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Construction of Zn_2GeO_4/Graphene Nanostructures with Dually-Protected Functional Nanoframes for Enhanced Lithium-Storage Performances

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ABSTRACT

Application products moving from small-sized devices to large-scale energy storage systems have pushed the development of lithium-ion batteries towards high-energy densities, high-power densities, and long cycle life. Germanium-based anode materials with high theoretical capacities are expected as promising anode candidates to fulfill those requirements, but suffer from the huge volume expansion upon lithiation, leading to serious material pulverization and capacity fading. Herein, a convenient and cost-effective strategy was conceived focusing on construction of dually-protected Zn_2GeO_4/graphene composites. The rationally designed composite was composed of hollowed Zn_2GeO_4 nanostructures and flexible graphene layers, which acted as two functional nanoframes to synergistically alleviate the volume change during lithiation/delithiation. As a result, the Zn_2GeO_4/graphene composite exhibited high specific capacities, excellent cycling stability and desirable rate capability. Specifically, the Zn_2GeO_4/graphene composite electrode delivered specific capacity of 702 mA h g^{-1} at 300 mA g^{-1} after 600 cycles with capacity retention of 85%. In addition, a high reversible capacity of 600 mA h g^{-1} was retained over 1000 cycles at a high current density of 800 mA g^{-1}. Those achieved-results suggested that rational design of electrode nanostructures offers an effective insight for obtaining high-performance batteries.

1. Introduction

Lithium-ion batteries (LIBs) with high-energy densities, high-power densities, and long cycle life are required for next-generation electric-energy storage systems, such as automobile industry, electric vehicles (EVs) and large-scale stationary electric energy applications [1,2]. However, the current commercial graphite electrode with limited capacity (~372 mA h g^{-1}) and poor rate capability is unable to satisfy the ever-increasing energy requirements. Thus, it is highly desirable to explore novel electrode materials to improve those hampers of LIBs. Recently, Germanium (Ge) as a promising alternative anode candidate has attracted much attention due to its intrinsic merits such as high theoretical specific capacity (1600 mA h g^{-1}), excellent electrical conductivity (100 times greater than Si) and ion diffusivity (400 times faster than Si) [3]. Nevertheless, the rare storage capacity and exorbitant price of Ge set the obstacles in industrial applications. Fabricating Ge-based ternary oxides with cheaper metal elements (Zn, Ca, Ba, etc.) is regarded as an efficient strategy to solve the problem. Considering theoretical specific capacity and reactivity of Ge-based ternary oxides during discharge-charge process, one of the most advisable choices for cheaper metal elements is Zn (theoretical specific capacity of ZnO: 978 mA h g^{-1}). Ge only accounts for 27 wt % in Zn_2GeO_4, effectively leading to the lower overall cost [4,5].

Although the Zn_2GeO_4 anode material showed these favorable properties over the commercial carbon materials, the practical applications of Zn_2GeO_4 are hindered by several critical obstacles such as severe pulverization and capacity fading, which are mainly caused by dramatic volume variation (~300%) during insertion/extraction of lithium-ions [6]. To address these challenges, nanostructured Zn_2GeO_4 such as nanowires, nanorods, and

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nanosheets have been synthesized which were demonstrated to accommodate the volume changes effectively [7–9]. Particularly, hollow nanostructures can not only accommodate the volume strain (huge hollow interior), but also shorten the diffusion paths of Li ions [10,11]. These nanostructured materials were shown to have enhanced specific capacity and cycle stability. However, the efficacy of mono-nanostructured electrode is finite to satisfy the demands of long-time cycling stability and high-rate capability for high-performance LIBs. In previous study, the incorporation of buffer phases like carbonaceous materials, C_3N_4, et al. into metal oxide electrodes could further increase the specific capacity and improve the cycling stability [12,13]. Those obtained nanocomposites consisting of multiple functional frameworks exhibited synergistic enhancement in conquering the shortcomings of poor mechanical stability and electrical conductivity. Inspired by this idea, combining hollowed Zn_2GeO_4 nanostructure and versatile graphene into composite is expected to endow Zn_2GeO_4 electrode with remarkable cycle life and cycle stability.

Herein, we reported a a convenient and efficient approach to scalable synthesis of Zn_2GeO_4/graphene composite. The dually-protected frameworks of hollowed Zn_2GeO_4 and flexible graphene layers exhibited excellent synergistic effect for alleviating the huge volume expansion upon insertion/extraction of Li ions. As expected, the Zn_2GeO_4/graphene composites rendered high specific capacity, excellent rate capability and long-term cycle stability. This synthesis conception interpreted that the 3D framework comprising multiple functional structures is beneficial for accommodating volume change upon lithiation/delithiation.

2. Experimental section

2.1. Preparation of hollow Zn_2GeO_4 nanostructures

All chemicals were commercial products with analytical grade without further purification. First, Na_2GeO_3 powder was prepared by a solid state reaction using Na_2CO_3 and GeO_2 at 900 °C for 12 h. Second, for synthesis of hollow Zn_2GeO_4 nanostructures, 83 mg Na_2GeO_3 and 219 mg $Zn(CH_3COO)_2$ were added into 20 ml DI water, respectively. After that, the mixture was stirred for 2 h and then transferred to a Teflon-lined autoclave. The hydrothermal synthesis was performed at 180 °C for 3 h, followed by natural cooling to room temperature. Then, the mixture was washed thoroughly by ethanol and DI water and dried in an oven at 80 °C.

2.2. Preparation of Zn_2GeO_4/Graphene Composites

Graphene oxide (GO) sheets were synthesized using a modified Hummer's method[14]. Zn_2GeO_4/graphene composites were constructed by freeze-drying technique and subsequent thermal reduction. The as-obtained Zn_2GeO_4 and graphene oxide (GO) were dispersed in 20 mL of tertiary-butanol solution (the mass ratio of Zn_2GeO_4 and GO were 4:1). Then the mixture was fully stirred and ultrasonic vibrated for 3 h. After that, the homogeneous mixture was quickly transferred into a freezer (−50 °C). After 10 minutes, the frozen Zn_2GeO_4/GO/tertiary butanol mixture was transferred into a vacuum drying oven (−50 °C, 0 Atm) and kept for 24 h to remove vapor and tertiary butanol solution. Finally, the dried Zn_2GeO_4/GO composites were calcined at 400 °C for 3 h under an argon atmosphere to obtain Zn_2GeO_4 and thermally reduced graphene composites.

2.3. Material Characterization

To determine the structure of the as-calcined products, powder X-ray diffraction (XRD) measurements were carried out on a Rigaku D8 advance X-ray diffraction-meter with Cu *Kα* radiation ($\lambda = 1.5418$ Å). The morphology analysis was characterized by scanning electron microscopy (SEM, LEO-1530, Oberkochen, Germany) and transmission electron microscope (TEM, JEM-2100F). Raman scattering was excited using the 633 nm radiation from He-Ne laser and was collected by a micro-Raman spectrometer in the $100 \sim 2000\ cm^{-1}$ range at room temperature. The X-ray photoelectron spectroscopy (XPS) was carried out on a PHI quantera scanning X-ray microprobe instrument employing monochromatic Al-Kα radiation as the excitation source.

2.4. Electrochemical Measurements

Electrodes were prepared by mixing active materials (70 wt %), acetylene black (20 wt %), and polyvinylidene difluoride (PVDF) binder (10 wt %). Then, the obtained slurry was smeared onto a copper foil and dried in a vacuum drying oven at 80 °C for 24 h to

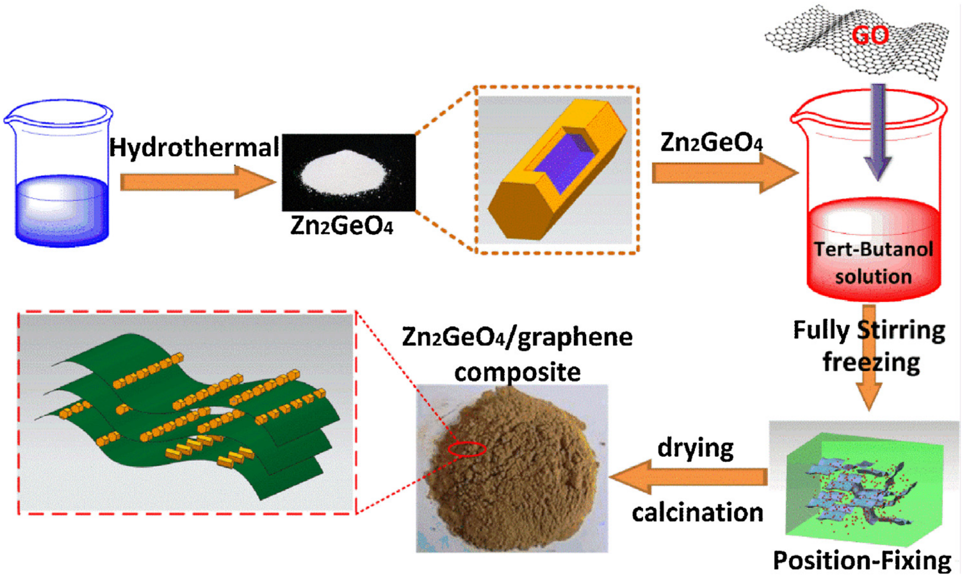

Fig. 1. Schematic illustration of the preparation of the Zn_2GeO_4/graphene composites.