-frequency semicircle, represent the SEI layer resistance and dielectric relaxation capacitance, respectively. The $R_{ct}$ and $CPE_2$ elements, corresponding to the middle-frequency semicircle, represent the charger transfer resistance between the electrolyte and the electrode and the associated double-layer capacitance, respectively, and $R_w$ is referred to the Warburg impedance, related to the Li-ion diffusion in the bulk electrode [38]. According to the fitting results, the values for $R_{SEI}$ and $R_{ct}$ of the bare SnSb electrode are 27.5 and 63.7 $\Omega$, respectively, whereas the SnSb/graphene electrode shows low $R_{SEI}$ and $R_{ct}$ values of 12.4 and 40.2 $\Omega$, respectively. The better wetting of the active material and restrained particle aggregation are responsible for the low $R_{ct}$ value for SnSb/graphene. The stabilization of the electrode by confining the particles between the graphene sheets is considered to account for the low $R_{SEI}$ value for SnSb/graphene. A lower $R_{ct}$ for SnSb/graphene can also explain its better rate capability than bare SnSb. In addition, a low $R_{SEI}$ value is also beneficial for reversible cycling of the electrode. As a result, the diffusion coefficients and EIS measurements agree well with the different electrochemical behaviors between bare SnSb and SnSb/graphene nanocomposite. The effect of graphene incorporation on the electrochemical performance of SnSb nanoparticles is thus clarified by these measurements.

4. Conclusions

A SnSb/graphene hybrid nanostructure has been successfully synthesized by a simple one-step solvothermal route. In this structure, the nanosized (30–40 nm) SnSb particles are loaded and confined by the graphene sheets. The SnSb/graphene composite shows improved cycling stability and rate capability compared to bare SnSb. The improvement in cycling stability can be attributed to the introduction of the flexible graphene that acts both as a buffer to alleviate the volume changes and as a separator to restrain the aggregation of the SnSb nanoparticles. The introduction of the graphene also supplies 2D conductive networks, enhances the wetting of the active material, and disperses the nanoparticles, leading
to improved rate capability. The results clearly indicate that the incorporation of graphene can improve the electrochemical properties of SnSb with a potential application as anode material for Li-ion batteries.

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