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Effects of electrodeposition synthesis parameters on the photoactivity of nanostructured tungsten trioxide thin films: Optimisation study using response surface methodology

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ABSTRACT

The main aim of this study was to synthesize and characterise nanostructured tungsten trioxide (WO_3) thin films via electrodeposition and subsequently, optimise the electrodeposition synthesis parameters using response surface methodology (RSM). Statistical Box–Behnken RSM design was used to investigate and optimise the effects of four independent electrodeposition synthesis parameters, namely: deposition time, precursor tungsten (W) concentration, annealing temperature and pH. In addition, the synergistic interaction between different electrodeposition synthesis parameters was identified and quantified in enabling a higher photoactivity achievable by nanostructured WO_3 thin films. Resultant nanostructured WO_3 thin films were characterised using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and photocurrent density measurements under one-Sun irradiation. From the electrodeposition synthesis process, it was found that there was a gradual increase in the nanocrystallites WO_3 size from 30 nm to 70 nm when the annealing temperature was varied between 400 °C and 600 °C. XRD results verified the existence of the same photoactive phase of monoclinic WO_3 with increasing annealing temperature with the preferred growth orientation along the {002} planar. Whilst from the Box–Behnken RSM design, it was found that the optimum deposition time, precursor W concentration, annealing temperature and pH were: 60 min, 0.15 mol/L, 600 °C, and pH 1.0, respectively. The highest photocurrent density of 120 μA/cm^2 was measured at 1 V (*versus* Ag/AgCl) for nanostructured WO_3 thin film synthesized at the optimum conditions as informed by the Box–Behnken RSM. Further analysis and validation of the Box–Behnken RSM model using analysis of variance (ANOVA) revealed that the RSM-derived statistical predictive model was robust, adequate and representative to correlate the various electrodeposition synthesis parameters to photocurrent density. This study highlights the importance to systematically optimise the electrodeposition synthesis parameters in order to achieve a higher photocurrent density on nanostructured WO_3 thin film for sustainable hydrogen production from photoelectrochemical water splitting reaction.

1. Introduction

Photoelectrochemical (PEC) water splitting is attractive owing to its potential for solar energy conversion without the need of energy derived from declining fossil fuel supplies [1]. To date, much of the researches being carried out are focused on solar energy conversion through PEC water splitting, which converts solar into renewable energy resource in the form of storable hydrogen energy [2]. During the PEC water splitting process, water molecule is photolysed into hydrogen (H_2) and oxygen (O_2) via the aid of semiconductor metal-oxide photocatalyst. Thus, the presence of semiconductor photocatalyst plays an important role in the solar-to-hydrogen energy conversion during the PEC water splitting process. Among the common photocatalysts used for PEC water splitting process, tungsten trioxide (WO_3) is increasingly used as a semiconductor photocatalyst for oxidative decomposition of water owing to its smaller bandgap energy of 2.6 eV [3]. Moreover, WO_3 has received a great deal of attention due to its good resistance against photo-corrosion, high stability

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in acid solution and the extended absorption into visible-light spectrum that rendered a better photoactivity. In the last 2 decades, WO_3 has been extensively studied from various fundamental science perspectives as well as a wide application in PEC water splitting process [4].

From the open literatures, various synthesis methods have been reported for the fabrication of nanostructured WO_3 thin films with bespoke physicochemical, optical, electronic and PEC properties, as well as improved photoactivity [5]. These include sputtering, thermal evaporation, chemical vapour deposition, sol-gel, electrodeposition and hydrothermal synthesis methods [6]. Most of these synthesis methods, however, are not suitable for scale-up processing and commercialisation [7]. Recently, the electrodeposition synthesis method has received much attention due to the advantages of low capital cost, ambient temperature and pressure conditions, direct control of film thickness and the possibility of scale-up processing and commercialisation [8]. During the electrodeposition process, different electrodeposition synthesis parameters such as deposition time, precursor W concentration, annealing temperature and pH are known to have dominant and synergistic effects on the eventual photoactivity of nanostructured WO_3 thin films, which were reviewed in our previous communication [7]. For instances, varying the deposition time can lead to different film thicknesses while a more stable crystal structure will be formed via heat treatment under different annealing temperature. Similarly, it is also known that both pH and precursor W concentration will have significant effects on the morphology and particle size.

Typically, in order to optimise the electrodeposition synthesis conditions for nanostructured WO_3 thin films, the experimental-based one-factor-at-a-time (OFAT) optimisation approach could be employed to verify the different optimum synthesis parameters. The OFAT approach has been traditionally used to achieve higher efficiencies by varying one independent experimental factor or parameter at a time while keeping the other independent factors constant. However, the major disadvantage of the OFAT approach is that it cannot depict the synergistic and interactive effects among the electrodeposition synthesis parameters and verify the optimum synthesis parameters without vast experimentation efforts [9]. Recently, the application of response surface methodology (RSM) is gaining immense attention as a robust statistical technique used for experiments design, predictive model development and evaluation of synthesis parameters and their interactions, as well as optimisation to yield the desirable response surfaces [10]. Generally, there are a number of RSM types that are widely used in the materials synthesis experiment design and optimisation, including: D-optimal [11], Central Composite Design (CCD) [12] Box–Behnken Design (BBD) [12] and others [13]. When compared among these RSM types, BBD statistical design is an independent, rotatable or nearly rotatable, quadratic design. The design combinations are placed at the midpoints of the edges and at the centre of the process space. This design requires less experimental runs and time to optimise parameters, as well as able to predict the optimal conditions to obtain high quality results from the experiments performed [11,12].

Thus, the main aim of this study was to synthesize and characterise nanostructured WO_3 thin films via electrodeposition and subsequently, optimise the electrodeposition synthesis parameters by using RSM. Previously, we had investigated the effect of heat treatment (*i.e.*, annealing temperature) through the OFAT approach on nanostructured WO_3 thin films and found that the highest photocurrent of 35 $\mu A/cm^2$ was achievable at 600 °C. This study constitutes the foremost study to systematically investigate and optimise the synthesis parameters for nanostructured WO_3 thin films via the electrodeposition synthesis route. Statistical Box–Behnken RSM design was used to investigate and optimise the effects of four independent synthesis parameters, namely: deposition time (X_1), precursor W concentration (X_2), annealing temperature (X_3) and pH (X_4). Resultant nanostructured WO_3 thin films were characterised using field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and photocurrent density measurements under one-Sun irradiation. For the RSM design, the measured photocurrent densities were assigned as the response outputs for the developed and validated Box–Behnken model. This study highlights the importance to systematically optimise the electrodeposition synthesis parameters in order to achieve a higher photocurrent density and thus, the photoactivity for nanostructured WO_3 thin films.

2. Materials and methods

2.1. Preparation of tungsten precursor solution

In this study, all the chemicals were used as received without further purification. Hydrogen peroxide 30% (H_2O_2) was obtained from HmbG Chemicals, USA. Tungsten (W) powder with particle size of 325 meshes was purchased from Chem Soln, USA. Platinum (Pt) black ($\geq$ 99.97%) with particle size $\leq$ 20 μm was also supplied by Chem-Soln, USA. All other miscellaneous chemicals were purchased from Merck, USA. Initially, the precursor solution was prepared by dissolving varying quantity of W powder in 50 mL of H_2O_2 and the reaction was allowed to continue up to 24 h. Thereafter, the excess H_2O_2 was decomposed by adding small amount of Pt black. The solution was further heated at 60 °C until no effervescence was evident. Then, the precursor solution was diluted to 50 mM via the addition of 150 mL of 50/50 (v/v) water/2-propanol. The function of propanol-2-ol was to extend the stability of precursor solution by preventing the precipitation of amorphous WO_3-based hydrated phase [13].

2.2. Synthesis of nanostructured WO_3 thin films

The electrodeposition synthesis of nanostructured WO_3 thin films was performed at room temperature using a conventional three-electrode electrochemical cell system (Metrohm, Netherland). Fluorine-doped tin oxide (F-SnO_2) glass slide (Chem Soln, USA; 2.5 cm $\times$ 2.0 cm size) was used as the working electrode (WE) after being cleaned with acetone and water; while a Pt rod was used as the counter electrode (CE) and Ag/AgCl (4 M KCl) as the reference electrode (RE). All the potentials used in the experiments were made reference to the Ag/AgCl (4 M KCl). During the electrodeposition synthesis, the effective immersion area of F-SnO_2 was fixed constant at 1.5 cm $\times$ 2.0 cm. The applied potential between WE and RE was –0.45 V controlled by the Autolab potentiostat/galvanostat (Metrohm, Switzerland). F-SnO_2 was rinsed using distilled water, followed by drying using clean air for 20 min (*i.e.*, heating and cooling rates of 10.0 °C/min and 2.5 °C/min, respectively). After the electrodeposition process, the as-deposited WO_3 film was removed from the suspension and annealed at 400–600 °C for 1 h to facilitate the phase transformation of amorphous WO_3 into nanocrystalline WO_3, as well as to enhance the adhesion strength between the nanostructured WO_3 thin film and F-SnO_2 electrode.

2.3. Characterisation of nanostructured WO_3 thin films

X-ray diffraction (XRD) was used to determine the in-situ phase composition of nanostructured WO_3 thin films (Philips X'pert Materials Powder Diffractometer; Cu Kα radiation; 45 kV; 40 mA). While the microstructure and chemical analysis was examined by using field-emission scanning electron microscopy (FESEM; FEI Nova NanoSEM; uncoated samples; secondary electron emission; accelerating voltage 5 kV). The PEC properties of nanostructured WO_3 thin films were measured in a dark-controlled and ambient temperature condition using the same Autolab potentiostat/galvanostat system. The only difference was that the peroxy-tungstic acid (PTA) electrolyte solution was replaced by sodium acetate (CH_3COONa) aqueous

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