Hydrothermal growth of Cobalt germanate/reduced graphene oxide nanocomposite as superior anode materials for Lithium-ion batteries

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ABSTRACT

Well dispersed Co_2GeO_4 (CGO) nanoplates and CGO/reduced graphene oxide (RGO) nanocomposites are prepared via hydrothermal method and characterized as novel lithium anode materials for the first time. Electrochemical measurements demonstrate that the CGO/RGO nanocomposites exhibit a large reversible capacity of 1250 mAh g^{-1} for the first cycle and a capacity retention of 1085 mAh g^{-1} after 100 cycles. Remarkable rate performance was also recorded. The superior electrochemical performance of the CGO/RGO nanocomposites electrode compared to the pure CGO electrode can be attributed to the well dispersed RGO which enhances the electronic conductivity and accommodate the volume change during the conversion reactions.

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1. Introduction

Lithium-ion batteries (LIBs) have been studied as one of the most promising energy storage devices because of their high theoretical capacity, high safety and low cost [1–3]. Much work has been done towards the exploration of different types of anode materials with high reversible capacity and long cycle life, nanotechnology is one of the key approaches to realize novel electrode materials with high electrochemical performance [4–6].

Germanium (Ge), as the anode material of LIBs, has a high theoretical capacity of 1600mAh g^{-1} by forming $Li_{2.2}Ge_5$ alloy and good electronic conductivity. Therefore Ge and Ge compounds may be promising candidates for the applications as anodes materials for LIBs [7–10]. However, pure Ge suffers from a serious capacity fading and the aggregation of Ge metal particles during lithium alloying and de-alloying process [11–13]. As a family of important functional materials, transition metal germanates have attracted attention as they have potential applications in catalysis, adsorption, ion exchange, humidity sensors and high energy laser systems [14–16]. Beyond that, transition metal germanates have also been proved to be promising anode materials for lithium ion batteries [17–23]. For example, Seung et al. [17] first discovered that transition metal oxide inclusion could improve the coulombic efficiency and capacity of GeO_2 by facilitating Ge re-oxidation to GeO_2. Yi et al. [18] carried out the synthesis of amorphous and crystalline Zn_2GeO_4 nanocrystals by an ion-exchange route, which exhibit a high reversible specific capacity and excellent rate capability. However, the huge volume change during the conversion reactions and the semiconductor character of germanates are believed to limits the cycling and rate ability [17].

Reduced graphene oxide (RGO) is well known due to its special 2D structure, superior electronic conductivity and large activated surface area. By compositing with RGO, the electrochemical performance of anode materials could be greatly enhanced [24–30]. As reported by Qiu the TiO_2-RGO nanocomposite possesses more stable cyclic performance, larger reversible capacity, and better rate capability, compared with that of the pure TiO_2 and TiO_2-GO samples [27]. The RGO serves not only as a conductive agent, but also as an inactive confining buffer to accommodate the volume change during charge/discharge cycling [28–30].

As far as we know, there is no report on CGO/RGO nanocomposites as an anode material for LIBs. In the present work, CGO/RGO nanocomposites were first constructed via hydrothermal method and tested as anode material of LIBs in comparison with pure CGO nanoplates. The CGO/RGO nanocomposites electrode showed higher specific capacity and improved capacity retention.

2. Experimental

2.1. Synthesis of graphene oxide, CGO nanoplates and CGO/RGO nanocomposites

All the concerned reagents were of analytic grade and used without further purification. The graphene oxide (GO) was synthesized from natural flake graphite power through a modified Hummers method [17]. CGO nanoplates: 2 mmol cetyltrimethylammonium bromide (CTAB), 1 mmol GeO_2 and 2 mmol $CoCl_2 \cdot 6 H_2O$ was dispersed in 70 ml distilled water and stirred for 30 min, the pH value of the resulting mixture was adjusted to 9 by adding ammonium hydroxide (28 wt%). Then, the mixture was transferred into a stainless steel autoclave with a Teflon liner of 100 mL capacity and heated in an oven at 160 °C for 24 h, followed by cooling to room temperature. CGO/RGO nanocomposites: 40 mg graphene oxide was ultrasonicated into 40 ml deionized water to form suspension A. 2 mmol CTAB, 1 mmol GeO_2 and 2 mmol $CoCl_2 \cdot 6H_2O$ was dispersed into 40 mL ethylene glycol (EG)-water (1:1 V/V) under continuous magnetic stirring for 30 min to form solution B. Then suspension A and solution B were mixed together under stirring, and the pH value of the resulting mixture was adjusted to 9 by adding ammonium hydroxide (28 wt%), then transferred to a 100 mL Teflon-sealed autoclave and maintained at 160 °C for 24 h, followed by cooling to room temperature. The obtained precipitation was separated by filtration, and washed with distilled water and ethanol for several times. Finally, the CGO nanoplates and CGO/RGO nanocomposites were obtained by annealing the precipitation at a ramp rate of 5 °C min^{-1} and holding at temperatures of 400 °C for 6 h under vacuum condition. The preparation procedure of CGO/RGO nanocomposites is illustrated in Scheme 1.

2.2. Sample characterization

The structure of samples were characterized with XRD patterns were collected by a Rigaku Dmaxrc diffractometer with Ni filtered Cu Ka radiation (V = 50 kV, I = 100 mA) at a scanning rate of 5 degree/min. Transmission electron microscopy (TEM, JEOL JEM-2100) and Zeiss SUPRA 55 for SEM. The morphology of the product was examined by a JEOL JEM-2100 TEM. The thermogravimetric analysis (TG) was performed on a PerkinElmer TGA-7 Thermo Analyzer under air flow at a rate of 5 °C min^{-1}, Raman spectra were recorded by a NEXUS 670 FT-IR Raman spectrometer with an excitation wavelength of 632 nm.

The electrochemical experiments were performed using 2016 coin cells. To prepare the working electrode, 70 wt% of the active material (CGO and CGO/RGO nanocomposites), 20 wt%
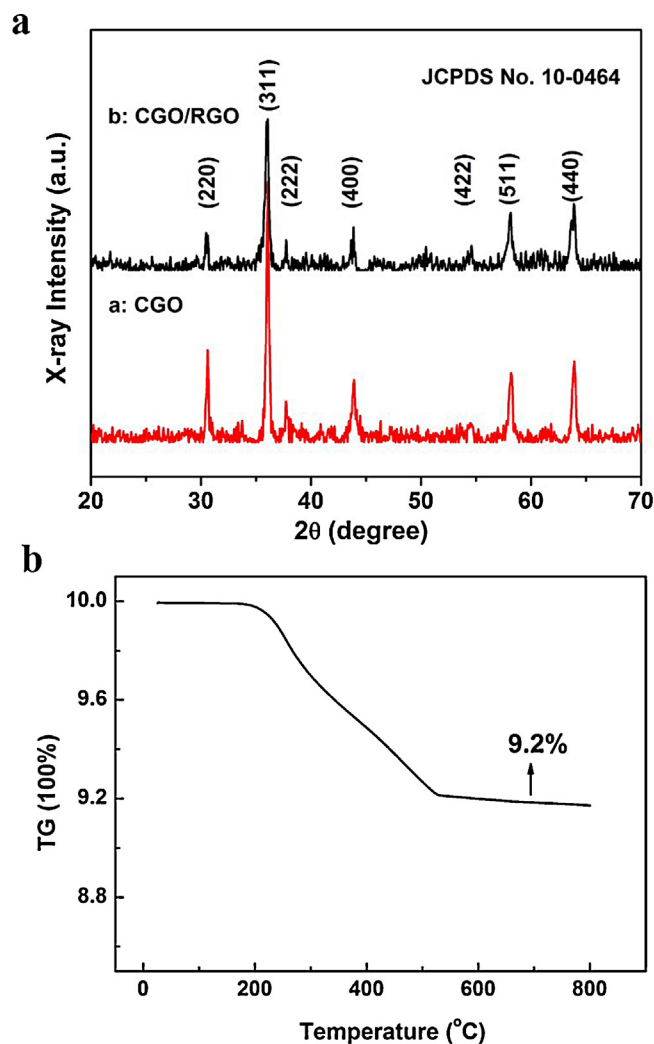
Fig. 1. (a) XRD patterns of as-synthesized CGO nanoplates and CGO/RGO nanocomposites. (b) TGA curve of CGO/RGO nanocomposites.

carbon black and 10 wt% carboxy methyl cellulose sodium (CMC) dissolved uniformly in distilled water were mixed to form a slurry. The resulting paste was cast on a Cu foil substrate and dried in a vacuum oven at 90 °C for 24 h to form the electrodes. Li foil was used as counter electrode, and Celgard 2400 as separator. The electrolyte was 1 M $LiPF_6$ dissolved in a 1:1:1 mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate with 5%
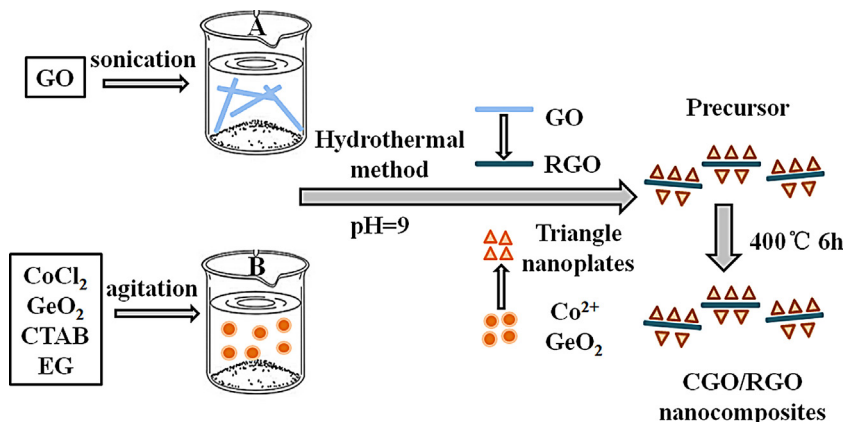
Scheme 1. Schematic drawing of the preparation process of CGO/RGO nanocomposites.