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Novel synthesis of Zn_2GeO_4/graphene nanocomposite for enhanced electrochemical hydrogen storage performance

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For the first time, a novel technique of preparing Zn_2GeO_4 nanostructures has been developed by using chemical precipitation method of $GeCl_4$ as a Ge precursor and acacen as a capping agent. Uniform and fine Zn_2GeO_4 nanoparticle was synthesized. The optimized Zn_2GeO_4 nanostructures anchored onto graphene sheets and Zn_2GeO_4/graphene nanocomposite synthesized through pre-graphenization, successfully. Hydrogen storage capacities of Zn_2GeO_4 nanoparticle and Zn_2GeO_4/graphene nanocomposite were compared, for the first time. Obtained results represent that Zn_2GeO_4/graphene nanocomposites have higher electrochemical hydrogen storage capacity than Zn_2GeO_4 nanoparticles. It was found that the synergistic effect between Zn_2GeO_4 nanoparticles and graphene sheets can improve the electrochemical performance of this hybrid composite electrode. After 29 cycles, the discharging capacities of the electrode reached to 2695 mAh/g. These results indicate that the Zn_2GeO_4/graphene nanocomposite can be potentially applied for electrochemical hydrogen storage.

Introduction

Zinc germanate (Zn_2GeO_4) as a ternary semiconductor oxide is a significant material due to its optical and electronic properties, which are suitable for application as hydrogen storage materials. In recent years, hydrogen storages are attracting universal scientific and technological interest because of their great energy density, renewable and green energy [1]. Although hydrogen storage has been drawn a great consideration for metal hydrides [2] and metal organic frameworks (MOFs) [3], less works have been reported for exploring the hydrogen-storage potential of nanostructured oxide materials. The various types of nanostructure materials are available for application as hydrogen storage materials such as: mesoporous nanostructured transition metal hydroxides [4], different oxides [5–7], metal sulfides [8], graphene nanocomposites [9], different alloys [10], CNT materials [11] and hydride compounds [2]. Zinc germanate (Zn_2GeO_4) is a good candidate due to its reasonable conductivity, excellent stability, facile synthesis, lower cost and especially their various morphology and sizes [12–14]. A variation of possible routes including high temperature solid state reaction [15], thermal evaporation [16], microwave-induced hydrothermal method with subsequent thermal decomposition [12], hydrothermal [13], solid-state method [17], Low temperature synthesis [18] and solvothermal [19] has been applied to obtain different sizes and morphologies. In the majority of studies of recent years, synthesized Zn_2GeO_4 nanostructures were used for

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diverse applications such as lithium ion battery [20], photocatalytic hydrogen generation [13], microwave dielectric [17], photo-degradation of organic pollutant [19] and Photoluminescence [15,16]. Graphene with a single atomic layer of graphite has various ideal usages because of its light weight, large surface area (2600 $m^2\ g^{-1}$), good mechanical and electrical conductivity properties, and high chemical stability. Graphene is usually used as the appropriate carrier for ternary oxide nanostructures [21]. Wang et al. [22] synthesized crystalline Zn_2GeO_4 nanorod/graphene composites as anode materials for high performance lithium ion batteries. Zou and co-workers [23] prepared sandwiched Zn_2GeO_4–graphene oxide nanocomposite as a stable and high-capacity anode for lithium-ion batteries. As aforementioned, although considerable progress has been made on Zn_2GeO_4/graphene nanocomposites as anode for lithium-ion batteries, its function as electrochemical hydrogen storage materials is not reported. It is the first report on the synthesis of Zn_2GeO_4 nanostructures by using $GeCl_4$ and chemical precipitation method in presence of acacen as a capping agent. Furthermore, the synthesized Zn_2GeO_4 nanostructure with optimized size and morphology and Zn_2GeO_4/graphene nanocomposite are proposed for the first time as electrochemical hydrogen storage material. Furthermore, it is also found that these Zn_2GeO_4/graphene nanocomposites exhibited high electrochemical hydrogen storage capacities at room temperature. After 29 cycles, the discharging capacities of the electrode still remain above 2695 mAh/g.

Experimental

Materials and physical measurements

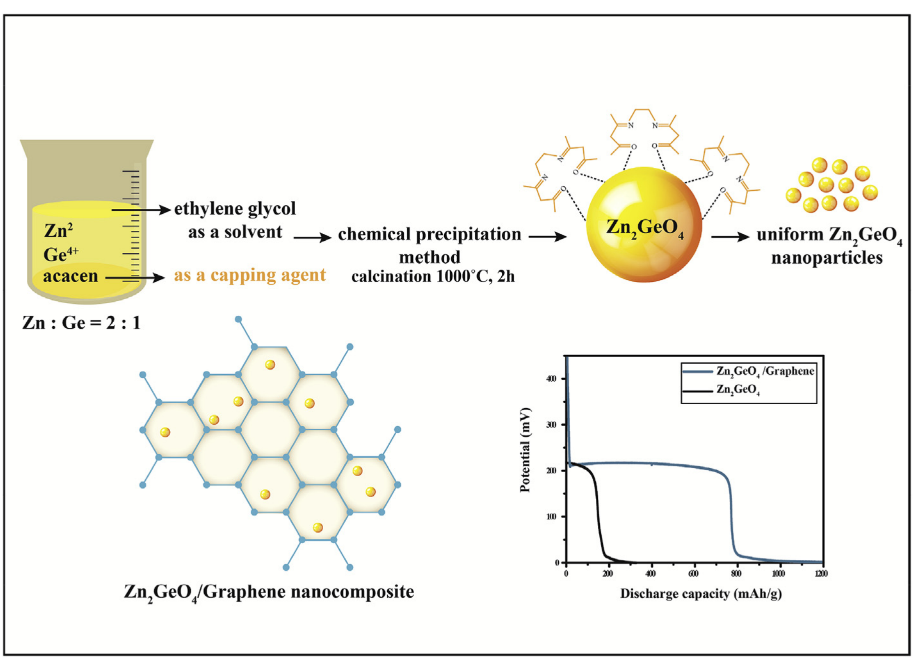
All the chemical reagents for the synthesis of zinc germanate nanostructures such as $Zn(NO_3)_2 \cdot 6H_2O$ and $GeCl_4$ were commercially available and employed without further refinement. Fourier transform infrared (FT-IR) spectra were detected on Shimadzu Varian 4300 spectrophotometer in KBr pellets. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Kα radiation. Scanning electron microscopy (SEM) image was applied on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The EDX analysis with 20 kV accelerated voltage was applied. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Transmission electron microscopy (TEM) image was achieved on a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. Optical analysis was performed using a V-670 UV–Vis–NIR Spectrophotometer (Jasco).

Preparation of Zn_2GeO_4 nanostructures

First, 0.5 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.1 g acacen Schiff base [24] were dissolved into ethylene glycol and was added to ethylene glycol solution of $GeCl_4$ with a molar ratio of Zn:Ge = 2:1. After that, the above solution was heated at 100 °C and stirred for 1–4 h. The precipitate was dried at 80 °C under vacuum for 2 h and then was calcined at 1000 °C for 2 h. In Scheme 1, schematic diagram of formation of Zn_2GeO_4 nanostructure and Zn_2GeO_4/graphene nanocomposite is

Table 1 – The reaction conditions for synthesis of Zn_2GeO_4 nanostructures.

Sample No.	Type of sample	Capping agent	Particle size/SEM
1	Zn_2GeO_4 nanoparticle	acacen	10–40 nm
2	Zn_2GeO_4 microstructure	–	Agglomerated particle
3	Zn_2GeO_4/graphene nanocomposite	acacen	10–40 nm particle/nanosheet



Scheme 1 – Schematic illustration for the growth mechanism of Zn_2GeO_4 nanostructures.

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