Catalysis Today 246 (2015) 165–171

Contents lists available at ScienceDirect

Catalysis Today

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

Synthesis of graphene-like MoS_2 nanowall/graphene nanosheet hybrid materials with high lithium storage performance

Jin Guo, Xiao Chen, Shaohua Jin, Mingming Zhang, Changhai Liang*

Laboratory of Advanced Materials and Catalytic Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

ARTICLE INFO

Article history:
Received 5 June 2014
Received in revised form
25 September 2014
Accepted 26 September 2014
Available online 28 October 2014

Keywords:
Graphene-like MoS_2
Graphene
Nanocomposites
Lithium ion battery

ABSTRACT

A facile method to synthesize graphene-like MoS_2 nanowall/graphene sheet (GL-MoS_2 nanowall/GNS) composites has been developed through a solvothermal method, and followed by annealing at 400 °C under Ar. The characterization results indicate that the thin flaky wall type GL-MoS_2 nanowall was supported well on the crumpled graphene flakes with good dispersion. The as-obtained nanowall-nanosheet hybrids are more robust and still retain the reversible capacity of 700 mA h g^{-1} after 100 cycles at a charge–discharge rate of 500 mA g^{-1}. The outstanding performance in electrochemistry is attributed to both the robust nanocomposite structure and the synergistic interactions between graphene and GL-MoS_2 nanowall, which makes it an efficient stable lithium storage material.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have aroused a wide variety of research interests around the world because they are the key components in portable electronic devices and stationary energy storage systems [1–7]. Graphite is the most popular commercial anode in LIBs owning to their flat potential profile for lithium intercalation and good structural stability during cycling. However, the theoretical maximum capacity of 372 mA h g^{-1} can hardly achieve the demands associated with the use in electric devices [8]. To meet the requirements in higher power densities and better cycling stability, significant efforts have been made to develop new electrode materials [9].

Molybdenum disulfide (MoS_2), a typical layered transition metal sulfide with an analogous structure to graphite, has recently received particular attention as a promising electrode material for LIBs because of their high specific capacities, unusual electronic and physical properties [10–14]. Generally, a bulk MoS_2 crystal is composed of three atom layers, a Mo layer sandwiched between two S layers, and the triple layers are stacked and held together by weak van der Waals interactions [15]. Precisely similar to the layered structure of graphite indicates that single-layer or few-layer MoS_2 flakes can be prepared. Rao and coworkers named the structure of MoS_2 and WS_2 with a single layer or a few layers graphene-like nanostructure [15]. In addition, it has been confirmed that the few-layer (particularly single-layer) MoS_2 nanosheets exhibit distinctively different chemical and physical properties in comparison with the bulk materials, owning to the changes in electronic properties with decreasing layer number [16–18]. Especially, the luminescence quantum efficiency of single-layer MoS_2 is about 10^4 greater than that of bulk MoS_2. GL-MoS_2 also has been investigated as a good cathode material for Li-ion batteries. For instance, Du et al. have prepared an exfoliated–restacked MoS_2 electrode with the superior cycle stability [19]. Lemmon and coworkers had obtained exfoliated MoS_2–PEO (polyethylene oxide) composite electrode exhibiting the improved cyclic performance and rate capability [20].

However, the single layer MoS_2 is easy to aggregate or restack during repetitive cycling and even in the drying process of electrodes due to the van der Waals interactions, which would lose its unique properties and give a negative effect on their performance in LIBs. To overcome these obstacles, many research groups introduced carbon based conductive additives into MoS_2 to improve the cyclability and rate capabilities of the material [13,21–27]. Among these carbon based conductive additive, graphene is a desirable matrix for improving the electrochemical performance owning its superior electrical conductivity, large surface area, excellent mechanical flexibility, and high thermal and chemical stability [28]. Thus, graphene composites with MoS_2 have been explored as LIB anode materials. The results generally showed some good promises such as high specific capacity and improvement of the cycle ability of MoS_2 [13,22]. However, to the best

* Corresponding author. Fax: +86 411 84986353.
E-mail address: changhai@dlut.edu.cn (C. Liang).

http://dx.doi.org/10.1016/j.cattod.2014.09.028
0920-5861/

of our knowledge, there are few reports on the synthesis of GL-MoS_2 nanowall/GNS nanocomposites (GL-MoS_2 vertically growth on the graphene surface). Hence, morphology-controlled synthesis of well-aligned graphene-like MoS_2 nanowall still remains a challenge by means of a simple, effective, and economical approach.

Herein, nanowall architectures constructed of GL-MoS_2 nanowall arrays on the graphene were firstly prepared by a facile in situ solvothermal reduction method. $Mo(dedtc)_4$ was used as a single source precursor to prepare GL-MoS_2 without the addition of any surfactants. The as-prepared GL-MoS_2 nanowall/GNS can not only prevent the agglomeration of MoS_2 flakes, but also restrict the growth of Mo nanoparticles during lithiation by the bond formed between MoS_2 nanowall and graphene. The limited growth of Mo nanoparticles can further suppress the lithiation product Li_2S to react with the electrolyte by the adsorption effect of Mo nanoparticles [29]. What is more, the vertical MoS_2 nanowall provides a shorter pathway for Li-ion and electrons. At the same time, the vertical MoS_2 nanowall can more effectively inhibit the aggregation of graphene sheets so that the conductivity of the composites can be further enhanced.

As a result, GL-MoS_2 nanowall/GNS exhibit outstanding reversible capacity and excellent rate performance (700 mA h g^{-1} after 100 cycles at a charge–discharge rate of 500 mA g^{-1} and reversible discharging capacity 380 mA h g^{-1} at 2000 mA g^{-1}), when applied as the anode material for lithium storage.

2. Experimental

2.1. Synthesis of GL-MoS_2 nanowall/GNS nanocomposites

Graphene oxide (GO) was prepared by a modified Hummers method [30] from natural graphite powder. Then exfoliation was carried out by ultrasonicating the GO dispersion in acetonitrile under ambient conditions.

For the preparation of GL-MoS_2 nanowall/GNS composites, 40 mL of a 1 mg mL^{-1} GO suspension was ultrasonicated for 0.5 h in acetonitrile, then 200 mg precursor $Mo(dedtc)_4$ was added into the suspension under vigorous stirring for 0.5 h. The precursor was prepared by our previous work according to a reported method with some modifications [31,32]. Typically, 1 g (3.8 mmol) $Mo(CO)_6$ and 2.25 g (7.6 mmol) bis(diethylthiocarbamoyl)disulfide were dissolved in 30 mL acetone under an oxygen-free argon atmosphere. The solution was stirred and refluxed at 58 °C for 2.5 h, after cooling to room temperature naturally for 5 h. The violet precipitate were collected and washed with pentane. Finally, the product was dried under vacuum at 120 °C to evaporate off residual impurities. The mass spectroscopy and molecular structure of precursor are shown in Fig. S1. The molecular weight of as-prepared $Mo(dedtc)_4$ is 689 g mol^{-1}.

The mixture was vigorously stirred for 0.5 h and sealed in a 50 mL Telfon-lined autoclave solvothermally treated at 220 °C for 12 h. After cooling naturally, the black precipitates were collected by centrifugation, and dried in a vacuum oven at 80 °C for 12 h. The GL-MoS_2 nanowall/GNS nanocomposites were obtained after annealing in conventional tube furnace at 400 °C for 4 h under Ar.

2.2. Characterizations

The materials were recorded with CuKα radiation by powder X-ray diffraction (XRD) using a D/MAX 2400 diffractometer. The 2θ angular regions between 5° and 80° were investigated at a scan rate of 8° min^{-1} with a step of 0.02°. The morphology of the samples was investigated by field–emission scanning electron microscope (FEI Nova Nano SEM 450) and transmission electron microscope (TEM, Philips CM200 electron microscope. The sample was dissolved in ethanol and the suspension was dropped onto a copper grid.). Raman measurements were obtained by an inVia Reflex Laser Micro-Raman spectroscope (Renishaw) with a 532 nm Ar laser.

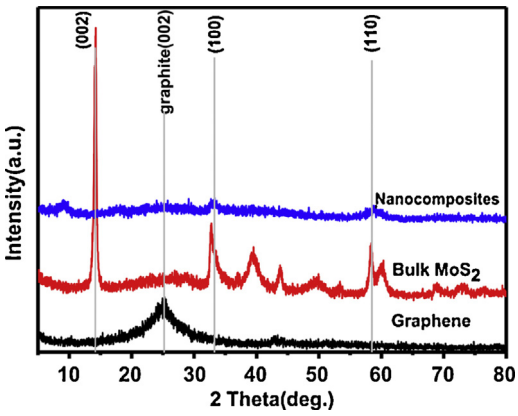

Fig. 1. XRD patterns of graphene, bulk MoS_2 and GL-MoS_2 nanowall/GNS nanocomposites.

2.3. Electrochemical measurements

The working electrodes were prepared by mixing 80 wt % active materials (GL-MoS_2 nanowall/GNS nanocomposites), 10 wt % acetylene black (super-p) and 10 wt % poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone. After coating the above slurry onto a copper foil current collector, it was dried under vacuum at 120 °C for 12 h and cut into pieces with a diameter of 14 mm before use. A Celgard 2300 membrane was used as a separator between the working electrode and the counter electrode (Li foil). The electrolyte was 1 M $LiPF_6$ in the mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1in volume). The working electrode, the separator, the electrolyte, and the counter electrode, were assembled to a coin-type cell (2016) in an argon-filled glovebox (Unilab 1200/780). Galvanostatic charge/discharge cycles of the cells were conducted between 0.01 and 3.00 V on a LAND CT-2001A battery cycler (Wuhan, China) after the catalytic material is stabilized at room temperature.

3. Results and discussion

The synthetic route of GL-MoS_2/GNS nanocomposites is schematically illustrated in Scheme 1. Oxygen-containing functional groups on graphene oxide (GO) sheets make it soluble and easily processable. The $Mo(dedtc)_4$ molecules adsorbed firstly on the oxygen-containing groups on the surface of GO through impregnation process in the acetonitrile. Then, GNS with uniformly dispersed MoS_2 nanosheets are generated by solvothermal treatment. The MoS_2 nanoflakes gradually convert to nanowall with curling up and growing vertically on the surface of the GNS as the reaction progress, and finally the GL-MoS_2 nanowall/GNS nanocomposites were obtained after annealing at 400 °C for 4 h under Ar.

For the as-prepared GL MoS_2/GNS nanocomposites and bulk MoS_2, all diffraction peaks are consistent with those of typical MoS_2 phase (JCPDS Card No.37-1492), demonstrating that the MoS_2 phases were formed after annealing at 400 °C. The broad and weak peaks of the (1 0 0) and (1 1 0) planes indicated the low crystallinity of MoS_2 in nanocomposites. Compared to bulk MoS_2 and pure graphene, as shown in Fig. 1, the (0 0 2) peaks located at 2θ = 14.4° and 25.3° could not be found for the GL-MoS_2/GNS composites sample, which demonstrated that MoS_2 nanosheets and graphene