Electrochimica Acta 186 (2015) 397–403

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Facile and large-scale preparation of sandwich-structured graphene-metal oxide composites as anode materials for Li-ion batteries

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ARTICLE INFO

Article history:
Received 9 October 2015
Received in revised form 30 October 2015
Accepted 1 November 2015
Available online 4 November 2015

Keywords:
Graphene
Metal oxide
Sandwich structure
Lithium-ion battery

ABSTRACT

Graphene-based metal oxides are desirable as potential anode materials for lithium-ion batteries (LIBs) owing to their superior electrochemical properties. In this work, sandwich-structured graphene-metal oxide (ZnO, NiO) composites are facilely synthesized on a large scale through self-assembly of graphene oxide nanosheets and metal ammine complexes, and then thermal decomposition of the self-assembled products. ZnO or NiO nanoparticles with diameters of 5~10 nm are immobilized between the layers of graphene nanosheets, which may provide the space for accommodating the volume change of metal oxides during cycles, and highly improve the electronic conductivity of the composites. Accordingly, these sandwich-structured composites exhibit enhanced electrochemical performances compared to metal oxide particles or stacked graphene nanosheets. This facile synthesis method is very suitable for the large-scale production of three-dimensional graphene-based composites as high-performance anodes for LIBs.

1. Introduction

Lithium-ion battery (LIB) is one of important energy storage and conversion devices owing to its outstanding advantages such as high energy density, long cycle life, no memory effect and environmental friendliness [1,2]. As promising anode materials for LIBs, metal oxides possess high theoretical capacities (e.g., 978 mA h g^{-1} for ZnO and 718 mA h g^{-1} for NiO), but their poor electronic conductivity and large volume change during cycles may lead to a rapid capacity fade and poor cycling stability [3,4]. Many strategies have been carried out to address these issues such as fabrication of nanosized or porous metal oxides, which may effectively buffers the stress caused by the volume change of metal oxides, shorten the diffusion path of Li ions, and increase the surface area in contact with the electrolyte. Another method is to prepare carbon-coated and -supported metal oxide composites because carbon component (e.g., carbon nanotube or nanofiber) can improve the electronic conductivity of the composite electrode as well as restrain the volume variation of metal oxides to some extent [5,6]. Besides, carbon supports can also prevent the aggregation of nanoparticles, thereby highly improving the cycle and rate performances of the composite [7,8]. Recently, a novel two-dimensional carbon material, graphene, displays some outstanding properties such as large specific surface area, unique mechanical property, and high electronic conductivity, and may hopefully replace traditional carbon materials in many fields [9,10]. It has been reported that graphene-supported metal oxides show better electrochemical behavior than pure metal oxides and some other carbon-supported metal oxides [11,12]. More importantly, the performance of graphene-based composites can further be improved by design of sandwich structure, which can further enhance the electron transfer rate in the composite and protect metal oxides against disintegration and aggregation during cycles [13,14]. Notwithstanding these advances, the traditional methods for the preparation of sandwich-structured graphene-metal oxide composites are too complicated and uneconomical to be applied in industry.

To design a sandwich structure of graphene-based metal oxide composite, nanosized metal oxides or graphene-based metal oxides are generally prepared and their surfaces are modified by amino groups if necessary, which makes metal oxides attached to the surface of graphene oxide (GO) through the strong electrostatic interaction [15,16]. Nevertheless, the synthesis of ultrasmall nanoparticles is difficult and the particle aggregation is inevitable, resulting in the formation of imperfect sandwich structure and a

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http://dx.doi.org/10.1016/j.electacta.2015.11.004
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decrease in the electrochemical performances [17,18]. Herein we describe a facile and scalable strategy for the large-scale preparation of sandwich-structured graphene-based metal oxides, which can avoid the previous preparation of metal oxide nanoparticles. GO nanosheets are first prepared and connected with metal ammine complexes to form a sandwich structure. After controllable calcination, sandwich-structured graphene-based ZnO and NiO (denoted as G-ZnO-G and G-NiO-G) are successfully fabricated and exhibit superior electrochemical performances compared to pure metal oxides (ZnO, NiO) and stacked graphene nanosheets (GN). Moreover, it is worth noting that the highest contents of metal oxides in the composites are related with the oxidation degree of GO, and the size of nanoparticles can be tuned by controlling the heating temperature. All these factors may influence the electrochemical properties of the composites and need to be optimized. This facile method for the large-scale synthesis of sandwich-structured graphene-based composites may be desirable for the applications in industry [19,20].

2. Experimental

GO was synthesized from natural graphite powders by a modified Hummer's method [21]. 0.01 g of GO was dispersed in 100 mL of deionized water by ultrasonication and 0.01 mol of $ZnCl_2$ or $NiCl_2$ was dissolved into 100 mL of deionized water. 20 mL of aqueous ammonia was then added into the $ZnCl_2$ or $NiCl_2$ solution to prepare metal ammine complexes and restrain the formation of hydroxides. Subsequently, 5 mL of above solution was added dropwise into 100 mL of GO solution with stirring. After 0.5 h, the precipitate was collected by centrifugation and dried at 60 °C. The black powder was transferred to a furnace and heated at 450 °C for 5 min under N_2 atmosphere. The heating rate is 10 °C min^{-1}. After cooling down to room temperature, G-ZnO-G or G-NiO-G was obtained. For comparison, ZnO or NiO powder was prepared by heating the graphene-based composites in air, and GN was prepared by heating staked GO nanosheets in N_2 gas. Moreover, 3 mL and 7 mL of prepared $ZnCl_2$ solution were used to synthesize G-ZnO-G with various contents of ZnO (denoted as G-ZnO-G-L and G-ZnO-G-H). The G-ZnO-G and G-NiO-G samples were also synthesized by calcination at higher temperature (600 °C), and denoted as G-ZnO-G-HT and G-NiO-G-HT, respectively.

Specimens were initially characterized using XRD on a Phillips X'pert Pro MPD diffractometer with Cu Kα radiation. X-ray photoelectron (XPS) spectra were recorded on a Shimadzu Axis Ultra spectrometer with an Mg Kα = 1253.6 eV excitation source. The thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC/PG thermal analyzer and carried out in air at a heating rate of 5 °C min^{-1}. Further characterization was

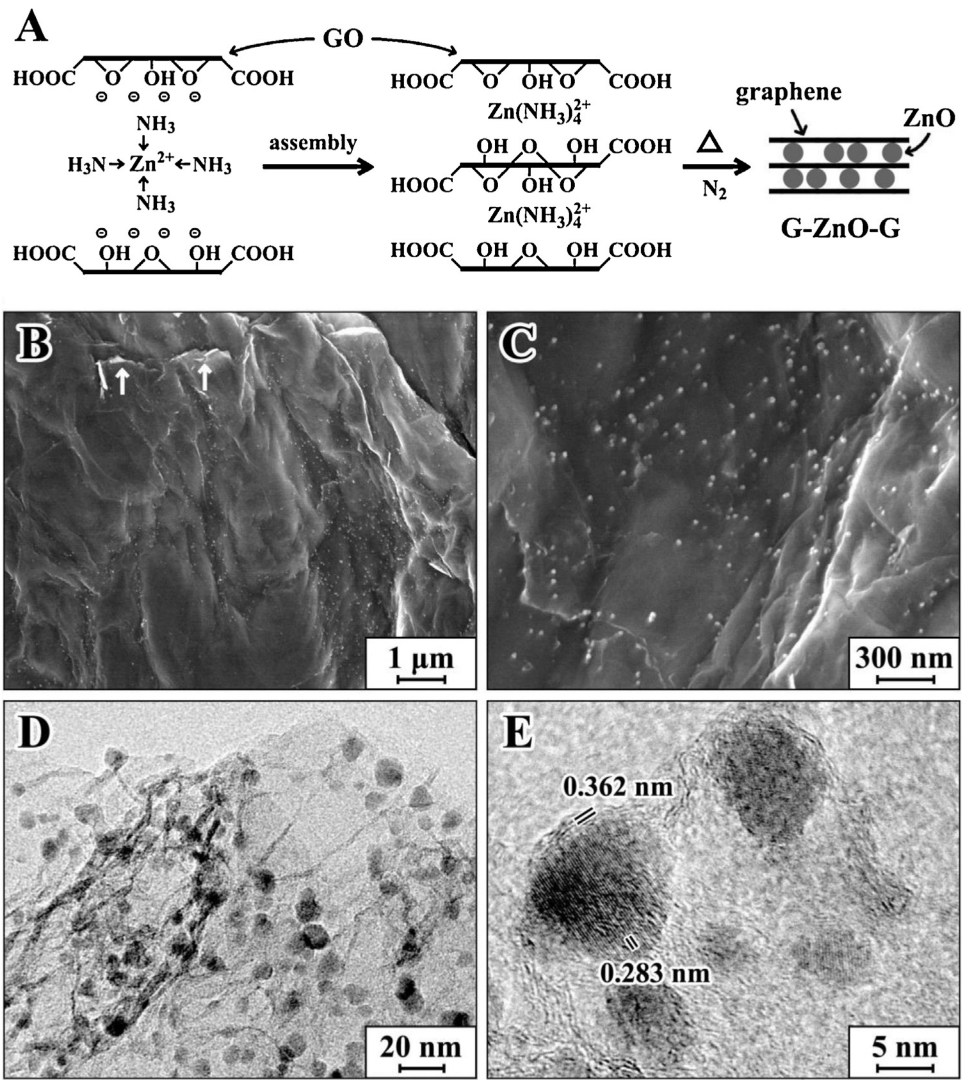

Fig. 1. (A) Schematic illustration of the synthesis route for G-ZnO-G. (B, C) SEM, (D) TEM and (E) HRTEM images of G-ZnO-G.