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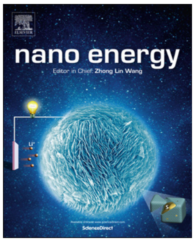

RAPID COMMUNICATION

Graphene-encapsulated selenium/polyaniline core-shell nanowires with enhanced electrochemical performance for Li-Se batteries

Jingjing Zhang[a,1], **Yanhua Xu**[a,1], **Long Fan**[a,1], **Yongchun Zhu**[a,*,1], **Jianwen Liang**[a,1], **Yitai Qian**[a,b,*,2]

[a] *Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China*
[b] *School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China*

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Abstract
A novel nanocomposite of graphene-encapsulated selenium/polyaniline core-shell nanowires (G@Se/PANI) has been designed and synthesized under the condition of low temperature without heating and investigated as a cathode material for Li-ion batteries. In this nanocomposite, selenium nanowires are well-sealed in the PANI layer with a thickness of ≈ 25 nm forming a core/shell structure and then the Se/PANI core-shell nanowires are uniformly encapsulated in the graphene nanosheets. As expected, the G@Se/PANI nanocomposite exhibits enhanced cycling performance and high-rate capability. The G@Se/PANI nanocomposite displays a reversible discharge capacity of 567.1 mA h/g at 0.2 C after 200th cycle and 510.9 mA h/g at 2 C, which could be associated with the highly electrical conductivity of graphene sheets and the unique PANI shell, together with the one-dimensional structure of selenium in the G@Se/PANI nanocomposite.

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[*] Corresponding authors at: Hefei National Laboratory for Physical Science at Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China. Tel.: +86 551 6360 1589; fax: +86 551 360 7402.
E-mail addresses: ychzhu@ustc.edu.cn (Y. Zhu), ytqian@ustc.edu.cn (Y. Qian).

[1] Tel: +86 551 63601589.

[2] Tel: +86 551 63607234.

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Introduction

Selenium, an element belonging to the same group as sulfur in the periodic table and showing a similar redox mechanism to sulfur [1], has been proposed to be a new promising cathode material for rechargeable lithium batteries, because it could provide several advantages over widely studied sulfur systems, including its higher electrical conductivity (10^{-5} S/cm; cf. 5×10^{-30} S/cm), comparable volumetric capacity (3253 A h/L based on 4.82 g/cm^3; cf. 3467 A h/L based on 2.07 g/cm^3), a higher output voltage (at least 0.5 V higher than Li-sulfur cells) and greatly alleviated dissolution of polyselenides [2-4]. Unfortunately, some fundamental problems remain to be resolved to further improve the performance of the Li-Se batteries, such as the low utilization of selenium, the drastic volume variation and low lithium ion and electron transport property during cycling [3,5].

Recently, extensive research has been focused on confining selenium in various carbon hosts via a melt-diffusion method over 260 °C to improve the electrical conductivity and utilization of selenium within the electrodes [3,5-10]. For example, using the hierarchically micro-mesoporous carbon spheres to encapsulate Se can improve the Se utilization and the cathodes maintain high reversible discharge capacities of 540 mA h/g at current density of 0.1 C after 100 cycles [7]. A Se composite confined within porous carbon nanospheres showed high volumetric capacity density of 3150 mA h/cm^3 and excellent rate capability (retains 57% of the theoretical capacity at 20 C) [8]. As our previous work, by dispersing moderate selenium in the interconnected porous hollow carbon bubbles this Se/C cathode also exhibited good cycling stability and favorable rate capability [10]. Noting that the structures and morphologies of these Se/C composites are all dependent on the carbon hosts. And the selenium is usually amorphous after high-temperature heating with the carbon hosts. Relatively little emphasis has been placed on confining selenium within the conducting polymer or carbon with controlled morphology, which maybe a more efficient strategy to improve the electrochemical performance. Among the various morphologies of selenium [11-14], selenium nanowires are extremely attractive since this special one-dimensional character not only can accommodate volume expansion without pulverization, but can facilitate axial charge transport and short radial Li ion diffusion distances, which have been verified by other electrode materials, such as Si, SnO_2, V_2O_5, etc [15-17]. And to keep the one-dimensional structure, the selenium nanowires composited with the conducting polymer or carbon should be operated at low temperature without heating because of the low melting point of selenium.

In this work, combined with the conducting polymers of PANI [17-20], and graphene with the superior electrical conductivity [21,22], we design and synthesize a superior nanocomposite of graphene-encapsulated selenium/polyaniline core-shell nanowires (G@Se/PANI) under the condition of low temperature without heating, which is very different from the traditional melt-diffusion method, as shown in Scheme 1. Starting from the 1D selenium nanowires, the conductive PANI was first closely covered onto the surface of the selenium nanowires forming a core/shell structure via an in situ chemical oxidative-polymerization method, resulting in the unique Se/PANI core-shell nanowires (Scheme 1a to b). Noting that the surface of the PANI shell is positively charged in the acidic solution because of the existence of amino functional groups. And when the negtively charged graphene oxide (GO) was mixed with the dispersible Se/PANI core-shell nanowires, electrostatic interactions existed between negatively charged hydrophilic GO nanosheets and positively charged PANI shell. GO sheets might encapsulate Se/PANI core-shell nanowires to form the GO@Se/PANI composites due to the favorable flexibility and strength of GO nanosheets (Scheme 1b to c). The GO was finally reduced to reduced graphene oxide (G) by chemical reduction, leading to G@Se/PANI. In this composites, selenium nanowires are well-sealed in the PANI layer with a thickness of ≈25 nm forming a core/shell structure. Elastic graphene sheets are then introduced to encapsulate the Se/PANI core-shell nanowires. When evaluated as cathode materials for Li-Se batteries, the as-synthesized GO@Se/PANI nanocomposite exhibits enhanced cycle stability (567.1 mA h/g at 0.2 C after 200th cycle) and high-rate capability (510.9 mA h/g at 2 C). This might open new avenues for the design of other electrode materials with large volume variations and low electrical conductivity in order to achieve high-performance lithium batteries.

Experimental

Materials synthesis

Preparation of selenium nanowires

Selenium nanowires were synthesized according to the literature with some modifications [23]. All the chemical reagents used here were analytical grade without further purification. In a typical reaction process, SeO_2 (0.25 g) and β-cyclodextrin (0.25 g) were added into a glass beaker containing 50 mL distilled water. The mixture was stirred for about 10 min to give a clear solution, which was promptly poured into another glass beaker containing ascorbic acid solution (50 mL, 0.028 M) under continuous stirring. After reacting for 4 h, the product was collected by centrifugation and washed with deionized water and absolute ethanol several times. Then it was re-dispersed in ethanol and allowed to age for 2 h without stirring. After that, the products were dried in a vacuum at 60 °C for 5 h.

Preparation of G@Se/PANI

GO was synthesised by a modified Hummers method [24]. The Se/PANI core-shell nanowires were prepared by an in situ chemical oxidative polymerization at the freezing temperature. The obtained selenium nanowires were dispersed into a mixed solution (27 mL distilled water and 3 mL acetone) in a round bottomed flask (150 mL) with sonication assistant. Aniline monomer (0.02 g) and dilute hydrochloric acid solution (10 mL, 2 M) were added into it and the mixture was stirred vigorously for 2 h. Subsequently, an aqueous solution of $(NH_4)_2S_2O_8$ (APS) (0.07 g dissolved in 10 mL distilled water) as an oxidant was added dropwise to the above reactant mixture under continuously stirring.