Electrochemical behavior of hydrothermally synthesized porous groundnuts-like samarium oxide thin films

S. B. Ubale¹ · T. T. Ghogare¹ · V. C. Lokhande² · T. Ji² · C. D. Lokhande¹

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Abstract

One pot hydrothermal method is used for synthesis of groundnuts-like samarium oxide (Sm_2O_3) thin film on stainless steel substrate. The Sm_2O_3 film is characterized by X-ray diffraction, water contact angle, UV–visible spectrophotometer, photoluminescence, and field emission scanning electron microscopy techniques. The hydrothermal method allows the formation of cubic Sm_2O_3 film with porous groundnuts-like morphology. The Sm_2O_3 film is hydrophilic with the optical band gap of 3.70 eV. Electrochemical capacitive behavior of Sm_2O_3 film is studied using cyclic voltammetry, galvanostatic charge–discharge measurement and electrochemical impedance spectroscopy. The Sm_2O_3 film exhibits maximum specific capacitance of 155 Fg^{-1} at 5 mVs^{-1} scan rate in 1 M KOH electrolyte.

Keywords Electrochemistry · Hydrothermal method · Samarium oxide · Supercapacitor · Thin film

1 Introduction

Periodic table contains seventeen rare earth elements including yttrium, scandium and lanthanide series elements. Most of the rare earth elements are found in China, Australia, and United States of America (USA) [1, 2]. The rare earth elements are thermally stable at high temperature and good refractory materials due to their physical and chemical properties [3]. The rare earths elements and their compounds have applications in devices such as supercapacitor and gas sensor [4], catalysis [5], magnetic and biochemical sensors [6, 7], solar cells [8] and luminescence [9].

The rare earth oxides and hydroxides in powder and thin film forms are synthesized using different chemical as well as physical methods such as atomic layer deposition (ALD) [10], metal organic chemical vapor deposition (MOCVD) [11] and pulsed layer deposition (PLD) [12].

The samarium is one of the rare earth elements having multiple oxidation states (Sm^{+3} , Sm^{+2} , Sm^{+1}) in various compounds. Antoinette and Israel [13] synthesized Sm_2O_3 nanostructured powder by combustion method and studied its optical properties. Roselin et al. [14] prepared Sm_2O_3 thin films by a spin coating method and investigated optical and luminescent properties. Yang et al. [15] synthesized Sm_2O_3 thin films using the epitaxial method and scrutinized dielectric properties. Also, Sm_2O_3 nanoparticles in powder form are synthesized using precipitation reaction method by Mehdi et al. [16] and hydrogen plasma-metal reaction method by Liu et al. [17]. Kumbhar et al. [18–20] synthesized of Sm_2S_3 thin films using the successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) methods and studied their supercapacitive properties.

As compared with reported synthesis methods, hydrothermal is a chemical method to prepare various metal oxide materials in thin film form with various porous

✉ C. D. Lokhande, l_chandrakant@yahoo.com | ¹Centre for Interdisciplinary Research, D.Y. Patil Education Society (Deemed To Be University), Kolhapur 416 006, India. ²Department of Electrical, Electronic Communication and Computer Engineering, Chonnam National University, Yongbong-Dong, Puk-Gu, Gwangju 500 757, South Korea.

nanostructured surface morphologies on different type of substrates (conducting or non-conducting). It is a convenient, facile and binder free method for large area deposition of different materials [21].

To the best of our knowledge, there are no reports on hydrothermally synthesised Sm_2O_3 thin films and their electrochemical study. In this communication, for the first time, Sm_2O_3 thin films are prepared by hydrothermal method and their electrochemical properties are evaluated. Also, the structural, water contact angle, optical, photoluminescence and morphological properties are studied.

2 Experimental

2.1 Materials used

AR grade samarium (III) chloride ($\text{SmCl}_3 \cdot 7\text{H}_2\text{O}$), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) and urea ($\text{CH}_4\text{N}_2\text{O} \cdot 5\text{H}_2\text{O}$) were used without further purification and double distilled water (DDW) was used as a solvent in the experiment. All solutions were freshly prepared and used for synthesis of Sm_2O_3 films.

2.2 Synthesis of Sm_2O_3 thin film

The one pot hydrothermal method was used for the synthesis of Sm_2O_3 thin films on the stainless steel (SS) (304 grade) substrate. The reaction bath contained solution mixture of 0.01 M samarium trichloride ($\text{SmCl}_3 \cdot 7\text{H}_2\text{O}$), 0.03 M urea ($\text{CH}_4\text{N}_2\text{O} \cdot 5\text{H}_2\text{O}$) and 0.05 M tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$). The well cleaned SS substrate was placed vertically in a reaction bath and this bath was kept in a hydrothermal autoclave at 394 K for 3 h. The whitish-gray colored Sm_2O_3 film was obtained after 3 h on SS substrate. The film was dried at room temperature (300 K) and used for further characterization as well as electrochemical evaluation. For optical characterization, glass substrate was used.

2.3 Sm_2O_3 thin film characterization

The crystallographic study of Sm_2O_3 film was carried out using X-ray diffractometer (Rikagu 600 mini flex). The surface morphology of Sm_2O_3 film was examined by field emission scanning electron microscope (model Crossbeam 1560 XBFIB workstation). The water contact angle was measured by Rame-Hart USA. The optical absorption study in the wavelength range of 200 to 800 nm was carried out using UV-Visible spectrophotometer.

Electrochemical behavior was tested in three electrode cell system using Sm_2O_3 thin film as a working electrode, platinum as a counter electrode and saturated calomel electrode (SCE) as a reference electrode using battery

cycler (ZIVE MP1 workstation, S. Korea). The cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) and electrochemical impedance (EIS) of system were studied in 1 M KOH electrolyte.

3 Results and discussion

Figure 1a shows the XRD pattern of Sm_2O_3 thin film. The peak positions corresponding to (211) and (222) planes of the cubic structure of Sm_2O_3 are identified (JCPDS no.88–2166). The crystallite size is determined by Scherer's relation as,

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where k is the proportional constant and its value is 0.89, λ is the wavelength of X-ray diffraction, β is the full width half maxima and θ is angle of diffraction. The estimated crystallite size is 8.3 nm using the plane (222). The peak in XRD pattern shown by the hash (#) corresponds to the SS substrate. The formation of cubic crystal structure of Sm_2O_3 film is also reported by other workers for hydrothermally deposited Sm_2O_3 thin films. Yan et al. [22] prepared Sm_2O_3 thin film on glass substrate and observed orientations along (222) and (211) planes. Kang et al. [23] also observed orientations along (222), (211) and (400) planes.

The water contact angle measurement was carried out to find out hydrophilic/hydrophobic property of film surface and it is found that Sm_2O_3 electrode exhibits a hydrophilic surface with a water contact angle of 28.6° , as shown in Fig. 1b. Kumbhar et al. [24] observed 45° water contact angle for α - Sm_2S_3 thin film synthesized using SILAR method. Pujari et al. [25] observed 49.7° water contact angle for ytterbium sulfide thin film synthesized by

Fig. 1 **a** X-ray diffraction pattern and **b** water contact angle measurement of Sm_2O_3 thin film

Fig. 2 **a** Plot of the absorbance (αt) versus wavelength (nm) of Sm_2O_3 film deposited on glass substrate. [Inset shows plot of $(\alpha h\nu)^2$ versus $h\nu$ (photon energy)] and **b** photoluminescence spectrum of Sm_2O_3 film

one pot hydrothermal method. For the supercapacitive performance, hydrophilic characteristic of electrode material is beneficial. The hydrophilic nature of surface electrode causes facile interaction between electrolyte ions and the electrode material surface [26]. Hydrophilic and nanocrystalline natures of material are the requirements for the enhancement of supercapacitive performance.

Figure 2a shows the variation of optical absorption (α) with wavelength (λ) for Sm_2O_3 film deposited on glass substrate. The optical spectrum indicates high absorption in the visible region. The band gap energy of Sm_2O_3 thin film is estimated using following relation.

$$\alpha = A(E_g - h\nu)^n / h\nu \quad (2)$$

where α is known as absorption coefficient, A is constant, E_g is optical band gap of material, ν is frequency of radiation and h is Planks constant, n is 2 for indirect band gap and 1/2 for direct band gap material. Inset of Fig. 2a shows plot of $(\alpha h\nu)^2$ versus $h\nu$ (photon energy). From this, the band gap of Sm_2O_3 electrode is found to be 3.70 eV. Huang et al. [27] reported band gap values of hydrothermally synthesized Sm_2O_3 electrode between 3.75 to 3.95 eV.

The photoluminescence spectrum of Sm_2O_3 electrode is illustrated in Fig. 2b, with excited wavelength in the range of 300–600 nm. The strong emission of Sm_2O_3 electrode is in the visible range of spectrum (575 nm). The luminescence characteristic of Sm_2O_3 electrode shows the presence of single defect level, which may be useful in LED applications [13].

The FE-SEM technique was used to examine surface morphology of Sm_2O_3 thin film. Figure 3a, b shows surface micrographs of Sm_2O_3 thin film at magnifications of 80 kX and 100 kX. The Sm_2O_3 film shows porous groundnuts-like morphology spread all over the substrate (Fig. 3a). The elongated groundnuts of about 150 nm in size are seen in inset of

Fig. 3 FE-SEM images of Sm_2O_3 thin film at **a** 80 kX and **b** 100 kX magnifications

Fig. 3b. The porous groundnuts-like structure offers a higher accessible surface area and more intercalation/deintercalation of electrolyte ions for enhancing of specific capacitance. Similar type of morphology is observed for manganese/carbon hybrid by hydrothermal method by Wang et al. [28]. Different types of morphologies of rare earth compounds, depending on method of preparation have been reported in the literature. Yadav et al. [4, 29] synthesized lanthanum oxide films by spray pyrolysis and chemical bath deposition methods and observed porous honey comb-like and rod shaped morphologies, respectively. Ghogare et al. [30] prepared lanthanum sulfide thin film by hydrothermal method and obtained nanopetals-like porous morphology. Patil et al. [29] obtained cinnamon-like lanthanum telluride thin films by chemical bath deposition method. Pujari et al. [25] obtained nanorod like surface morphology of ytterbium sulfide thin film by hydrothermal method, while Kumbhar et al. [31] observed barley-like morphology for chemically deposited samarium telluride films.

The electrochemical behavior of Sm_2O_3 electrode is studied in 1 M KOH electrolyte at different scan rates using cyclic voltammetry (CV). As shown in Fig. 4a, current area under the curve increases with increasing scan rate in negative potential window of -1.2 to -0.5 V/SCE.

The electrochemical capacitance is determined by following equation,

$$(C_s) = \frac{\int_{V_1}^{V_2} I(V) dv}{s \times m \times (V_2 - V_1)} \quad (3)$$

where $\int_{V_1}^{V_2} I(V) dv$ is the integrated current response of Sm_2O_3 electrode, s is a scan rate in mVs^{-1} , m represents the mass of difference between before and after film deposition in mgcm^{-2} . V_1 and V_2 represent initial and final potential in volt, respectively. The maximum electrochemical

Fig. 4 **a** The CV curves of Sm_2O_3 electrode at different scan rates in 1 M KOH electrolyte, **b** plot of specific capacitance versus scan rate and **c** galvanostatic charge–discharge curves of Sm_2O_3 electrode at current densities 0.2–0.5 mAcm^{-2}

capacitance of 155 Fg^{-1} is observed at scan rate 5 mVs^{-1} . This value is comparable with reported values for other rare earth chalcogenides. Ghogare et al. [30] reported specific capacitance of 121.42 Fg^{-1} in 1 M Na_2SO_4 electrolyte for $\beta\text{-LaS}_2$ thin films whereas Yadav et al. [29] obtained specific capacitance of 147 Fg^{-1} in 1 M KOH electrolyte for La_2O_3 thin films. In electrochemical study, specific capacitance (C_s) is based on nature of electrolyte ions and potential window. The intercalation/deintercalation of electrolyte ions with Sm_2O_3 electrode is represented as follows,

Figure 4b illustrates the plot of specific capacitance versus scan rate. The maximum specific capacitance of 155 Fg^{-1} is achieved at scan rate 5 mVs^{-1} . Increased specific capacitance at lower scan rate is due to of high intercalation/deintercalation of charges/ions between electrode surface and electrolyte [26]. Figure 4c shows that the galvanostatic charge/discharge (GCD) curves are non-linear at the current densities of 0.2–0.5 mAcm^{-2} , which confirm the pseudocapacitive nature of Sm_2O_3 electrode [32]. The maximum specific capacitance of 120 Fg^{-1} is exhibited at 0.2 mAcm^{-2} current density. The porous groundnuts-like nanostructure helps to more intercalation/deintercalation of electrolyte ions and improves the capacity of charge storage

Fig. 5 Nyquist plot (Inset shows the equivalent circuit) of Sm_2O_3 thin film

The Nyquist plot is used to study of basic properties of electrode material for electrochemical performance. The Nyquist plot in Fig. 5 shows high impedance in the frequency range 0.1 to 1000 Hz at A.C. amplitude 10 mV. It shows an almost vertical line in the low-frequency region, representing the preferred capacitive behavior. The equivalent series resistance (ESR) of $1.2 \Omega \text{ cm}^{-2}$, charge transfer resistance (R_{ct}) of $2.39 \Omega \text{ cm}^{-2}$ and Warburg resistance (W) $2.14 \text{ k} \Omega$ are estimated from the Nyquist plot. An equivalent circuit for the total equivalent impedance is shown in the inset of Fig. 5. The values of solution resistance and equivalent charge transfer resistance for Sm_2O_3 electrode are comparable to the values of $\beta\text{-LaS}_2$ [30].

4 Conclusions

The porous groundnuts-like Sm_2O_3 thin film is synthesized on stainless steel substrate using inexpensive one pot hydrothermal method. The Sm_2O_3 film exhibits cubic crystal structure. The groundnuts-like morphology combined with hydrophilic nature of film, result in electrochemical capacitance of 155 Fg^{-1} . This study indicates that Sm_2O_3 electrode is a promising candidate as an anode material for next generation asymmetric supercapacitor devices.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interests.

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