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Flexible Bismuth Selenide /Graphene composite paper for lithium-ion batteries

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A B S T R A C T

A flexible Bi_2Se_3/Graphene (BSG) composite paper has been prepared through a simple vacuum filtration method and a thermal reduction together. The BSG composite paper was directly used as anode electrode for lithium-ion batteries, without using any polymer binders or conduction additives. In contrast to the pure Bi_2Se_3, the BSG exhibits high reversible lithium ion storage capacities and superior cyclic capacity retention. It proposed that the superior lithium storage performances would be attributed to the special construction of the as-prepared BSG paper, in which the graphene can not only act as conductive network for electrodes, but also act as a frame to alleviate volume expansion or aggregation of Bi_2Se_3 nanosheets during lithiation/delithiation. The as-prepared BSG paper shows a great potential as an anode materials for flexible Li-ion batteries.

1. Introduction

In recent decades, lithium-ion batteries (LIBs) has been widely applied to portable electronics and electric/hybrid devices because of its high energy density, high rate capability and environmentally friendly properties [1–3]. And with recent advances in the technology of various types of soft portable electronic instrument, there remains a strong market demand for ultra-thin and flexible Li-ion batteries to offer power [4–6]. However, due to the lack of material, which possess electronically superior conductivity, high mechanical flexibility and high electrochemical stability, hence, most materials are inappropriate as a flexible electrodes [7].

Graphene, a one-atom-thick two-dimensional (2D) carbon material, has gained high attention due to its high surface area, structural flexibility and chemical stability [8]. In addition, graphene oxide (GO) paper and graphene paper have been successfully fabricated by filtration of individual GO or graphene sheet [9,10]. What's more, recent program demonstrated that graphene paper have an excellent lithium cycle performance when used as an advanced anode material in LIBs [5,11–13] However, when the graphene paper directly as anode material for Li-ion batteries, the capacities are very poor, although they show a good cycling stability. It indicates that the graphene paper is not suitable for the application as the anode material for Li-ion batteries by itself [14].

Bismuth selenide (Bi_2Se_3), crystallizes in a layered structure, and the Li ion can be inserted into its gaps, making it can applicable in Li-ion batteries [15–17]. For example sheet-like and microrods structure showed discharge capacity of 725.6 and 870 mAh g^{-1} in fist cycle, but the capacity loss rapid [18,19]. In addition, Yang et al. [20] reports Bi_2Se_3 nanosheet and Bi_2Se_3-S_X with a discharge capacity of 123.4 and 235.1 mAh g^{-1} after 30 cycles. Zou et al. [21] and Li et al. [22] synthesis In-Bi_2Se_3 and Bi_2Se_3-S hierarchical nanostructures with a 163.3 mAh g^{-1} after 50 cycles and 109.4 mAh g^{-1} after 100 cycles, respectively. However, owing to the poor cycle performance of Bi_2Se_3, it is unsuitable to practical application as anode Recently, graphene has been used to form composite materials (like SnO_2 [23,24], TiO_2 [25], Si [26] and ect) as electrode materials, and exhibited a better cycling stability because of the hybridizing with graphene which has excellent mechanical strength and elasticity, high surface area, and superior electronic conductivity. So, integrating Bi_2Se_3 with the graphene paper is a practical way to fabricate flexible free-standing Bi_2Se_3/Graphene composite paper, and improve the capacity of Bi_2Se_3 based Li-ion batteries. However, to our best knowledge, there are no reports about Bi_2Se_3/graphene composite paper as anode for Li-ion battery.

In the present work, we have successfully prepared flexible free-standing Bi_2Se_3/Graphene composite paper through a simple vacuum filter method. When directly served as anode electrode for lithium batteries, it delivered a high cycle stability 203 mAh g^{-1} after 100

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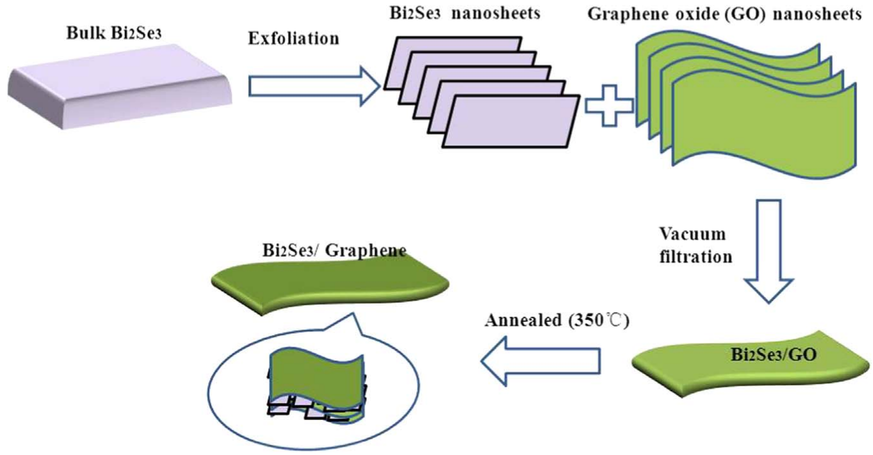

Fig. 1. Schematic illustrations about formation process to prepare BSG composite paper.

cycles. The composite paper showed an excellent electrochemical discharge/charger performance, indicating their potential applications in Li-ion batteries.

2. Experimental section

2.1. Preparation of Bi_2Se_3 nanosheets

Bi_2Se_3 nanosheets were prepared by a hydrothermal exfoliation method based on our previous work [27,28]. In a typical procedure, 0.23 g Bi_2Se_3 and 0.2 g LiOH was added into 30 ml ethylene glycol, after that the mixture was constantly stirred about 1 h. Then the solution was transferred into a 50 ml Teflon-lined autoclave under 200 °C for 24 h. The resulting products were collected after washing with acetone and deionized water for several times, then dried in vacuum.

2.2. Preparation of Bi_2Se_3/Graphene composite paper

Graphene oxide (GO) was synthesized from purified natural graphite by using modified Hummers method [29]. Here, we adopted a simple vacuum filtration and thermal reduction method to obtain a flexibility Bi_2Se_3/Graphene (BSG) composite paper. In detail 10 mg GO was dispersed into 10 ml Bi_2Se_3 (1 mg ml^{-1}) aqueous suspension, then ultrasonic for more than one hour to form a uniform Bi_2Se_3/GO suspension solution. Then the solution by vacuum filtered to get a thin of self-supporting Bi_2Se_3/GO composite paper. The paper was dried in air and peeled off from the filter membrane and subsequently reduced at 350 °C for 3 h [30]. GO reduced turn to graphene after the annealing process, and Bi_2Se_3/Graphene (BSG) nanocomposite have been gained. In order to get the optimal sample, different mass ratio between graphene and Bi_2Se_3 nanosheets had been prepared. The BSG paper with graphene to Bi_2Se_3 mass ratio of 1/2, 1/1 and 2/1 are noted as BSG12, BSG11 and BSG21, respectively.

2.3. Materials characterizations

Raman spectrum which was collected by using the Renishaw InVia system with a laser operating at λ=532 nm. The morphologies of as-prepared samples were characterized by using scanning electron microscope (SEM, VEGA3 SBH, Tescan).

2.4. Electrochemical measurements

Electrochemical measurements of the samples were performed by fabricating CR2025 coin cells in an argon-filled glove box. Pure lithium foil was used as the counter electrode and reference electrode, the BSG composite paper was cut into a suitable size and used as a working electrode. By comparison, the Bi_2Se_3 nanosheets electrode was prepared by dissolving the samples, carbon black, and poly (vinylidence difluoride) (PVDF) in N-methy-2-pyrrolidinone (NMP) with a weight ratio of 80:10:10 and spreading the slurry on pure copper foil (99.6%). After dried in a vacuum at 120 °C for 12 h, the copper foil cut into circular strips, and finally pressed under the pressure of 10 MPa. The electrolyte was 1 mol L^{-1} of $LiPF_6$ solution in dimethyl carbonate (DMC) and ethylene carbonate (EC) with a volume ratio of 1: 1. Galvanstatic charging and discharging were conducted based on a multichannel (NEWARE BTS-610) battery tester between 0.001 and 3.000 V at a current density of 50 mAg^{-1}. Cyclic voltammogram (CV) measurements were performed on an electrochemical workstation (CHI660E) with a voltage range from 0.001 to 3.000 V at a scan rate of 0.1 mV s^{-1}. And the electrochemical impedance spectroscopy was also tested by electrochemical workstation, with the frequency range from 0.01 to 100 kHz.

3. Results and discussion

The details of synthesis procedure are described in Fig. 1. Firstly, the GO dispersed into Bi_2Se_3 aqueous solution by sufficient ultrasound to obtain a stable dark brown suspension. Secondly, the composite suspension was filtered through an Anodisc membrane filter (47 mm diameter, 0.2 µm pore size, Whatman). Finally, the composite paper was peeled off from the filter membrane and then anneal.

Fig. 2(a) shows the photographs of as-prepared BSG paper, it is clear that the composite paper was flexible and free-standing, it can be cut into an appropriate shape for electrochemical testing. Fig. 2(b) is the corresponding high resolution SEM images of Bi_2Se_3 nanosheets after exfoliation. Through the image we find the size of nanosheets is about 0.5 ~2 µm and the thickness less than 50 nm. Fig. 2(c) and (d) show the cross-section SEM images of BSG paper. Form Fig. 2(c), we can obviously observed that the fracture of the paper exhibits a layered structure through the entire cross-section. In addition Bi_2Se_3 nanosheets are well distributed between graphene layers as showed in Fig. 2(d). Owing to this unique layered composite structure, the Bi_2Se_3 can effectively prevent the graphene sheets stacking, simultaneously, graphene can work as a buffer to prevent Bi_2Se_3 volume expansion during the Li^+ insertion/extraction process [31].

Raman spectrum was employed to confirm the composition of the BSG. Fig. 3 exhibits the Raman spectrum of pure Bi_2Se_3, precursor GO, and as-prepared BSG, respectively. The Raman spectrum of pure Bi_2Se_3 has three characteristic peaks (72, 131 and 173 cm^{-1}), in which the peak at 72 and 173 cm^{-1} correspond to A_{1g}^{1} and A_{1g}^{2} mode, while the peak at 131 cm^{-1} can be assigned to the E_g^2 mode [32,33] These modes were also observed in the Raman spectrum of as-prepared BSG.