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Short Communication

Porous network of samarium sulfide thin films for supercapacitive application

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ABSTRACT

In the present letter, a novel aqueous chemical method is employed to prepare thin film of Sm_2S_3 material containing porous network of interconnected nanoparticles for supercapacitive application. The orthorhombic phase formation of Sm_2S_3 film is concluded from X–ray diffraction study. The chemical states of samarium and sulfur are determined using X–ray photoelectron spectroscopy study. The pseudocapacitive behavior of Sm_2S_3 showed a maximum specific capacitance of 248 F g^{-1} in 1.5 M $LiClO_4$ electrolyte prepared in propylene carbonate electrolyte. The nature of charge and discharge curves confirmed pseudocapacitive behavior of film electrode. The highest power and energy densities of 15.6 kWh kg^{-1} and 54.6 Wh kg^{-1}, respectively are obtained. An electrochemical stability of 94% is retained after 1500 cycles.

1. Introduction

Electrochemical supercapacitors are developing rapidly to replace the low energy density conventional dielectric capacitors and low power density batteries. The supercapacitor bridges the gap between dielectric capacitors and batteries [1]. Present research is focused in tuning the physicochemical properties of both electrode material and electrolyte so as to have best of the possible supercapacitive devices. Such supercapacitors can be used in hybrid electrical vehicle, cell phones, military missile systems etc [2]. The supercapacitors are classified depending upon charge storage mechanism namely electric double layer capacitors (EDLC), pseudocapacitors and hybrid supercapacitors. The EDLCs store charges using non–faradaic reactions and possess highest electrochemical stability. The supercapacitors based on activated carbon, carbon aerogels etc., belong to EDLCs [3]. The pseuocapacitors use metal oxides like MnO_2, RuO_2 etc., as electrode material in which cation undergoes transition of oxidation states to store charges [4]. The hybrid supercapacitors make use of both faradic and non–faradic reactions for charge storage [5].

The metal sulfides are emerging as a new class of pseudocapacitve materials. Recently, CuS, NiS etc. are studied as supercapacitive electrode materials but their potential window is limited due to lower reduction potential of metal cation involved and use of aqueous electrolytes [6,7], which results into poor energy and power densities. The rare earth element like samarium is widely studied as a dopant for its application in fuel cells and photoluminescence [8,9]. The samarium having higher reduction potential and multiple oxidation states when combined with sulfur to form a samarium sulfide can be used as supercapacitve electrode to improve the potential window of supercapacitors. The present paper reveals preparation of Sm_2S_3 thin films using modified chemical deposition method and their

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supercapacitive parameters evaluation in non aqueous $LiClO_4$: propylene carbonate electrolyte.

2. Experimental

The Sm_2S_3 thin films were deposited using a simple and inexpensive successive ionic layer adsorption and reaction (SILAR) method. The commercially available AR grade samarium nitrate ($Sm_2(NO_3)_3$) and sodium sulfide (Na_2S) were used for the deposition of Sm_2S_3 thin films. A 10 ml of 0.1 M $Sm_2(NO_3)_3$ solution (pH∼5) was used as a source of cations and 10 ml of 0.15 M Na_2S solution (pH∼13) was used as a source of anions. The process of Sm_2S_3 deposition was carried out in four steps. In the first step, well cleaned stainless steel substrate was dipped into cationic bath of $Sm_2(NO_3)_3$ solution for 30 s in order to to adsorb Sm^{3+} ions onto the substrate. In the second step, substrate was rinsed in double distilled water (DDW) for 20 s to remove loosely adsorbed Sm^{3+} ions. In the third step, the substrate was dipped in anionic Na_2S solution 30 s where S^{2-} ions react with preadsorbed Sm^{3+} ions. Finally, the substrate was again rinsed in DDW for 20 s to remove unadsorbed S^{2-} ions and loosely bound Sm_2S_3 particles. This completes one deposition cycle. Such 90 cycles were repeated and maximum film thickness of 0.36 μm was obtained. These films were annealed at 473 K for 4 h to improve grain growth and crystallinity.

The crystal structure of films was examined using a Bruker AXS Advance X-ray diffractometer with primary monochromatic radiation from CuK_α ($\lambda = 1.54$ Å). The chemical state of the elements was determined from X-ray photoelectron spectrometer (ThermoVG Scientific, United Kingdom). The surface morphology was observed using field emission scanning electron microscope (FESEM, JEOL 6360, Japan). The automatic battery cycler system (WBCS–3000) and electrochemical impedance analyzer (model, CHI6112D) were employed to determine supercapacitive parameters.

3. Results and discussion

The X-ray diffraction (XRD) pattern of Sm_2S_3 film is shown in Fig. 1(a). The peaks corresponding to the reflections

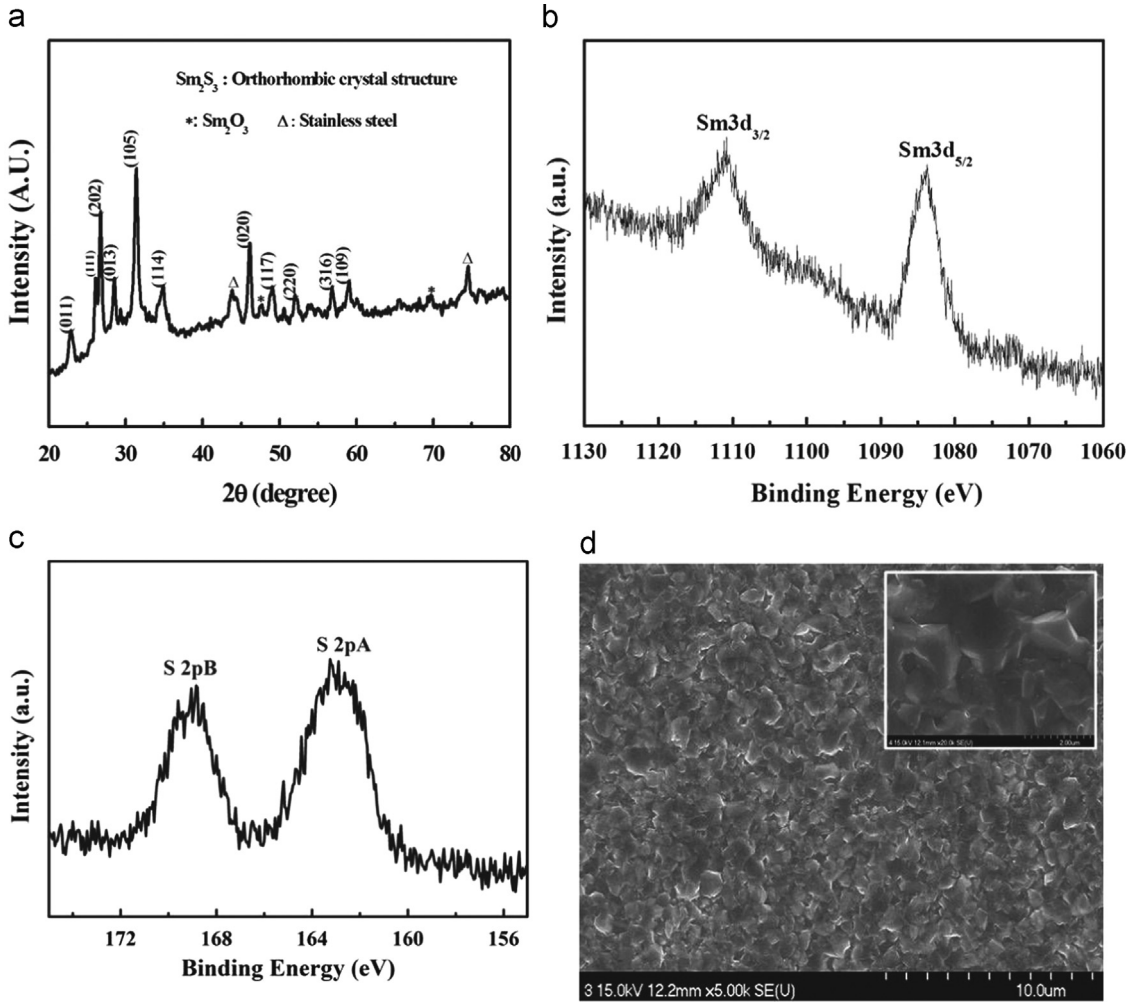

Fig. 1. (a) The XRD pattern of Sm_2S_3 film, XPS spectra of (b) Sm3d region, (c) S2p region of Sm_2S_3 film and (d) FESEM image of Sm_2S_3 at 5000 × magnification. Inset shows same image with 20,000 × magnification.