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Hydrothermal assisted growth of vertically aligned platelet like structures of WO_3 films on transparent conducting FTO substrate for electrochromic performance

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ABSTRACT

Controlled growth of nanostructured metal oxide films growing on the conducting substrates with good adhesion in a single step process via hydrothermal method is still challenging. In the present work, WO_3 platelets were deposited on transparent conducting fluorine doped tin oxide substrates by single step hydrothermal process via tailoring the reaction time (8 h, 12 h and 16 h) and reaction temperature (120 °C and 180 °C). X-ray diffraction analysis showed that the WO_3 thin films grown at 120 °C for 8 h and 12 h reaction time comprised with mixed phases of hexagonal and monoclinic system, whereas 16 h of reaction time produced single phase monoclinic system. However the WO_3 films deposited at 180 °C for 8 h, 12 h and 16 h reaction time acquired monoclinic system. Raman spectrum showed the stretching and bending modes of WO_3. The WO_3 films deposited at 120 °C and 180 °C for different reaction time 8 h, 12 h and 16 h exhibited various surface morphology such as buds like, bricks like, platelets like and sheets with platelets like structures. Optical studies showed that the transmittance of WO_3 film is decreased with increase in the reaction temperature. The WO_3 film deposited at 120 °C for 12 h reaction time acquired transmittance of about 86% at 463 nm whereas the film deposited at 180 °C for 12 h reaction time showed transmittance of about 75% at 465 nm. The direct and indirect optical band gap of the deposited WO_3 films varies in the range 2.5 eV– 2.9 eV and 2.6–2.75 eV respectively with varying growth parameters. The electrical properties of WO_3 film deposited at 120 °C for 12 h showed relatively low resistivity (1.8×10^{-3} Ωcm) and high carrier concentration (9.3×10^{19} cm^{-3}). The electrochromic studies carried out for the WO_3 film synthesized at 120 °C for 16 h exhibits high peak current density, diffusion coefficient and fast switching kinetics with respect to other deposited films.

1. Introduction

Electrochromic materials attracted great interest ever since the discovery of electrochromism for about four decades ago [1]. Various groups working elsewhere have been taking efforts to synthesis novel electrochromic (EC) materials and to improve the electrochromic property of the materials to make them suitable for various applications in EC displays [2], smart windows [3,4], dye-sensitized solar cells [5,6], sensors [7,8] and lithium ion batteries [9,10]. Semiconducting metal oxides in the form of thin films with various nanostructures have paved the ways for improving the electrochemical property. Thus active research has been carried out on semiconducting metal oxides like NiO_2, IrO_2, V_2O_5 and WO_3 to use them as cathodic and anodic electrodes in electrochromic applications [11]. Among the various metal oxides, WO_3 has been recognized as one of the most important and promising inorganic cathode electrode materials due to its distinct electrochromic response, high cyclic stability, high coloration efficiency and intercalation property [12,13]. The WO_3 also finds applications in photocatalytic degradation [14,15], lithium ion batteries [16], photoluminescence [17] and gas sensors [18,19]. The nanostructured arrays aligned vertically on the conducting substrates offer large surface area with improved properties than that of the bulk materials because of their intrinsic structural features [20].

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The nanostructured arrays also enhance the interaction between electrochromic materials and electrolytes (H^+ or Li^+) which lead to accelerate the ion and electron intercalation and de-intercalation process [11,21]. Nanostructured arrays of WO_3 thin films with different surface morphologies such as nanorods [22–24], nanowires [25–27], nanoplates [28–30], nanoflowers [1] and nanobricks [31] formed on the conducting FTO substrates have been fabricated by many researchers inorder to improve the electrochromic properties of WO_3. Vertically aligned 1D/2D nanostructured WO_3 thin film has been prepared on the FTO substrate which enhanced the conductivity and showed improved electrochromic property [32].

Many deposition methods have been employed in depositing WO_3 thin films which include spray pyrolysis [33], e-beam evaporation [34,35], sputtering [36], hydrothermal [20,37], solvothermal [26], electrodeposition [1] and pulsed laser deposition [38] methods. Among the numerous deposition methods reported to prepare WO_3 nanostructured films, hydrothermal method is a versatile one because of its cost effectiveness, facile and ability to control over the size and growth at low temperature. The deposition of WO_3 thin films over the WO_3 seed layer coated conducting substrates effectively control the morphology, density and orientation of nanostructured arrays. However the lattice mismatch between the FTO (lattice constant a = 4.75 Å and c = 3.196 Å; JCPDS card no: 77-0451) and the WO_3 (lattice constant for hexagonal a = b = 7.324 Å and c = 7.662 Å; JCPDS card no: 85-2460 and for monoclinic a = 7.300 Å, b = 7.538 Å, c = 7.689 Å and β = 90°; JCPDS card no: 85-0950) results in a long time response and poor cyclic stability, thus thereby supressing the electrochromic properties. Junchen Zhou et al. [20] reported that WO_3 nanoplate like structures deposited on the FTO substrate by adjusting the amount of HCl in the precursor solution revealed better photoelectron chemical cell (PEC) performance and better methyl orange degradation activities. Kondalkar et al. [39] reported that the nanometric WO_3 thin film prepared on ITO substrate by Langmuir-Blodgett technique showed improved electrochromism and fast switching kinetics for coloration and bleaching. Hung et al. [40] reported that 3-D hexagonal WO_3 nanowires synthesized on FTO substrate acquired high electrical conductivity, high optical modulation, fast switching time and long cyclic stability suitable for the large area smart window applications. Li et al. [41] reported that self-seeded WO_3 films grown on FTO substrate showed improved electrochromic performance than WO_3 thin film deposited on WO_3 seed layer assisted FTO substrate. Photocurrent density of nanostructured WO_3 films deposited on FTO substrate was reported [42–45].

However achieving controlled growth of various nanostructured WO_3 thin films on FTO substrate and WO_3 seeded FTO substrate via single step hydrothermal method is challenging. Hence in the present work we have made an attempt to synthesize vertically aligned WO_3 films directly on the FTO substrate with good adhesion by single step hydrothermal method using ammonium oxalate as a structure directing agent. The effect of hydrothermal reaction temperature (120 °C and 180 °C) and reaction time (8 h, 12 h and 16 h) on the structural, morphological, optical and electrical properties of WO_3 films is investigated. The correlation of these properties with electrochemical activity such as cyclic voltammetry, cyclic stability and response time of WO_3 films is discussed.

2. Experimental

2.1. Materials

Sodium tungstate dihydrate ($Na_2WO_4{\cdot}2H_2O$), hydrochloric acid (HCl) and ammonium oxalate ($(NH_4)_2C_2O_4$) procured from Sigma Aldrich were used as received. The bare FTO conductive glass substrates (7 Ω/cm^2) were used.

2.2. Preparation of WO_3 platelets on FTO substrate

The WO_3 films were deposited on FTO substrates by hydrothermal method. Sodium tungstate dihydrate of 0.231 g was dissolved in 30 ml double distilled water under constant stirring at room temperature. The pH of the solution was adjusted to ~2 by adding 3 M 10 ml HCl drop by drop. Ammonium oxalate (0.2 g) was added to the prepared solution under constant stirring. Further 40 ml of distilled water was added to the above solution with continuous stirring for about one hour which yielded 70 ml solution. Then the solution was transferred to 50 ml Teflon lined stainless steel autoclave. The FTO glass substrates cleaned with methanol in ultrasonicator and then dried in hot air oven at 60 °C were used. FTO substrates with the conducting side facing downwards and inclined to about 45° angle against the inner wall of the Teflon vessel were immersed into the solution. The substrates were placed upside down during the growth of the film with an inclination of 45° because the angle of inclination plays an crucial role on the surface morphology of the film whereas the position of the film upside down retains the germinated WO_3 nanocrystals [46,47]. The sealed autoclave was placed inside the muffle furnace and hydrothermal synthesis was carried out at reaction temperatures 120 °C and 180 °C in separate experiments and each experiment was carried out for different reaction time (8 h, 12 h and 16 h). After completion of reaction the autoclave was naturally allowed to cool to room temperature. The deposited WO_3 films were rinsed with double distilled water and ethanol and dried at 60 °C. The dried WO_3 films were annealed at 550 °C for one hour in a muffle furnace and characterized. The thickness of the WO_3 film deposited at 120 °C (8 h, 12 h and 16 h) varies from 1.52

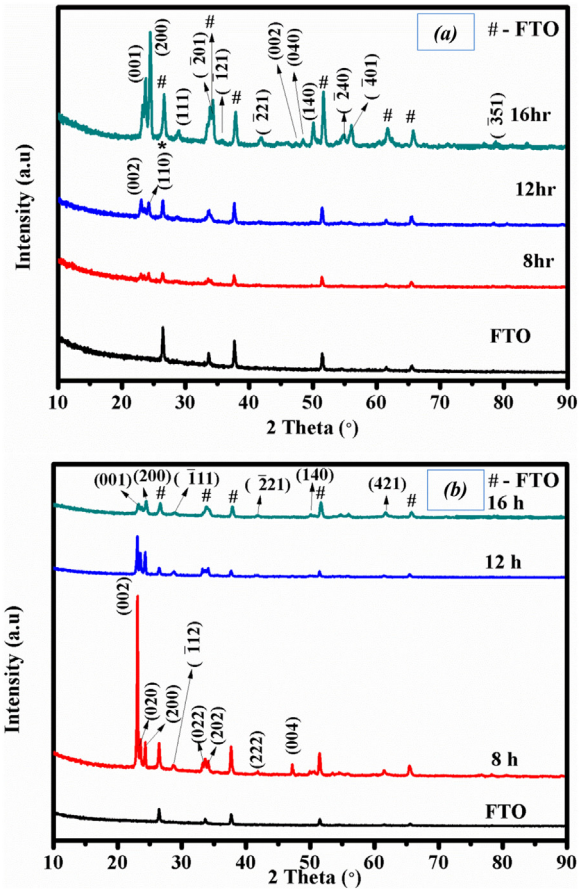

Fig. 1. XRD pattern of the WO_3 films prepared at (a) 120 °C (b) 180 °C for different reaction time 8 h, 12 h and 16 h.

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