Materials Letters 223 (2018) 45–48

Contents lists available at ScienceDirect

Materials Letters

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

Self-assembled samarium selenide nanorods as a new electrode material for reliable supercapacitors

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ARTICLE INFO

Article history:
Received 8 February 2018
Received in revised form 18 March 2018
Accepted 3 April 2018
Available online 4 April 2018

Keywords:
Nanorods
Samarium selenide
X-ray techniques
XPS
Supercapacitors
Specific capacitance

ABSTRACT

For the first time, cross-linked nanorods of samarium selenide (Sm_2Se_3) were self-assembled using the chemical route for reliable supercapacitors. The X-ray diffraction and X-ray photoelectron spectroscopy techniques confirmed the formation of crystalline Sm_2Se_3. The formation of Sm_2Se_3 across-linked nanorods was confirmed by field emission scanning electron microscopy technique. The cyclic voltammetry, charge-discharge, and electrochemical impedance spectroscopy were used to study the supercapacitive properties of the electrode. The highly porous network of the electrode resulted from this assembly exhibited excellent capacitive behavior with a maximum specific capacitance (316 F g^{-1}) and cycling stability (87%) for 1000 charge-discharge cycles.

1. Introduction

Ever enhancing demand for reliable and safe energy for the hybrid electric vehicle, power backups, and portable devices have led to focus more attention on energy storage devices [1,2]. Recently investigated supercapacitors are turning out to be one of the best energy storage devices for various appliances. The prime requirements for electrodes in supercapacitors are high conductivity, well-defined redox states and highly porous microstructure [3]. Basically, electrode materials such as conducting carbon allotropes, metal oxides, and conducting polymers are employed in supercapacitors. The carbon-based supercapacitors also called an electric double layer capacitor (EDLC) involve adsorption-desorption of charges (non-faradaic processes) at the electrode-electrolyte interface. On the contrary, metal oxide or conducting polymer-based supercapacitors perform fast and reversible redox reactions (faradic processes) and are called as pseudocapacitors [4,5]. Recently hybrid capacitors were developed in which electrodes are composite of carbon-based nanostructured material and metal oxide/conducting polymer [6]. None of these have been able to fulfill desired power and energy requirements.

There are various key factors associated with an electrochemical performance of any supercapacitor cell. The first and foremost is the ohmic loss arising as a result of higher equivalent series resistance which depends on the intrinsic resistance of electrode and contact resistance between the electrode and current collector [7]. For example, if horizontally aligned graphene nanosheets to the current collector are used as an electrode in supercapacitors, it enhances contact resistance and thereby puts a limitation on energy and power density of supercapacitors [8]. Another is lower working potential due to an aqueous electrolyte and low redox potential of electrode also reduces these densities. Therefore, there is need of new electrode material exhibiting more conductive nature, higher redox potential with multiple oxidation states and the porous microstructure having fairly vertical alignment of the nanostructure to a current collector.

The metal chalcogenides are emerging as the new class of materials for energy storage application [9]. Out of these, metal selenides are more conductive than its sulfide and/or telluride and therefore may be used in supercapacitors with reduced ohmic losses. But there are very few articles related to the metal selenide based supercapacitors [10,11]. In this communication, we demonstrate direct assembly of samarium selenide (Sm_2Se_3) nanorods to the current collector and their application for supercapacitors. In addition to conductive nature of samarium selenide, an extra advantage of higher reduction potential and multiple oxidation

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https://doi.org/10.1016/j.matlet.2018.04.016
0167-577X/

states of samarium have been taken to enhance supercapacitive properties like specific capacitance, working potential window, power and energy densities using non-aqueous $LiClO_4$-propylene carbonate electrolyte.

2. Experimental section

The AR grade chemicals of $Sm(NO_3)_3$, TA, selenium and sodium sulfite (Na_2SO_3) were used for the deposition. Initially, 10 ml of 0.1 M $Sm(NO_3)_3$ aqueous solution was prepared and complexed by addition of an appropriate amount of tartaric acid. To this, a separately formed 0.15 M Na_2SeSO_3 solution (see ESI) was added dropwise. The pH of the resultant solution was controlled to 12 (±0.1) using ammonia (NH_4OH) solution. The bath was heated slowly to attain a temperature of 353 K and then well cleaned stainless steel substrates were dipped into the bath. At the temperature of 353 K, the precipitation started in the bath and onto the substrate forming Sm_2Se_3 nanorods.

3. Results and discussion

Fig. 1 shows the schematic for the formation of Sm_2Se_3 cross-linked nanorods. Initially, nucleation took place by combing the Sm^{3+} and Se^{2-} ions on the substrate surface (heterogeneous nucleation) and/or in the solution (homogeneous nucleation). It was then followed by growth of nucleation sites that resulted in a

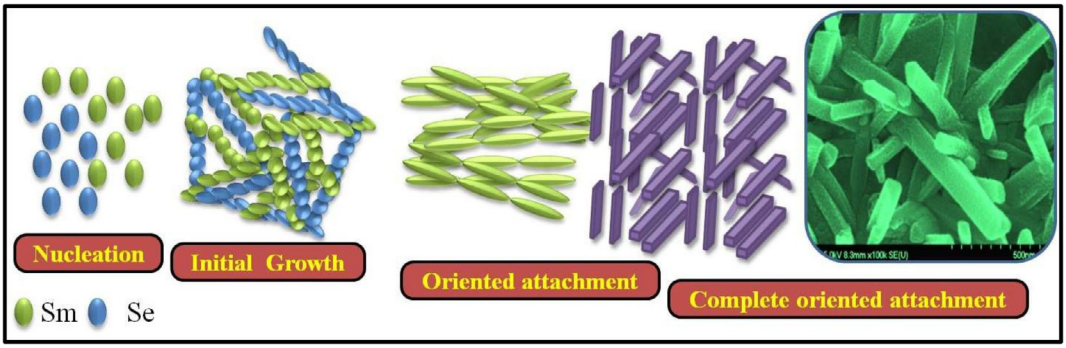

Fig. 1. Schematic for the formation of Sm_2Se_3 nanorods.

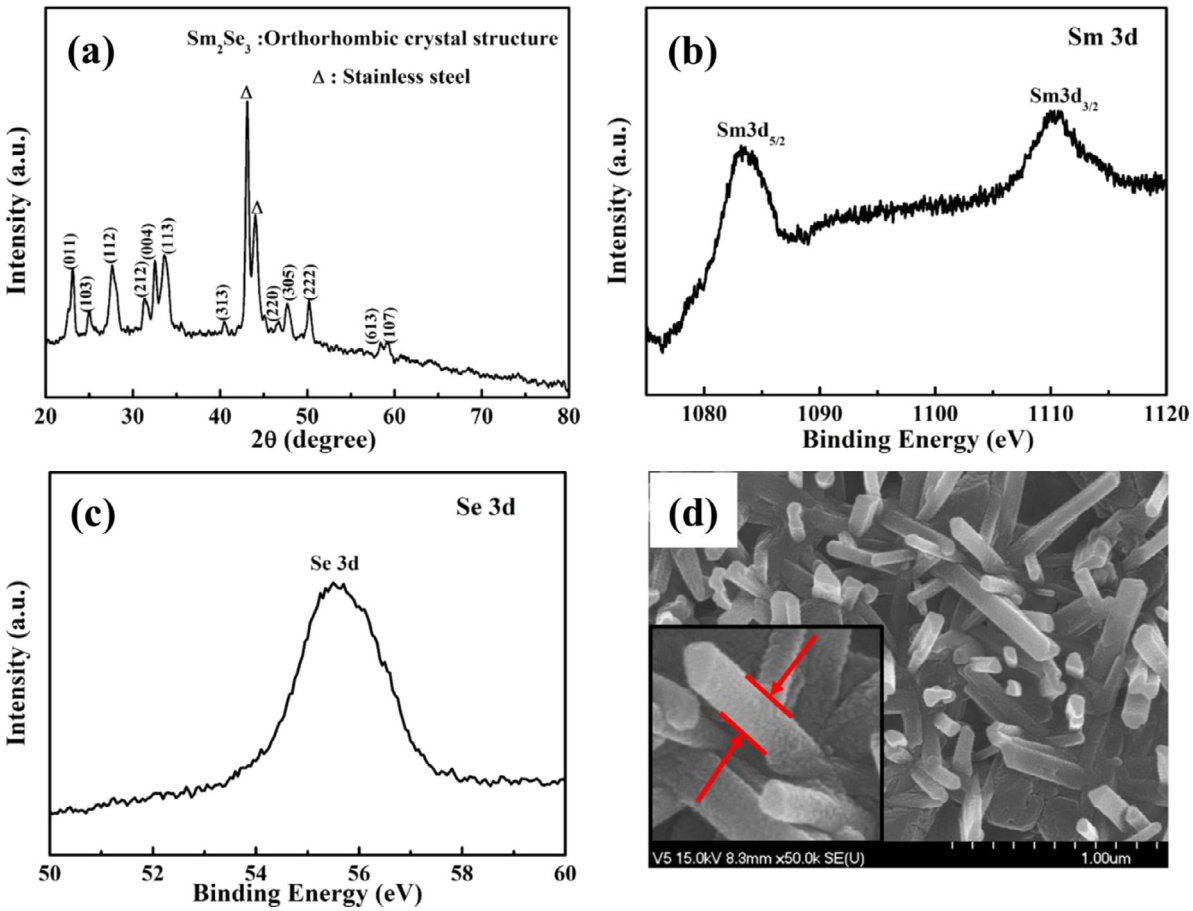

Fig. 2. (a) XRD pattern, (b) XPS spectra of Sm 3d, (c) XPS spectrum of Se 3d regions of Sm_2Se_3 and (d) FE-SEM image of the Sm_2Se_3 nanorods. (Inset shows the magnified high resolution image).