Synthetic Metals 217 (2016) 138–143

Contents lists available at ScienceDirect

Synthetic Metals

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

Preparation and lithium ion batteries properties of SnS_2 nanoparticle/reduced graphene oxide nanosheet nanocomposites using supercritical carbon dioxide

Keyu Li[a], Shancheng Yan[a,*], Zixia Lin[b], Xiubin Dai[a], Peng Qu[c,**]

[a] School of Geography and Biological Information, Nanjing University of Posts and Telecommunications, Nanjing 210023, PR China
[b] National Laboratory of Solid State Microstructures, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, PR China
[c] Henan Key Laboratory of Biomolecular Recognition and Sensing, College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, PR China

ARTICLE INFO

Article history:
Received 18 January 2016
Received in revised form 14 March 2016
Accepted 21 March 2016
Available online 1 April 2016

Keywords:
Supercritical CO_2
SnS_2 nanoparticle
Nanocomposites
Anode materials
Lithium-ion batteries

ABSTRACT

Graphene-based nanocomposites have been widely investigated as promising anode materials because of the high specific capacity and good rate capability. However, effective distributing the nanomaterials into graphene conductive network still remains some challenges. In this study, the supercritical carbon dioxide (SC-CO_2) route as a good strategy is developed to prepare SnS_2/reduced graphene oxide (RGO) nanocomposites, which integrates the complementary effect of ultrasmall SnS_2 nanopaticle and RGO nanosheet in the nanocompositions. The SnS_2/RGO nanocomposite exhibits high initial discharge capacity of 1466.1 mA h g^{-1} (100 mA g^{-1}), good capacity retention of about 492 mA h g^{-1} (100 mA g^{-1}) after 70 cycles and good rate capacity as an anode material for lithium ion batteries. These results demonstrate that supercritical CO_2 (SC-CO_2) possess significant technological value to enhance the energy storage properties of other two-dimensional (2D) nanocomposites.

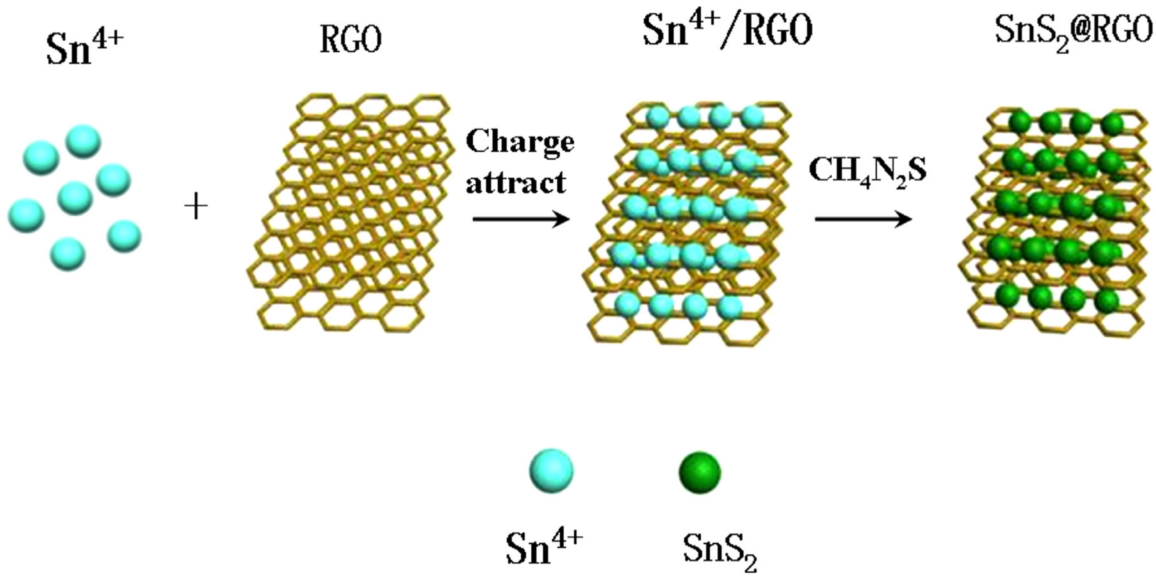
1. Introduction

Rechargeable lithium ion batteries (LIBs) with high energy density, stability and environmentally friendly is playing a critical role in portable electronic devices, electric vehicles and hybrid electric vehicles, which have been widely studied for power source [1–6]. Graphene has been used for the application of lithium ion battery due to its unique two dimensional (2D) single layer structures, high thermal conductivity and high surface area [2,7,8]. However, the relatively low theoretical capacity (372 mA h g^{-1}) of graphite can not fully meet the requirements for high-power rechargeable LIBs application, which cause the rise of alternative higher capacity materials, such as SnO_2, MoS_2, SnS_2, WS_2, etc. [1–3,9]. Among them, SnS_2 has attracted much attention as anode material of LIBs battery via hydrothermal, solvolthermal and reflux synthesis techniques [1,4,8–12]. Nevertheless, the electrical conductivity and rate capability of SnS_2 are restricted from the volume expansion and capacity fading in the process of ion insertion and extraction [8,12–15]. Thus, the graphene with unique properties can be used as a conductive matrix to enhance electron transport and buffer the volume expansion, resulting in the rapid development of graphene-based nanocomposites [8,14–20]. The typological nanocomposites are supposed to maximize structure compatibility and obtain greater capacity than the individual components [14]. In addition, the simple, fast, cost-effective and environmentally friendly synthetic method still is a challenge [8].

Herein, the supercritical carbon dioxide (SC-CO_2) route as a good strategy has been developed to synthesis SnS_2/RGO nanocomposites, owing to its advantages, such as low viscosity, low interfacial tension, outstanding wetting of surfaces and high diffusion coefficients. Meanwhile, the SC-CO_2 also possesses near-zero surface tension and excellent penetration ability, which can help to prevent the restacking of RGO nanosheets and to reinforce the contact between the SnS_2 nanoparticles and RGO nanosheets [7,21,22]. These characteristic can be fully utilized to control of the solubility of a solute in SC-CO_2 by changing the pressure and temperature [21]. The formation of SnS_2/RGO nanocomposites using these reactants of $SnCl_4 \cdot 5H_2O$, RGO and thiourea via SC-CO_2 process can be seen in Scheme 1. The SnS_2/RGO nanocomposites exhibit high irreversible initial discharge capacity and a higher reversible capacity as anode materials for lithium ion batteries. The superior performance and good rate capacity demonstrate that the

* Corresponding author.
** Corresponding author.
E-mail addresses: yansc@njupt.edu.cn, 289946930@qq.com (S. Yan), qupeng0212@163.com (P. Qu).

http://dx.doi.org/10.1016/j.synthmet.2016.03.027
0379-6779/



Scheme 1. The formation of SnS_2/RGO nanocomposites using SC-CO_2 route.

SC-CO_2 synthesis techniques for the formation of SnS_2/RGO nanocomposites are believed to function synergistically energy storage of the anode material.

2. Experimental details

2.1. Preparation of SnS_2 and SnS_2/RGO nanocomposites

All chemical reagents were analytical grade and used without further purification. $SnCl_4 \cdot 5H_2O$ and thiourea were all purchased from Aladdin Industrial Corporation. GO was made by the modified Hummers method, and exfoliated using a high pressure homogenizer, then annealed at 300° C for 3 h under Ar atmosphere. The final product is called reduced graphene oxide (RGO).

In a typical reaction, the solution used to prepare SnS_2/RGO nanocomposites was first composed of 0.1753 g $SnCl_4 \cdot 5H_2O$, 0.0952 g thiourea, 0.0292 g of RGO. The solvent was 30 mL ethylene glycol. The mixture was transported to a preheated (100 °C) stainless steel reactor (50 mL), and CO_2 was charged into the reactor to the desired pressure (15 MPa). The mixture was reacted in the SC-CO_2 for 120 min. Subsequently, the products were cooled at room temperature, separated by centrifugation, washed several times with distilled water, and then dried in a vacuum at 60 °C for 4 h.

2.2. Materials characterizations

Field emission scanning electron microscopy (JSM-7000F) was used to determine the morphology of the samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a JEOL model JEM2100 instrument at an accelerating voltage of 200 kV.

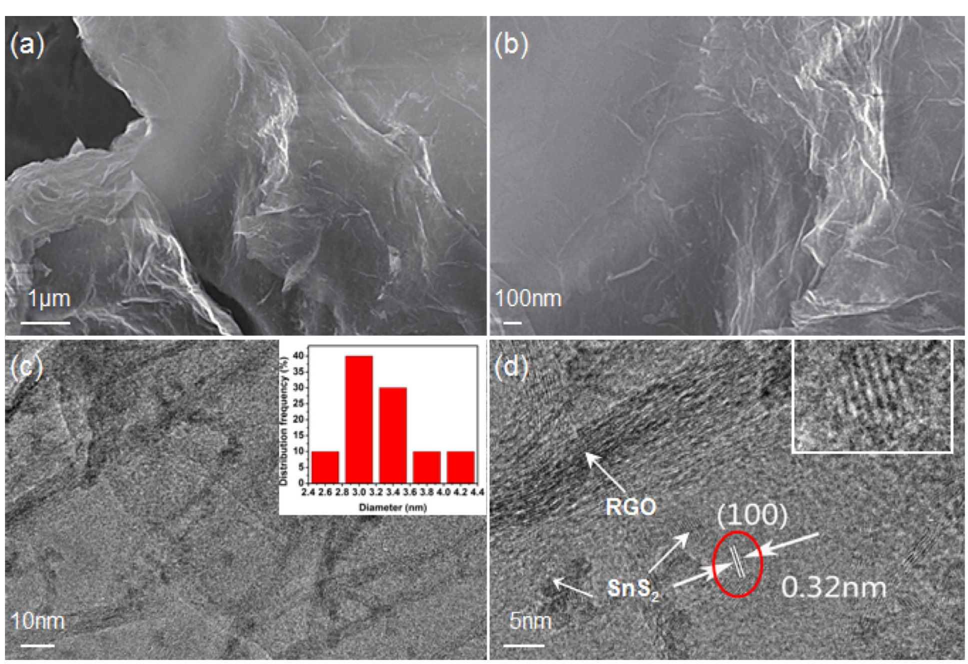


Fig. 1. (a) and (b) SEM images of SnS_2/RGO nanocomposites, (c) TEM image of SnS_2/RGO nanocomposites and (d) Its HRTEM image.