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Research paper

Graphene-wrapped Porous Sb Anodes for Sodium-Ion Batteries by Mechanochemical Compositing and Metallomechanical Reduction of Sb_2O_3

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ABSTRACT

Antimony metal nanoparticles wrapped with a-few-layer graphene coat (Sb@Gn) were fabricated from their oxide form (Sb_2O_3) in a micrometer dimension using a novel two-step ball-milling process. The first mechanochemical process was designed to decrease the particle size of Sb_2O_3 microparticles for ensuring advantages of nano size and to subsequently coat the Sb_2O_3 nanoparticles with a-few-layer graphene (Sb_2O_3@Gn). The second metallomechanical ball-milling process reduced the oxide to its metal form (Sb@Gn) by the help of Zn as a metallic reductant. The graphene layer (@Gn) blocked the alloying reaction between Sb and Zn, limiting the size of Sb particles during the metallomechanical reduction step. During reduction, oxygen species were transferred from of Sb_2O_3 through @Gn to Zn along redox transfer pathways rather than direct mass transfer via unsaturated vacancies in the @Gn. the redox transfer involving oxidation of @Gn by O^{2-} is plausible routes for O^{2-} transfer in the metallomechanical reduction. The Sb@Gn anode exhibited outstanding capacity retention along charge/discharge cycles and improved rate capability in sodium-ion batteries. The @Gn provided conductive pathways to the Sb core and limited size expansion during sodium-lithium alloying.

1. Introduction

Metal elements have multiple oxidized states. Atmospheric oxygen (O_2) and moisture (H_2O) easily oxidize metals. Therefore, the oxidized states of metals are thermodynamically stable so that the oxides are abundant in deposits. The reduction of oxides to metals has been the most important and a challenging process to human beings. One of the most popular reduction processes is based on using hydrogen gas as a reducing agent at high temperature [1]. Metallothermic reduction processes were implemented as a risk-free alternative to the hydrogen process. As suggested by the nomenclature, easily oxidizable metals at extremely negative reduction potentials (e.g., Mg, Al, Ca and Zn) are used as reducing agents in the metallothermic processes. Recently, this method was used to obtain high-capacity metal anode materials for lithium ion batteries (e.g., Si and Ge) from their oxide sources [2–6]. Metallothermic reduction processes involve significant challenges even if they benefit from high efficiency and scale-up feasibility: (1) metal alloy formation between the metal of interest and the metal reducing agent, (2) metal particle aggregation and crystal growth encouraged by high-temperature operational conditions and (3) energy costs to maintain the high reaction temperature. In this work, we present a novel reduction method based on the metallomechanical reduction by using high energy ball milling with a metal reducing agent [7,8]. The advantage of the metallomechanical reduction over its thermal counterpart (the metallothermic reduction) is that additional energy input is not required to maintain high operational temperature [9]. Additionally, metal alloy formation and particle aggregation are prevented during the metallomechanical reduction process by implementing the pre-step to wrap each oxide particle with a-few-layer graphene layers [10].

Recently, sodium-ion batteries (SIBs) have been touted as a promising candidate for next-generation energy storages to replace lithium-ion batteries (LIBs) since sodium is non-toxic, cost-effective and abundant when compared with lithium [11–13]. However, the implementation of SIBs is limited yet. Graphite, the most popular anode material for LIBs, is sodiated at ~35 mAh g^{-1},

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which is significantly lower than the lithiation capacity (372 mAh g^{-1}). The inferior sodiation capacity of graphite is attributed to the radius of Na^+ (0.102 nm) that exceeds that of Li^+ (0.076 nm) [14–16]. It is difficult to intercalate larger-sized Na^+ into the interlayer space of graphite. Metals that are alloyed with sodium have been selected as alternatives to intercalation materials, including tin, antimony and bismuth [12,17–19]. Antimony (Sb) is characterized by unique puckered-layer structures having a low stacking density at 39%. It exhibits high theoretical capacity of 660 mAh g^{-1} and 1890 mAh cm^{-3} at 0.7 to 0.8 $V_{Na/Na+}$ for sodiation [16,18,20]. However, the high capacity inevitably leads to a large theoretical volume expansion of > 390% during sodiation. The volume change results in particle pulverization, electrode fracture and electrolyte decomposition on freshly exposed Sb surface, leading to capacity decay [16,21–23]. Various strategies have been developed, including surface modification (carbon or metal oxide coating; hybridized with carbon materials), nanostructural design (1D, 2D and 3D nanostructures) and alloying with other metals (Sn-Sb and Bi-Sb) [24–35].

Herein, we had Sb nanoparticles coated by an a-few-layer graphene via a two-step process: (1) the mechanochemical coating of graphene on Sb_2O_3 (producing Sb_2O_3@Gn) and (2) the metallomechanical reduction of Sb_2O_3 to Sb metal (producing *m*-Sb@Gn where *m* indicates metallomechanical). Both steps were performed in the same ball mill to grind precursors including Sb_2O_3, graphite and zinc metal by high energy (Scheme 1). The kinetic energy of moving stainless steel balls was transferred to the reactants in the high-energy ball milling. As control, the Sb_2O_3@Gn prepared from the first step was metallothermically reduced to Sb@Gn (denoted as *t*-Sb@Gn where *t* indicates metallothermic) by vaporized Zn reductants using the same Zn powder at 450 °C for 3 h.

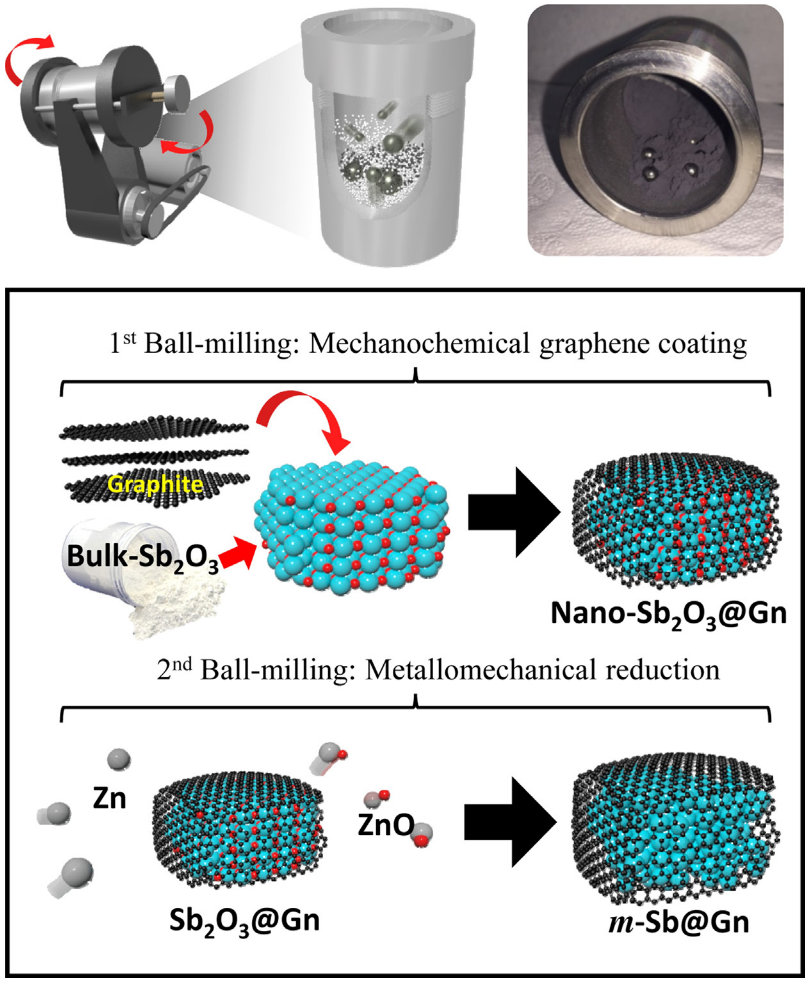
2. Experimental Section

2.1. Sb_2O_3@Gn synthesis

A mixture of 1 g Sb_2O_3 (99.9%, Sigma Aldrich) and 0.1 g graphite (KS6, Timcal) were introduced to a stainless-steel vial with and 6 stainless steel balls (diameter in 4 mm). Then, the vial was filled with argon gas. The mixture was ball-milled by using a high-energy ball miller (SPEX 8000D) for 6 h.

2.2. m-Sb@Gn synthesis

A mixture of the as-synthesized Sb_2O_3@Gn and zinc powder (99.9%, Alfa Aesar) (2:3 in mol) was ball-milled in the same way used for synthesizing Sb_2O_3@Gn for 3 h. The resultant product was stirred in a 1 M HCl solution at 30 °C for 1 h to remove the ZnO by-products. Subsequently, the solution was filtered by vacuum and



Scheme 1. High-energy ball milling used for *m*-Sb@Gn synthesis. Two-step synthesis process of mechanochemical graphene (Gn) coating followed by metallomechanical reduction of Sb_2O_3 to Sb metal. Specifically, Zn is converted to ZnO in the second step, and this reduces Sb_2O_3 to Sb metal. Furthermore, Sb_2O_3@Gn and Sb@Gn indicate graphene-wrapped Sb_2O_3 and Sb, respectively.