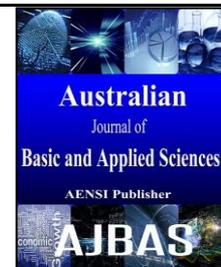




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Effect of Annealing Temperature on Photogenerated Charge Transfer in Electrochemically-Synthesized Nanostructured Tungsten Trioxide Thin Films

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ABSTRACT

Background: Various nanostructured thin films on photoelectrodes have been utilised in photoelectrochemical (PEC) water splitting process for solar hydrogen fuel conversion. However, the overall solar conversion efficiency is still relatively low and this could be due to the rapid recombination of photogenerated charge carriers at molecular level. **Objective:** The main aim of this paper was to understand the effect of annealing temperature on the photogenerated charge transfer in nanostructured tungsten trioxide (WO_3) thin films synthesized via electrochemical deposition route. **Results:** Amorphous WO_3 films were annealed between 100°C and 600°C . It was found using electrochemical impedance spectroscopy (EIS) that both the charge-transfer and transport resistances decrease with increasing annealing temperature. **Conclusion:** This study concluded that a properly controlled annealing treatment is crucial in regulating the nanocrystals growth, which subsequently enhances the photogenerated charge transfer and solar conversion efficiency for sustainable hydrogen production from water splitting.

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INTRODUCTION

Tungsten trioxide (WO_3) is an n-type semiconductor material and has found application as the new generation photocatalyst owing to its unique chemical characteristic of having high resistance in most aqueous media (Liu *et al.*, 2012). In addition, the band gap energy of semiconductor WO_3 photocatalyst is relatively lower of 2.6eV than the gold standard titanium dioxide (TiO_2) of 3.2eV and thus, can absorb 12% into the visible light spectrum (Kalanur *et al.*, 2013). Theoretically, the valence band position of semiconductor WO_3 is energetic enough to induce oxygen evolution during water electrolysis reaction and thus, is commonly regarded as the oxygen-evolution catalyst (OEC). Based on this aspect, previously many scientists have focused on the application of semiconductor WO_3 as the OEC in a standard photoelectrochemical (PEC) cell for solar energy fuel conversion during the water splitting process (Amano *et al.*, 2013). Thermodynamically the splitting of water molecules is an uphill process where, water molecules will either gain or lose electrons (Zhu and Chong, 2015). Meanwhile, in the PEC-assisted water splitting process, the redox reaction is directly related to the positioning of valence band (VB)/conduction band

(CB) of the semiconductor photocatalyst used (Phuan *et al.*, 2014). In this instance, the CB position of semiconductor WO_3 photocatalyst makes it a non-suitable hydrogen-evolution catalyst (HEC) used at cathode when compared to the ideal VB position of semiconductor WO_3 photocatalyst as OEC at anode (Kamat and Bisquert, 2013). Thus, the mismatching in the CB positioning of semiconductor WO_3 photocatalyst has seriously impaired the potential hydrogen evolution from PEC-assisted water splitting process.

Since the water splitting process mostly occurs in aqueous solution, the surface of the electrode containing photoelectrocatalyst thin film is quite important, as well as the bulk structure. This is owing to that the former can provide active sites for absorption of water molecules while; the latter is responsible to prevent the recombination of photogenerated charge carriers in semiconductor WO_3 photocatalyst. Therefore, the careful synthesis of a thin nanostructured WO_3 film over the anodic surfaces can regulate both the surface morphology and structural in determining the overall PEC-assisted water splitting efficiency. Previously, it was known that a number of synthesis factors are affecting the surface morphology and structural during the synthesis of a thin nanostructured WO_3

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film over photoelectrode such as precursor solution concentration, pH, applied potential, annealing treatment and others. In our previous communication, we had reviewed the effects of different synthesis factors on the size, composition and thickness of electrochemically-synthesized nanostructured WO₃ thin films (Zhu *et al.*, 2014). Among the various electrochemical synthesis factors, annealing treatment at elevated temperature is known to have a significant impact on the eventual nanostructured WO₃ thin films in terms of surface morphology, crystal structure and phase transition. For instances, Liu *et al.* (2012) explained that the low photoactivity is due to the poor crystallisation in the annealed WO₃ films. They found that the photoactivity of WO₃ is enhanced when the annealing temperature was increased to 450°C and this was linked to the better crystallisation state and decrease in surface defects of WO₃.

To date, there is no systematic study on the effect of annealing temperature on electrochemically-synthesized nanostructured WO₃ thin films. Thus, the main aim of this study was to investigate the effect of annealing temperature on the physicochemical property and the eventual photogenerated charge transfer of nanostructured WO₃ thin films prepared via electrochemical deposition route. Primarily the effect of annealing temperature on the photogenerated charge transfer of nanostructured WO₃ thin films synthesized at different annealing temperature was examined in this study using electrochemical impedance spectroscopy (EIS). This work constitutes a more fundamental approach towards understanding the effect of annealing temperature on the electrochemically-synthesized nanostructured WO₃ thin films in improving the overall PEC-assisted water splitting efficiency.

Experimental Procedure:

Preparation of precursor solution:

In this study, all chemicals were used as received without further purification. Hydrogen peroxide (H₂O₂, 30%) was obtained from HmbG Chemicals, USA. Tungsten (W) powder with particle size of 325 meshes was purchased from ChemSoln, USA. Platinum (Pt) black (purity $\geq 99.97\%$) with particle size $\leq 20 \mu\text{m}$ was supplied by ChemSoln, USA. All other miscellaneous chemicals were purchased from Merck, USA. In this study, the preparation of precursor solution for the electrochemical deposition method was in accordance to a previous study (Baek *et al.*, 2003). Initially, the precursor solution was prepared by dissolving 1.8 g of W powder in 50 mL of H₂O₂ and allowed to dissolve up 24 h. After that, the excess H₂O₂ was decomposed by adding small amount of Pt black. The solution was further heated at the optimum temperature of 60°C until no gas bubbles were evident (Murau, 1961). This was followed by diluting the precursor solution to the concentration of 50mM via the addition of 150mL of 50/50 (% v/v) of water/2-propanol. The function of 2-propanol is to

extend the stability of precursor solution by preventing the precipitation of an amorphous WO₃-based hydrated phase (Kwong *et al.*, 2012).

Preparation of nanostructured WO₃ thin films:

The electrochemical deposition of nanostructured WO₃ thin films was performed at room temperature using a conventional three-electrode electrochemical cell system, PGSTAT204 Applied Potentiostat (Metrohm, Netherlands). FTO glass slide (ChemSoln, USA; 14Ω/sq; 2.5cm×1.5cm) was used as the working electrode (WE) after being cleaned with acetone and water, while Pt was used as the counter electrode (CE) and Ag/AgCl (4M KCl) as the reference electrode (RE). In this study, all the measured potentials were made reference to the Ag/AgCl (4M KCl) electrode. During the electrochemical deposition process, the immersed area of FTO was fixed constant at 2cm×1.5cm. The applied potential between the WE and RE was fixed at -0.45V (vs SCE), as controlled by the PGSTAT204 Applied Potentiostat unit (Kwong *et al.*, 2012). After the electrochemical deposition process, the as-deposited amorphous WO₃ films on FTO were rinsed using distilled water, dried by clean air and subsequently annealed at different temperature ranging from 100°C to 600°C in air for 20 min (i.e. at heating and cooling rates of 10.0°C/min and 2.5°C/min, respectively).

Characterisation of nanostructured WO₃ thin films:

FE-SEM on uncoated samples with an accelerating voltage of 5kV (FEI Nova NanoSEM, Country). Whilst the PEC properties of the samples were measured at room temperature in a dark box using the same PGSTAT2014 Applied Potentiostat unit and FTO glass slide as the WE. However, the peroxy-tungstic acid (PTA) electrolyte solution was replaced by 0.1 mol/L sodium acetate (CH₃COONa) aqueous solution for the measurement of PEC properties. During the measurement of PEC properties, illumination from a 100 W halogen lamp restricted at a frequency of 0.05 Hz was used as the light source. The intensity of incident light was measured using a digital light meter to be 8700 mW/m² at a light source-to-sample distance of 10 cm. The linear potentiodynamic voltammetry was applied at a scan rate of 5 mV/s with a step size of 1mV.

RESULTS AND DISCUSSION

Field Emission – Scanning Electron Microscopy (FE-SEM):

The as-deposited amorphous WO₃ films were subjected to annealing treatment under different temperature, ranging from 100°C to 600°C. Figure 1 shows the surface morphology, crystal size and structure of the nanostructured WO₃ thin films formed under different annealing temperature.

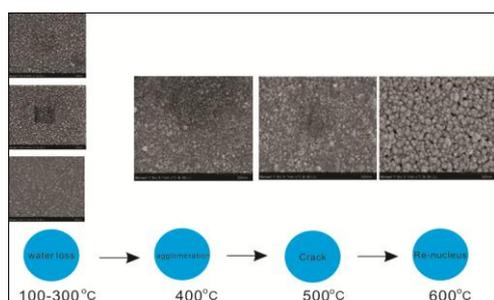


Fig. 1: FE-SEM images of nanostructured WO₃ thin films formed under different annealing temperatures of 100°C to 600°C.

From Figure 1, it can be observed that the surface morphology of nanostructured WO₃ thin films was significantly altered by the annealing treatment. In this study, it was observed that the nanostructured WO₃ thin films experiences four major physical transformation stages of: (1) loss of surface-adsorbed and chemisorbed water molecules; (2) agglomeration of WO₃ nanocrystals; (3) physical cracking and; (4) formation of closely-uniform and homogeneous nucleus-shaped WO₃ nanocrystals. During the first physical transformation stage, the average WO₃ nanocrystals size of 30 nm was observed after the amorphous WO₃ film was subjected to heat treatment at 100-300°C. As outlined, such a change could be attributed to both the oxidation of surface-adsorbed water molecules and phase transformation of WO₃ crystalline process that was accompanied by the loss of water molecules in vapor form (Ng *et al.*, 2013). For the annealed sample at 400°C, it was found that the smaller WO₃ nanocrystals agglomerated to form larger and irregular-sized WO₃ crystals. When the sample was annealed at 500°C, however, it was observed through the FE-SEM image that indicated the presence of physical cracks on the surface of the annealed WO₃ thin films. These physical cracks were absent in the as-deposited amorphous WO₃ film, which indicates that they were thermally generated during the heat treatment or cooling processes. Similar observation on the presence of physical cracks was also reported in a previous study by Rahman and Joo (2012). They concluded that the presence of physical cracks would lead to a higher photoactivity, as they will generate more surface active sites for the contact between the interfaces of WE and aqueous solution. The final stage of annealing treatment at 600°C resulted in the disappearance of physical cracks, while producing closely-uniform and homogeneous nucleus-shaped WO₃ nanocrystals as evidenced from the FE-SEM image shown in Figure 1.

Electrochemical Impedance Spectroscopy (EIS):

Generally EIS is a useful characterisation method for the analysis of efficient photogenerated charge-transfer process. This is a steady-state method for measuring the current response to the application

of AC voltage as a function of frequency. Previously, this EIS method has been used to study the charge-transport kinetics in the PEC-assisted water splitting process [14]. In this study, we have performed the EIS measurements on the nanostructured WO₃ thin films annealed at temperature ranging from 100°C to 600°C. Due to the unstable nanostructured WO₃ thin films formed at 100°C to 300°C, the EIS measurements were not performed for these samples. Figure 2(a) shows the Nyquist plot from the EIS measurements of nanostructured WO₃ thin films annealed at 400°C to 600°C under constant light illumination of 8700 mW/cm². Meanwhile, Figure 2(b) shows the Bode phase plot for the enlargement of high-frequency region in Figure 2(a). From Figure 2(a), it can be observed that the Nyquist plot exhibits two-semicircles including a large-semicircle at low-frequency and a small-semicircle at high-frequency. In this instance, the large-semicircle in the Nyquist plot was fitted to a charge-transfer resistance (R_{ct}) and subsequently, assigned at the interfaces of electrolyte/WO₃ electrode. Whilst the small-semicircle in the high-frequency region was fitted to a transport resistance (R_w), which was ascribed for the accumulation/transport of injected electrons and the charge transfer across the WO₃/WE interface. Table 1 shows the variation in the measured R_{ct} and R_w values with increasing heat treatment from 400°C to 600°C.

From Table 1, it was observed that the nanostructured WO₃ thin film annealed at 600°C was having lower charge-transfer and transport resistances than the annealed WO₃ thin films at 400°C and 500°C. This indicated that the photogenerated charge transfer was optimum for the annealed WO₃ thin film at 600°C, as more efficient electrons transfer process is occurring. In this instance, the higher measured charge transfer and transport resistances in the nanostructured WO₃ thin film annealed at 500°C can be linked to the presence of physical cracks and relatively disordered film structure. Hence, these could result in a loose mechanical adhesion between the nanostructured WO₃ thin film annealed at 500°C and the working FTO electrode.

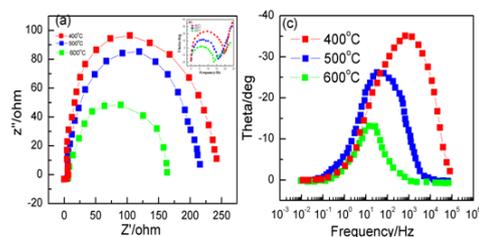


Fig. 2: EIS spectra of nanostructured WO₃ thin films annealed at varying annealing temperatures ranging from 400°C to 600°C. (a) Nyquist plot; (b) Enlargement of high-frequency region (**Inset** in a) and; (c) Bode phase plot.

Table 1: Kinetic parameters for the recombination reaction of nanostructured WO₃ thin films annealed at 400°C to 600°C.

Samples	R _{ct} (Ω)	R _w (Ω)	τ(ms)
WO ₃ (400°C)	150.38	51.51	0.31
WO ₃ (500°C)	120.36	31.51	2.31
WO ₃ (600°C)	78.23	20.56	3.65

The poor mechanical adhesion between the nanostructured WO₃ thin film and working FTO electrode might leads to higher resistances and lower photocurrent density. Correspondingly, the characteristic frequency peaks (1-103 Hz) for nanostructured WO₃ thin films annealed at 500°C and 600°C in the Bode phase plot are shown in Figure 2(c).

From Figure 2(c), it was observed that the characteristic frequency peaks for nanostructured WO₃ thin films annealed at 400°C, 500°C and 600°C have shifted to lower frequencies sequentially. In this instance, the corresponding low frequency peaks (f_{max}) were located at 66.5Hz and 34.3Hz. Theoretically, the characteristic frequency is related to the inverse of recombination lifetime (τ) in nanostructured WO₃ thin films and is given by the following equation:

$$\tau = 1/\omega_{min} = 1/2\pi f_{max}$$

where τ is the recombination lifetime (ms), ω_{min} is the applied sine wave frequency (Hz) and f_{max} is the low-frequency peak (Hz).

From Table 1, it can be seen that the recombination lifetime for the nanostructured WO₃ thin film annealed at 600°C was 3.65ms, which was more prolonged than annealed WO₃ thin films at 500°C (i.e. 2.31ms) and 400°C (i.e. 0.31ms). This also implies that the formation of closely-uniform, homogeneous nucleus-shaped and highly-crystalline WO₃ crystals at 600°C results in a higher photogenerated charge transfer ability due to the longer electrons lifetime. This could effectively prolong the recombination of electron-hole pairs at the surfaces of WO₃ and subsequently, lead to an enhancement in the overall PEC-assisted water splitting efficiency. Phuan *et al.* (2014) explained that this was thermodynamically linked to the increase in average WO₃ nanocrystals size and reducing WO₃ grain boundaries during the annealing treatment that leads to the suppression of electron-hole pairs recombination rate. In overall, the annealed WO₃ thin film at 600°C was found to be optimum due to the increase in average WO₃ nanocrystals size, reducing voids, suppression of electron-hole pairs recombination, allowing lower resistances and thus, higher photogenerated charge transfer at molecular level.

Conclusions:

In this study, nanostructured WO₃ thin films were successfully synthesized via the electrochemical deposition method. From the study, it was observed that the as-deposited amorphous WO₃ films on FTO were transformed in terms of the average WO₃ nanocrystals size, surface morphology

and uniformity, as well as the photogenerated charge transfer ability when subjected to annealing treatment at varying temperature of 100°C to 600°C. Overall the effect of annealing treatment will increase the average WO₃ nanocrystals size, reduce the voids, suppress the electron-hole pairs recombination that result in higher photogenerated charge transfer at molecular level. It is anticipated that this study provides the basic platform in the electrochemically-synthesis of nanostructured WO₃ thin films for further surface modifications in enabling a higher PEC-assisted water splitting efficiency.

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