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One-pot environment-friendly synthesis of boron doped graphene-SnO_2 for anodic performance in Li ion battery

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High specific capacity, availability of tin oxide (SnO_2) and improved electrical conductivity and rate capability of boron-doped graphene sheets (*BG*) promises the composite of the two as a potential anode material for Li ion battery. We report for the first time, one-pot synthesis of SnO_2 dispersed boron-doped few layer graphene (SnO_2/*BG*-I) in an environment friendly, hazardous-harmful reducing agent free, hydrogen assisted reduction technique in comparison to complicated two-step conventional process. In addition, a two-step, wet chemical free, greener approach is also employed to achieve SnO_2 nanoparticles over *BG* support (SnO_2/*BG*-II). Both the materials as anode showed enhanced performance compared to un-doped graphene supported SnO_2 nanoparticles (SnO_2/G). One-pot synthesized SnO_2/*BG*-I as anode in Li ion battery shows comparable performance with a reversible capacity of 348 mAh g^{-1} at a current density 200 mA g^{-1}, while SnO_2/*BG*-II with higher amount of boron doping, exhibits higher stability over cycles with an excellent reversible capacity of 558 mAh g^{-1} due to the uniform distribution of SnO_2 over boron-doped graphene sheets.

1. Introduction

Li ion battery (LIB) is one of the most widely used rechargeable devices in portable electronics as well as hybrid vehicles for its advantages such as light weight, high energy density and long cycle life. Low theoretical capacity (372 mAh g^{-1}) of graphite restricts the LIB performance by reducing the ability of providing higher energy and power density despite of its commercial realization as the anode material. The challenge to the battery community is to develop an anode material with high capacity and cyclic stability at lesser cost [1,2]. Various nanostructures of metals, metal oxides, and alloys have been used for a long time now, as the anode material for LIB with enhanced performance but problems like swelling during intercalation/de-intercalation leading to low stability and short cycle life still exists [3–5]. SnO_2 is one of the most preferred anode materials due to its environmental benignity, availability in nature at low price, and higher theoretical capacity (781 mAh g^{-1}). However, ~300% volume change of tin particles [6,7] over lithiation/delithiation process results in cracking and pulverization, ensuing electrical contact loss between the conducting additive/active material/current collector foil. Fragmented nanoparticles also do have probability of traveling through the separator to the cathode side, leading to self-discharge or aggregate to form thick solid-electrolyte interphase (SEI) deposit by draining the electrolyte [8], further degrading the anodic performance over cycles. Conducting carbon nanomaterials such as carbon nanotubes [9], graphene [10,11] has been reported to be engaged as the passive element in the SnO_2 electrode, improving the cycle life and capacity by counter balancing the semiconducting nature of the nano-structured metal oxides. The carbon support also controls the SEI layer formation by preventing nanoparticle agglomeration and volume change [12] over cycles. Two-dimensional flexible structure of graphene is interesting in this aspect because of its high surface area, porosity, electrical conductivity and chemical inertness compared to carbon nanotubes [13]. Heteroatom doping into graphene is reported to enhance its electronic property as well as Li storage property [14,15]. Tin oxide nanoparticles decorated over nitrogen-doped carbon has been investigated thoroughly [16], however their synthesis process are quite complicated with less yield. Boron-doped graphene have been reported to show improved anodic performance with higher rate capability and stability compared to few layer pristine graphene [14,17]. Liu et al.

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showed 2D core-shell structure with carbon coating shell for boron-doped SnO_2/graphene as a high performance anode material for Li ion battery [18]. However, the investigated material was synthesized in a multistep, long time consuming process of glycol reduction, hydrothermal and thermal treatment. Using phenylboronic acid or boric acid as dopant precursor, achieved boron doping level in the carbon backbone of the composites were 4% and 3% respectively. In here, wet chemical free, simple, environment friendly, hydrogen assisted reduction method has been used to construct 2D composite with tin oxide nanoparticles as spacers, incorporated in between boron-doped graphene layers in very less time and minimum number of steps. Two different routes of synthesis were employed for obtaining the rationally intended structure of tin oxide decorated boron-doped graphene (SnO_2/*B*G) from equal amount and same set of precursors. SnO_2/*B*G-I was synthesized for the first time, in a novel, one-pot technique, where boron doping (2.2%) and dispersion of nanoparticles takes place in a single process. For the other method, doped (7.1%) -graphene support synthesis in first step and subsequent nanoparticles dispersion over the support in the second, leads to the realization of SnO_2/*B*G-II. SnO_2/*B*G-I and SnO_2/*B*G-II both are employed as anode material for LIB. The combining effect of boron doping and nanostructure of SnO_2 is studied on the respective anodic electrochemical performances.

2. Experimental

2.1. Material synthesis

Tin oxide nanoparticles decorated over boron-doped graphene sheets were achieved in two distinct ways. SnO_2/*B*G-I and SnO_2/*B*G-II, both the materials used same set of precursors in equal amount for synthesis. Graphite oxide (GO), boric acid (H_3BO_3) and tin chloride dihydrate ($SnCl_2$, $2H_2O$) were used as the source of graphene sheets, boron and tin respectively. GO was prepared from graphite powder (Sigma Aldrich, < 45 μm), using modified Hummers' method [19]. Boric acid and tin chloride dihydrate were used as received without any further treatment. Toxic and wet chemical free, hydrogen assisted reduction technique was used in both the processes for achieving the desired material.

Nanoparticles decoration over graphene sheets together with boron doping into the carbon framework takes place in a single process for SnO_2/*B*G-I. For this, graphite oxide was mixed with boric acid in a mass ratio of 2:1. Tin chloride dihydrate, in calculated amount was mixed together with the earlier composition. The uniform mixture was then sprinkled over a quartz boat and placed inside a quartz tube, having provision of controlled temperature and gas flow. Argon gas was flushed for the first 15 min at room temperature and hydrogen (99.99%) gas was allowed at elevated temperature of 250 °C for 30 min. H_2 flow was stopped and the temperature was increased to 700 °C for additional 30 min in Ar atmosphere. Heating was switched off and the material inside was furnace cooled to room temperature in Ar atmosphere. The as-synthesized sample was collected from the furnace and treated to remove B_2O_3 [14], the unwanted by-product of boric acid. The sample was further heat treated at 200 °C in air atmosphere to get oxygen-deficiency free crystalline phase of SnO_2. This final product was labeled as tin oxide decorated boron-doped graphene-I (SnO_2/*B*G-I).

SnO_2/*B*G-II was prepared in customary two-step process. Firstly, boron-doped graphene sheets (*B*G) were achieved in an environment friendly method, as reported by us earlier [14]. Tin precursor was mixed with *B*G sheets in calculated amount to get the desired loading and placed in a tubular furnace as earlier. After the initial Ar flushing of 15 min in room temperature, furnace temperature was increased to 250 °C in hydrogen atmosphere for 30 min. Heating was then turned off and furnace was allowed to cool down in Ar flow. The inside material was collected and air-treated at 200 °C. The final product was labeled as tin oxide decorated boron-doped graphene-II (SnO_2/*B*G-II). Decoration of SnO_2 nanoparticles over un-doped graphene support was achieved in the similar process of earlier second step of SnO_2 dispersion over *B*G support. Calculated amount of graphite oxide, instead of *B*G was mixed with $SnCl_2$, $2H_2O$ to acquire the precursor assembly for final product of SnO_2/G.

2.2. Physical characterizations

The X-ray diffraction (XRD) measurements were carried out in a PANalytical X'Pert Pro X-ray diffractometer with nickel filtered Cu-K_α radiation as the X-ray source in the 2θ range of 5° − 90° with a step size of 0.016°, to check the phase of the synthesized materials. X-ray photoelectron spectroscopy (XPS) study was performed to explore the level of boron doping and tin oxide phases in the hybrid composite, using SPECS instrument with Mg-K_α as the X-ray source and PHOIBOS 100MCD as the analyzer at ultrahigh vacuum (10^{-10} mbar). The powder sample was uniformly bedecked over one side adhesive carbon tape for the XPS studies. The obtained data were deconvoluted using CasaXPS software with Shirley background correction. LabRAM HP 800 UV Raman spectrometer was used to study the vibrational modes of the samples with 632 nm, He-Ne laser as excitation source in the range of 1000–2000 cm^{-1}. Thermogravimetric analysis was carried out in a SDTQ600 (TA instruments) in zero air atmosphere from room temperature (30 °C) to 1000 °C. The elemental mapping of the sample was characterized by INSPECT F. Transmission electron microscope (FEI Technai G^2 20 STWIN, 200 keV) was used to get the detailed morphology of the materials. The TEM samples were prepared by drop-casting few drops of the ethanol-dispersed material over 200-mesh gold coated copper grid.

2.3. Electrochemical characterization

The working electrode slurry was prepared by mixing active material (SnO_2/*B*G-I or SnO_2/*B*G-II) in a ratio of 75:15:10 with polyvinylidene fluoride (PVDF) binder and conductive graphite (MTI corporation, USA < 5 μm) in N-methyl-2-pyrrolidinone solvent. The slurry was coated uniformly on copper foil using doctor blade technique and dried at 120 °C in vacuum oven for 6 h. 12 mm diameter disk was cut from this dried composite to proceed as anode. CR2032 type coin cell in half-cell configuration with lithium metal as the counter electrode, Celgard 2400 membrane as separator, standard $LiPF_6$ (1 M) dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1: 1 v/v) as the electrolyte and the coated coin as anode were assembled in a high pure argon (>99.999%) filled glove box (mBRAUN, Unilab; H_2O and O_2 < 1 ppm) for the electrochemical measurements. Galvanostatic charge–discharge measurements were carried out at room temperature using a Solartron electrochemical workstation between 3 V and 0.01 V at various current densities. The electrochemical ac impedance spectra were obtained by applying a sine wave with amplitude of 5 mV over the frequency range from 100000 Hz to 0.01 Hz in an Autolab PGSTAT302 instrument with NOVA software.

3. Results and discussion

Schematic illustration of Fig. 1 shows the difference in the synthesis process for SnO_2/*B*G-I and SnO_2/*B*G-II. Tin oxide decorated on boron-doped graphene in the one-pot synthesis process has been obtained through direct 1a to 1c pathway. To the best of