



Activation of electrochemical lithium and sodium storage of nanocrystalline antimony by anchoring on graphene via a facile in situ solvothermal route



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HIGHLIGHTS

- We synthesize Sb/graphene nanohybrid by an in situ one-pot solvothermal route.
- The nanohybrid exhibits improved Li and Na-storage properties than bare Sb.
- The graphene offers buffering, conducting, and immobilizing effects for Sb.

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ABSTRACT

A Sb/graphene nanohybrid has been synthesized by a facile in situ solvothermal route using SbCl_3 and graphite oxide as the precursors and NaBH_4 as the reducing agent. Microstructural observation reveals the sheet-like nanostructure consisting of Sb nanocrystals (50–100 nm) attached on few-layer graphene nanosheets. The in situ introduced graphene uniformly disperses the Sb nanocrystals, while the attached Sb nanocrystals hinder the restacking of the graphene nanosheets. The introduction of graphene remarkably improves the electrochemical Li and Na-storage properties of Sb due to the combined buffering, confining and conducting effects of graphene. The underlying mechanism for the enhanced Li and Na-storage properties has been investigated by chemical diffusion coefficient and electrochemical impedance spectroscopy measurement.

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1. Introduction

Compared with conversional carbon-based anode materials, some metals or alloys materials can yield a much higher specific capacity via a Li-alloying/de-alloying mechanism [1,2]. Among these anodes, Sb-based materials have received a special interest because they exhibit well-defined potential plateaus, in addition to the high theoretical capacity (660 mAh g^{-1} for metallic Sb). These materials, however, suffer from a rapid capacity fade due to the large volume changes during the alloying/de-alloying processes. A

volume increase of over 100% is observed during the conversion from Sb to Li_3Sb [1]. Since Tirado's group reported that CoSb_3 showed an improved cycling stability than bare Sb [3], a great attention has been paid to some Sb-based alloys, SbM_x [4–10], where M represents a Li-inert element, which acts as a buffering matrix for the volume changes. The electrochemical Li-storage performance of these Sb or Sb-based alloys could be further improved by loading them onto carbon matrices, such as carbon nanotubes [11,12], TiC/C [13], $\text{Cr}_3\text{C}_2/\text{C}$ [14], MO_x/C (M = Al, Ti, and Mo) [15], acetylene black [16], and pyrolytic carbon [17,18].

Na-ion batteries have long been considered as alternatives to Li-ion batteries because of the natural abundance of Na sources [19–21]. Although graphite can also be used as the matrix to host Na ions, its Na-storage capacity is limited to NaC_{70} [22], much lower compared with that of Li storage (LiC_6), due to the large radius of Na ion. Compared with graphite, hard carbon is a more suitable

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Na-storage host due to its higher capacity [23–26]. However, the Na-storage capacity of hard carbon is not satisfactory yet, typical below 300 mAh g⁻¹. Similar to the case of Li storage, the material based on a Na-alloying reaction can also store Na ions. A theoretical Na-storage capacity of 847 mAh g⁻¹ can be achieved by forming Na₁₅Sn₄ alloy [27]. A first charge capacity as high as 410 mAh g⁻¹ was obtained for Sn/C [28]. Recent work has showed that Sb-based materials also exhibit a high Na-storage capacity by forming a maximum Na₃Sb composition [29–33]. Similarly, better Na-storage properties of these Sb-based anodes could be realized by using carbon-based matrices, such as Super P carbon [31], SiC/C [33], and carbon-fiber/carbon-black [32], to buffer the volume change which is as high as 390% [30].

From the above discussion, it is obvious that for both Li and Na storage, carbon materials play an important role in improving the electrochemical performance. Compared with the conventional carbon materials, graphene, a new two-dimensional carbon material [34], is more suitable to serve as the matrix to support active materials, especially those in nanoscale. The flexible graphene acts not only as the buffer to accommodate the volume changes but also as the separator to restrain the particles aggregation because of its large specific surface area [35] and high mechanical strength [36]. Besides, graphene affords conducting channels owing to its high electronic conductivity [37]. The work on some Sn-based materials, such as metallic Sn [38,39], tin oxides [40,41], and tin alloys [42,43] has indicated that the Li-storage performance could be significantly improved by anchoring them onto graphene. The Na-storage performance of SnO₂ could also be improved by using graphene as the support [44].

To our best knowledge, however, the effect of graphene on the Li-storage properties of Sb-based materials was rarely studied [45]. No report is available about the effect of graphene on the Na-storage properties of Sb-based materials. Herein, we report a facile one-pot solvothermal route to prepare Sb/graphene (Sb/G) nanohybrid. The effect of graphene on the Li and Na-storage properties of Sb will be investigated. The mechanism for the electrochemical improvement by graphene incorporation and the reason for the different Li and Na-storage behaviors of Sb and Sb/G will be explored.

2. Experimental

2.1. Preparation of Sb/G nanohybrid

Graphite oxide (GO, 50 mg), which was prepared by the modified Hummer's method [46], was dissolved in 60 mL of ethylene glycol (EG) with sonication for 3 h to form a homogeneous solution. Then, 337.35 mg of SbCl₃ was added into the above solution with sonication for another 0.5 h. After adding sufficient NaBH₄ (800 mg), the mixed solution was transferred to a Teflon-lined stainless steel autoclave and heated in an electric oven at 180 °C for 24 h. The resulting product was separated by centrifugation, washed repeatedly with deionized water and absolute ethanol, and dried at 40 °C under vacuum overnight. For comparison, bare Sb was also prepared using the same procedure except that GO was not added during the synthesis. Microsized Sb was prepared by ball-milling commercial Sb powder.

2.2. Materials characterization

The crystalline phases of the products were identified by X-ray diffraction (XRD) on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu K_α radiation (λ = 0.1542 nm). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOS AXIS ULTRA-DLD spectrometer with a monochromatic Al

K_α radiation (hν = 1486.6 eV). The morphologies of the products were observed by field emission scanning electron microscopy (FE-SEM) on a FEI-sirion microscope and transmission electron microscopy (TEM) on a JEM 2100F microscope. Raman spectra were collected on a Jobin-Yvon Labor Raman HR-800 Raman system using Ar-ion laser of 514.5 nm at 10 mW. The carbon content analysis was conducted on a Flash EA 1112 tester. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bruker Vector 22 Fourier infrared spectrometer. The powder sample was mixed uniformly with KBr with a weight ratio of 1:100, and pressed into a pellet before the FTIR measurements.

2.3. Electrochemical measurements

The electrochemical Li and Na-storage properties of the products were evaluated by galvanostatic cycling using CR2025-type coin cells. The electrode slurry was made by mixing 75 wt% active material (Sb/G, Sb), 15 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) with magnetic stirring for 2 h. The slurry was then coated onto Ni foam and dried at 100 °C under vacuum overnight to make the working electrodes. The electrodes were then assembled into half cells in an Ar-filled glove box using Li (or Na) foil as the counter electrode and Celgard 2300 polypropylene membrane as the separator. The electrolyte was 1 M LiPF₆ (or NaPF₆) dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume). The cells were charged and discharged at various current densities between 0.005 and 1.5 V vs. Li/Li⁺ (or Na/Na⁺) on a Neware battery tester (Shenzhen, China). The specific capacity of Sb/G was calculated based on the total weight of Sb and graphene. Electrochemical impedance spectroscopy (EIS) measurements were performed on a CHI660C electrochemistry workstation after the cells have been charged and discharged for desired cycles. The impedance plots were recorded by applying an ac voltage of 5 mV amplitude in the frequency range from 10 mHz to 100 kHz at de-lithiated states after the cells have been equilibrated at open circuit voltage for 10 h. Cyclic voltammetry (CV) scanning was carried out on an Arbin BT2000 system between 0.005 and 2.0 V vs. Li/Li⁺ (or Na/Na⁺) at various scan rates using three-electrode beaker cells with Li foil (or Na foil) as both the counter and reference electrodes. All of the electrochemical measurements were carried out at room temperature.

3. Results and discussion

Fig. 1a shows the XRD patterns of Sb/G and bare Sb. All the diffraction peaks can be indexed to hexagonal Sb (space group R3m, JCPDS No. 85-1324) for Sb/G and bare Sb. The diffraction peak of graphene that should appear at around 2θ = 25° is absent in Sb/G, suggesting that the restacking of the graphene sheets is restrained by uniformly loading Sb particles in between the graphene sheets. The electrostatic attraction between the positively charged Sb³⁺ ions and the negatively charged graphene oxide [47] in the precursors plays a critical role in uniformly attaching Sb particles on graphene in the final product. The content of graphene in Sb/G is estimated to be 15.9 wt% by carbon content analysis.

The Raman spectra of Sb/G, graphene, and GO are given in Fig. 1b. All the three samples exhibit two bands at 1350 and 1580 cm⁻¹, corresponding to the D line and G Line, respectively, of carbon materials. The G line is due to the E_{2g} phonon of the sp² carbon atoms, and the D line is a breaking mode of κ-point phonons of A_{1g} symmetry [48,49]. Note that both Sb/G and graphene show an increased D/G intensity ratio compared with GO, due to the decreased average size of the sp² domains and the increased number of these domains during the conversion from GO into graphene [50]. It should be noted that the G peak exhibits an

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