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Effect of solution chemistry on the characteristics of hydrothermally grown WO_3 for electroactive applications

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ABSTRACT

Hydrothermally grown tungsten trioxide coatings were prepared at 95 °C using different metal sulfates. Morphology of the oxides was altered from grains to flower- and urchin-like structures using potassium sulfate, sodium sulfate and lithium sulfate, respectively. The flower-like structures presented the highest deintercalated charge, 35 mC cm^{-2} with time response of 96 s. In addition, they indicated a charge transfer resistance across the tungsten trioxide–electrolyte interface of 752 Ω. These outcomes imply that they are promising candidates for electroactive applications.

1. Introduction

Many attempts have been made for the growth of nanostructures because they offer potential advantages in technological applications due to their large surface area and size-dependent properties [1]. Towards this direction, the hydrothermal method has attracted attention because the nanoscopic morphologies can simply be controlled by the solution properties, growth time and temperature [2–5]. In addition, it is a cost-effective and environmental friendly technique as no toxic chemicals are required and the growth temperature can be as low as 95 °C.

Among the various metal oxides, tungsten trioxide (WO_3) is a versatile wide bandgap semiconductor with many valuable applications in gas sensors [6], photocatalysts [4], electrochromics [7], batteries [8] and capacitors [9]. Hexagonal form of WO_3 is of great interest owing to its well-known tunnel structure, which has been investigated as an intercalation host for obtaining hexagonal tungsten bronzes M_xWO_3 ($M = Li^+$, Na^+, K^+ etc.). Hence, the crystal structure, dimensionality and size of the WO_3 nanostructures can be regarded as critical factors that may provide novel performances [10–16].

The preparation of oriented hexagonal WO_3 nanotrees on tungsten plate substrate has been reported by Shibuya and Miyauchi [17,18]. However, their photoelectrochemical application is limited by the opacity of the substrate. Hexagonal WO_3 nanowire arrays have been synthesized on fluorine doped tin dioxide (FTO) substrates by solvothermal technique. In this case, the relative amount of H_2O, oxalic acid and urea in the precursor solution played an important role in determining the morphological characteristics of the oxide [1]. Furthermore, a crystal seed assisted hydrothermal method has been employed for assembling plate and brick-like $3WO_3 \cdot H_2O$ nanostructures on FTO glass substrate through sodium sulfate (Na_2SO_4) [19]. Other salts such as lithium sulfate (Li_2SO_4) [20] and potassium sulfate (K_2SO_4) [21,22] have been utilized for the growth of single-crystal nanowires of hexagonal WO_3. Though the use of salts is promising for the solution approach enabling the synthesis of WO_3 nanostructures, not much has been explored on how to control the growth conditions to prepare different WO_3 crystal structures.

In this paper, we report the hydrothermal growth of WO_3 with diverse crystal structures and morphologies on FTO glass substrates at 95 °C through the amount of K_2SO_4 and the presence of Na_2SO_4 and Li_2SO_4. The correlation of these properties with the electrochemical activity comprising charge storage, durability, time response and impedance capability through the as-deposited WO_3 coatings is discussed.

2. Experimental details

The hydrothermal growth of WO_3 was carried out on FTO glass substrates. Prior to deposition, all substrates were ultrasonically cleaned with propanol, acetone, ultrapure H_2O and dried with N_2. The solution preparation involved the stirring of 0.003 mol, Na_2WO_4 with 100 ml, ultrapure H_2O (18.2 MΩ cm at 25 °C), followed by the addition of 2 M, hydrochloric acid (HCl) to adjust the pH solution at 1. Then different K_2SO_4 amounts of 0, 0.001, 0.002, 0.003, 0.004, 0.006, 0.007 and 0.008 mol were added to the above solution under

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stirring until they were completely dissolved. Afterwards, the solution was placed in a Pyrex glass bottle with propylene autoclavable screw cap with the substrate positioned on the bottom of the bottle and placed in a regular laboratory oven at 95 °C for 24 h. A second series of experiments was also performed using 0.007 and 0.009 mol of Na_2SO_4 and Li_2SO_4 respectively, keeping the other growth conditions constant. At the end of the induction period, the samples (regarded as the FTO substrate with the WO_3 coating on the top) dried in air at 95 °C for 10 min.

X-ray diffraction (XRD) characterization was performed using a Siemens D5000 Diffractometer with CuKα (λ = 1.54056 Å), 2-theta = 20.0–60.0°, step size 0.05°, step time 60 s/° and a glancing angle of 1°. The morphology of the samples was examined using a Jeol JSM-7000F field-emission scanning electron microscope (FE-SEM) at an operating voltage of 15 kV. In this case, all samples were over-coated with a thin film of gold prior to analysis to avoid charging. Finally, the cyclic voltammetry (CV) [23–26] and the electrochemical impedance spectroscopy (EIS) measurements were done using a three-electrode cell. The CV curves were accomplished in 1 M, lithium perchlorate ($LiClO_4$)/propylene carbonate solution for a scan rate of 10 mV s^{-1} through the potential range of −1 V to +1 V. In this case, the working electrode corresponded to the WO_3 coating grown on FTO glass substrates. The area of this electrode exposed to the electrolyte was 1 cm^2. The lithium ion intercalation/deintercalation process with respect to time was also studied using chronoamperometry at −1 V and +1 V for a step of 200 s. Finally, the EIS curves were obtained in the same instrument as CV with AC amplitude of 5 mV over the frequency range of 35 kHz–100 mHz.

3. Results and discussion

In order to understand the growth mechanism of WO_3, the amount of K_2SO_4 was varied keeping the growth temperature (95 °C) and period (24 h) constant. The total absence of sulfate ions in the reaction medium led to the complete lack of oxide growth. In particular, the overall experimental parameters indicated that 0.006 mol, K_2SO_4 was required in the solution for the deposition of adhesive and durable coatings. Regarding the highest amounts (0.007 and 0.008 mol), material was detached during the sample's removal from the Pyrex bottle due to the creation of cracks on the surface of the substrate. Finally, only the as-grown coatings for 0.006 mol, K_2SO_4, 0.007 mol, Na_2SO_4 and 0.009 mol, Li_2SO_4, presented similar properties (structural, morphological and electrochemical) after approximately 6 months indicating their stability with time.

The XRD patterns of the as-grown WO_3 samples for 0, 0.002, 0.003 and 0.004 mol of K_2SO_4 present reflections only due to the FTO glass substrate at 26.5°, 33.7°, and 37.1° with respective Miller indices (110), (101), and (200) [27] and at 45.6°, 51.75° and 54.52° due to the Al holder (not shown for brevity). These peaks are also observed for those grown using 0.007 and 0.008 mol, K_2SO_4 indicating that they are largely amorphous. This is an expected behavior if one realizes their poor surface coverage. On the other hand, a weak peak at 24.42° appears only for the 0.006 mol sample (Fig. 1), which is consistent with the orthorhombic $WO_3{\cdot}H_2O$ [28]. Regarding the effect of alkali ions on the structure of WO_3, intense and sharp peaks are shown in the presence of 0.007 mol, Na_2SO_4, due to the hexagonal WO_3 crystal phase [19] (Fig. 2). Based on the reflections observed, the lattice constants a and c are calculated to be equal to 7.288 Å and 3.889 Å respectively, which agreed well with those reported in the literature (JCPDS card no. 33-1387 card). On the other hand, the as-grown WO_3 using 0.009 mol, Li_2SO_4 (Fig. 2) presents similar behavior as with Na_2SO_4, but with the presence of two extra peaks related with the orthorhombic $WO_3{\cdot}H_2O$ [28].

To summarize, different phases of WO_3 can be generated i.e. amorphous orthorhombic $WO_3{\cdot}H_2O$ to pure hexagonal WO_3 to mixed phases of hexagonal WO_3 and orthorhombic $WO_3{\cdot}H_2O$, through the gradual increase of K^+ and the presence of alkali ions such as Na^+ and Li^+.

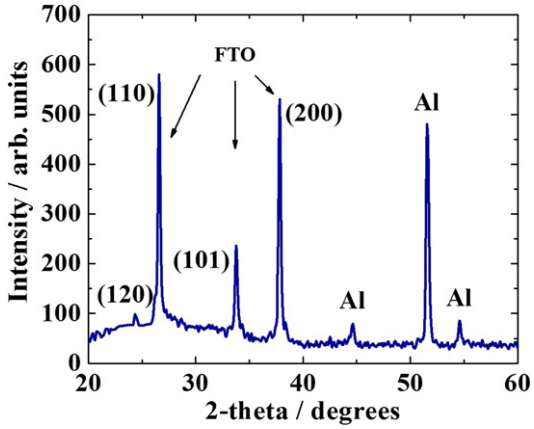

Fig. 1. XRD pattern of orthorhombic $WO_3 \cdot H_2O$ grown on FTO glass substrate at 95 °C using 0.006 mol, K_2SO_4. Peaks corresponding to FTO substrate and Al holder are indicated.

FE-SEM analysis of the as-grown WO_3 coatings using different amounts of K_2SO_4 is shown in Fig. 3. In the absence of K_2SO_4, only few grains are obtained. With an increase in the dosage of K_2SO_4 to 0.004 mol, the surface of the substrate is covered by the grains forming a layer. On the other hand for 0.006 mol, their agglomeration occurred. In terms of the highest amount of K_2SO_4, only the substrate is shown due to the detachment of the material after the sample's removal from the Pyrex bottle (Fig. 3 inset).

Other metal sulfates, such as Na_2SO_4 and Li_2SO_4 are also examined presenting the formation of flower- and urchin-like structures, respectively (Fig. 4). It is believed that the different radius of Na^+ and Li^+ cations induced various interactions between the cations and WO_3 crystals, which led to the different morphologies of the products [20]. However, more in-depth studies are necessary to further understand their growth process, which can provide important information for structure design and morphology-controlled synthesis of WO_3 and other oxides.

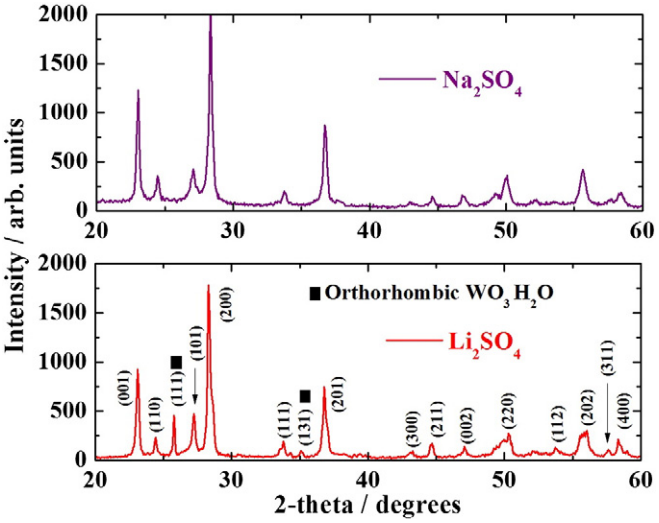

Fig. 2. XRD patterns of hexagonal WO_3 grown on FTO glass substrate at 95 °C using 0.007 mol, Na_2SO_4 and 0.009 mol, Li_2SO_4. Orthorhombic $WO_3 \cdot H_2O$ peaks are indicated with black squares.