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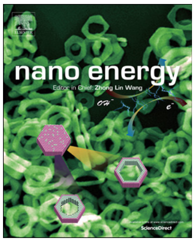

RAPID COMMUNICATION

In situ TEM characterization of single PbSe/reduced-graphene-oxide nanosheet and the correlation with its electrochemical lithium storage performance

Jian Xie[a,b], **Fangfang Tu**[a,b], **Qingmei Su**[c], **Gaohui Du**[c,**], **Shichao Zhang**[d], **Tiejun Zhu**[a], **Gaoshao Cao**[b], **Xinbing Zhao**[a,b,*]

[a] *State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*
[b] *Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, China*
[c] *Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China*
[d] *School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, Beijing 100191, China*

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Abstract

In this work, in situ transmission electron microscopy (TEM) technique has been applied to investigate the structural and phase evolutions of lead selenide (PbSe) nanocrystals loaded on reduced graphene oxide (rGO) nanosheets. An all-solid-state nano lithium battery composed of a single PbSe/rGO sheet cathode, Li_2O electrolyte and Li anode has been fabricated to real time monitor the electrochemical lithiation/de-lithiation process of PbSe. It is found that few-layered rGO is a suitable support for PbSe during the in situ TEM observation due to its large surface area and good Li ion and electron conductivity. Based on the in situ characterization, a lithiation/de-lithiation mechanism of PbSe has been proposed. In situ characterization results are correlated with the electrochemical performance of PbSe/rGO. The role that rGO plays in modifying the electrochemical performance of PbSe has also been clarified by the in situ TEM characterization.

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[*] Corresponding author at: State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China. Tel./fax: +86 571 87951451.

[**] Corresponding author. Tel./fax: +86 571 87951451.

E-mail addresses: gaohuidu@zjnu.edu.cn (G. Du), zhaoxb@zju.edu.cn (X. Zhao).

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Introduction

Rechargeable Li-ion batteries have been considered as promising power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs) in recent years [1-3]. A challenge is still remaining to develop high-capacity anode materials in order to meet the ever increasing high-energy-density requirement for EVs and HEVs. Although Sn or Si-based materials can yield a rather higher capacity than conventional carbon-based materials by forming Li-Sn and Li-Si alloys [4-6], these anodes generally show a rapid capacity fade due to the large volume changes during alloying/de-alloying process. An effective method to improve the cycling stability is to use nanostructured materials [7-9], because of their large surface area, short Li ion diffusion pathway, and enhanced mechanical strength [9]. Nanomaterials, however, are easy to aggregate upon repeated cycling owing to their large surface energy. In addition, particle pulverization and exfoliation still occur for nanomaterials after long-term cycling. A practical method is to confine the nanomaterials within a matrix that inhibits the pulverized particles from aggregating and exfoliating.

Graphene, a new two-dimensional (2D) carbon material [10], is an ideal matrix to support nanomaterials due to its large surface area [11], giant mechanical strength [12], and high electronic conductivity [13]. Besides, graphene also contributes to the overall capacity for the composites [14-16]. The work on some Sn-based materials, such as metallic Sn [17-19], tin oxides [20-23], tin sulfide [24-27] and tin alloys [28-30] has found that the electrochemical Li-storage properties could be remarkably improved by anchoring them on the graphene sheets. The electrochemical performance of nanosized Si and Ge could also be enhanced by using graphene as the matrix [31-34]. It is generally accepted that the improved electrochemical performance could be attributed to a combination of conducting, buffering and confining effects offered by graphene. The above effects are closely related to spatial relationship between the active particles and graphene and its evolution during the electrochemical process. Nevertheless, the intrinsic mechanism is not well understood so far owing to the lack of the effective in situ characterization techniques.

In situ TEM has provided a powerful tool to real time observe the electrochemical process of the electrode materials by fabricating a nano battery inside a TEM chamber. It has been successfully applied to in situ monitor the structural and phase evolutions for some typical electrode materials with an alloying/de-alloying Li-storage mechanism, such as SnO_2 [35,36], Si [37-39], Ge [40] and Ge/Si [41]. To date, the materials suitable for in situ TEM characterization are limited to those with special morphology, mainly one-dimensional (1D) nanomaterials [35-41], or that attached on 1D materials [42]. For a single nanoparticle, a supporting matrix is preferred for easy fabrication of the in situ characterization device. Du et al. found that reduced graphene oxide (rGO) is an ideal support for nano-Fe_2O_3 to in situ investigate its electrochemical lithiation/de-lithiation mechanism [43] due to the fact that rGO can supply a large surface area [11], rapid Li ion and electron conducting channels [13,44], and a strong couple with the guest materials [45].

Similar to Si, Ge and Sn, Pb in the same IVB group also exhibits a large Li-storage capacity by forming Li-rich Li-Pb alloy [6]. However, its electrochemical Li-storage mechanism and performance have been rarely investigated. In this work, a PbSe/rGO nanohybrid has been synthesized by an solvothermal route and an all-solid-state Li-Li_2O-PbSe/rGO nano lithium battery has been fabricated to real time monitor the structural and phase changes of PbSe and the role that rGO plays in altering the electrochemical performance of PbSe. The rGO has a double function for in situ TEM characterization of PbSe: (i) rGO is a good support for easy loading and characterization of PbSe nanocrystals by offering a large surface area and rapid Li ion and electron conducting channels; (ii) the effect of rGO on the electrochemical performance of PbSe can be reflected by its spatial relationship with PbSe which can be monitored during in situ TEM characterization.

Material and methods

Preparation of PbSe/rGO nanohybrid

Graphite oxide (GO, 60 mg), prepared by a modified Hummers method [46], was added into 50 mL of ethylene glycol (EG) under ultrasonic agitation to form a uniform dispersion. Then, 0.5 mmol of $Pb(NO_3)_2$ and 0.5 mmol of Se powder were added to the above dispersion with magnetic stirring for 24 h. The mixed solution was then transferred to a Teflon-lined stainless steel autoclave (100 mL in capacity) and heated in an electric oven at 180 °C for 36 h. The resulting precipitate was collected by centrifugation, washed with deionized water and absolute ethanol repeatedly, and dried at 40 °C under vacuum for 10 h. Another sample with low rGO content (PbSe/rGO1) was prepared by a similar route by decreasing the GO to 30 mg in the precursor while keeping other conditions unchanged. Bare PbSe was also prepared with a similar route without the addition of GO in the precursor.

Materials characterization

The phases of the products were analyzed by X-ray diffraction (XRD) on a Rigaku D/Max-2550pc powder diffractometer equipped with Cu K_α radiation (λ=1.541 Å). The Raman spectra were collected on a Jobin-Yvon Labor Raman HR-800 using Ar-ion laser of 514.5 nm. X-ray photoelectron spectra (XPS) were measured on a KRATOS AXIS ULTRA-DLD spectrometer with a monochromatic Al K_α radiation ($h\nu$=1486.6 eV). The morphologies of the products were observed by field-emission scanning electron microscopy (SEM) on a FEI-sirion microscope and transmission electron microscopy (TEM) on a JEM-2100F microscope. The carbon content analysis of PbSe/rGO was conducted on a Flash EA 1112 tester.

In situ TEM characterization

In situ TEM observation was performed on the JEOL JEM-2100F TEM using the Nanofactory TEM-scanning tunneling microscopy (STM) holder. The TEM-STM holder integrates a fully functional STM probe. The STM probe can be driven by the piezopositioner to approach the other electrode at fine steps when the holder is inserted into the TEM column.