



# Synthesis and characterisation of a novel bilayer tungsten trioxide nanojunction with different crystal growth orientation for improved photoactivity under visible light irradiation



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## ABSTRACT

The main aim of this study was to prove the concept and elucidate the effect of a bilayer tungsten trioxide (WO<sub>3</sub>) nanojunction with different crystal growth orientation for improved photoactivity under visible light irradiation. For the first time, the concept of a bilayer WO<sub>3</sub> nanojunction with different crystal growth orientation was demonstrated. A layer-by-layer assembly for the bilayer WO<sub>3</sub> nanojunction with the same monoclinic  $\gamma$ -WO<sub>3</sub> crystal structure, but with two different crystal growth orientation of {002} at 600 °C and {200} at 500 °C was synthesized via the controlled electrodeposition-annealing method. Photocurrent measurements showed that the individual photoactivity of WO<sub>3</sub> thin film with {002} crystal growth orientation was higher than that of WO<sub>3</sub> thin film with {200} crystal growth orientation, while the bilayer WO<sub>3</sub> nanojunction with different crystal growth orientation exhibited the highest photoactivity. To further characterise the bilayer WO<sub>3</sub> nanojunction, X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), high resolution-transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and photocurrent density measurements were performed. Based on the findings, a theoretical postulation model was proposed in explaining the transfer of photogenerated charge carriers in bilayer WO<sub>3</sub> nanojunction that leads to improved photoactivity under visible light irradiation.

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## 1. Introduction

Solar-driven photoelectrochemical (PEC) water splitting process for hydrogen (H<sub>2</sub>) production utilising semiconductor-based photoelectrodes is attractive and sustainable to potentially resolve the projected energy shortage issue in the coming decades [1,2]. To date, however, it was reported that most of the semiconductor-based photoelectrodes are having a low solar-to-hydrogen (STH) efficiency, and also not being sufficiently energetic in driving the overall PEC water splitting reaction into H<sub>2</sub> and oxygen (O<sub>2</sub>) [3]. Over the years, numerous researches have been carried out to

improve the STH conversion efficiency of PEC water splitting process but with limited success [4]. This is because the STH efficiency is mainly limited by the low efficiency in photogenerated charge carriers separation before any redox reaction can proceed on the semiconductor surfaces [5]. Generally, it was known that the efficient separation of photogenerated charge carriers is highly dependent on the surface and structural properties of the semiconductor photoelectrode used [6–8]. Thus, the manipulation of surface physicochemical properties of semiconductor photoelectrode used for PEC water splitting process is one of the key factors to determine the eventual STH efficiency [9].

To date, various semiconductor-based photoelectrodes have been extensively investigated for the application in PEC water splitting process [4,10]. For instances, the photoanodes fabricated from *n*-type semiconductor metal oxides were employed, such as titanium dioxide (TiO<sub>2</sub>) [11,12], hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [1] and tungsten

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trioxide ( $\text{WO}_3$ ) [13] due to their high chemical stability, high availability, low-cost and environmental benign [1,11,13]. Among them,  $\text{WO}_3$  is an *n*-type semiconductor having an indirect band gap of 2.5–2.8 eV that could harness approximately 12% of the solar spectrum and absorb light with wavelength of up to 500 nm [13]. Based on these requirements,  $\text{WO}_3$  is considered as a suitable semiconductor photoanode material that can be used for PEC water splitting process than  $\text{TiO}_2$  that possess an indirect band gap of 3.0–3.2 eV [14]. Whilst  $\text{TiO}_2$  absorbs only in the ultraviolet (UV) region of the solar light spectrum, and could harness approximately 4% of the total solar irradiation [11]. In comparison, the theoretical maximum STH conversion efficiency in a PEC water splitting device using  $\text{TiO}_2$  photoanode was only 2.2% while  $\text{WO}_3$  achieved a STH efficiency of 4.8% when being used as the photoanode [11]. Additionally,  $\text{WO}_3$  also exhibits high resistance against photocorrosion, having a moderate hole diffusion length (~150 nm) when compared to  $\alpha\text{-Fe}_2\text{O}_3$  (2–4 nm) and  $\text{TiO}_2$  ( $10^4$  nm), and inherently good electron transport properties [15].

Although the semiconductor  $\text{WO}_3$  photoanodes have been proven to exhibit a higher PEC water splitting performance, the corresponding STH efficiency is still relatively low and far from practical realisation for large-scale solar  $\text{H}_2$  production [16]. One of the main intrinsic factors that limit the STH efficiency is the back reaction of intermediate chemical species that recombine to form water molecules. A viable strategy that can be used to mitigate performance losses from back reaction of intermediate chemical species is to create internal electric fields, which will separate the photogenerated charge carriers more efficiently [5]. It is well-known that these internal electric fields created within semiconductor photoelectrodes are associated with bespoke surfaces and interfaces engineering, including the electrolyte solution/photoelectrode interfaces, metal cocatalyst-photoelectrode junctions, and *p-n* junction in nanocomposite photoelectrodes. There are also internal electric fields created at phase boundaries, including *p-n* junctions and polar surfaces termination that refer to the influence of structure and composition on their physicochemical properties. Additionally, a surface or interfacial junction can also be formed between two different polymorphs of a photoactive phase with exactly the same chemical composition. This is owing to that the polymorphs have different crystallographic structures, and these will lead to different surface electronic properties [17,18]. Furthermore, the close interaction between different polymorphs of a photoactive phase embedded in an interfacial junction has the potential to facilitate the efficient separation of photogenerated charge carriers and thus, improve the overall photoactivity [5,19,20].

Based on this proposition, we demonstrated a novel approach for creating an internal electric field within the semiconductor  $\text{WO}_3$  photoelectrode and improving its photoactivity for potential application in PEC water splitting process. In this study, a bilayer  $\text{WO}_3$  nanojunction with different crystal growth orientation was obtained by a layer-by-layer assembly of the same monoclinic  $\gamma\text{-WO}_3$  crystal structure, but with two different crystal growth orientation of {002} at 600 °C and {200} at 500 °C achieved via controlled electrodeposition-annealing method. In order to further characterise the bilayer  $\text{WO}_3$  nanojunction, X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), high resolution-transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and photocurrent density measurements were performed. Finally, a theoretical postulation model was proposed in explaining the transfer of photogenerated charge carriers in bilayer  $\text{WO}_3$  nanojunction that leads to improved photoactivity under visible light irradiation.

## 2. Experimental

### 2.1. Preparation of precursor solution

All the chemicals were used as received without further purification. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 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 the other miscellaneous chemicals were purchased from Merck, USA. The preparation of precursor solution used for the cathodic electrodeposition synthesis method was in accordance to our previously published study [6,9]. Briefly, the precursor solution was prepared by dissolving 1.8 g of W powder in 50 mL of  $\text{H}_2\text{O}_2$  and allowed to dissolve up to 24 h. After that, the excess  $\text{H}_2\text{O}_2$  was decomposed by adding small amount of Pt black. The solution was further heated at 60 °C until no gas bubbles were evidenced [21]. This was followed by diluting the precursor solution to the concentration of 50 mM by adding 150 mL of 50/50 (% v/v) of water/2-propanol. The function of 2-propanol was to extend the stability of precursor solution by preventing the precipitation of an amorphous  $\text{WO}_3$ -based hydrated phase [22].

### 2.2. Cathodic electrodeposition synthesis of $\text{WO}_3$ thin films

The cathodic electrodeposition synthesis of  $\text{WO}_3$  thin films was performed at room temperature using a conventional three-electrode electrochemical cell system of PGSTAT204 Applied Potentiostat (Metrohm, Netherlands). FTO glass slide (ChemSoln, USA;  $14 \Omega/\text{sq}$ ;  $2.5 \text{ cm} \times 1.5 \text{ cm}$ ) was used as the working electrode (WE) after being cleaned with acetone and extra-pure water, while Pt was used as the counter electrode (CE) and Ag/AgCl (4 M KCl) as the reference electrode (RE). During the cathodic electrodeposition synthesis process, the immersed area of FTO in the precursor solution was fixed at  $2 \text{ cm} \times 1.5 \text{ cm}$ . The applied potential between the WE and RE was fixed at  $-0.45 \text{ V}$ , as controlled by the PGSTAT204 Applied Potentiostat [22]. After the cathodic electrodeposition synthesis process, the amorphous  $\text{WO}_3$  films were rinsed using distilled water, dried by clean air, and subsequently annealed at different temperature ranging from 500 to 600 °C in air for 20 min (i.e. at the heating and cooling rates of  $10.0 \text{ }^\circ\text{C}/\text{min}$  and  $2.5 \text{ }^\circ\text{C}/\text{min}$ , respectively).

### 2.3. Characterisation of $\text{WO}_3$ thin films

XRD measurements were carried out at room temperature using Cu  $K\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) with a potential of 40 kV and a current of 30 mA (Philips PW1830, Netherlands). The surface microstructural of  $\text{WO}_3$  thin films was examined using FE-SEM on uncoated samples with an accelerating voltage of 5 kV (FEI Nova NanoSEM, USA). For HR-TEM, the samples were dispersed in ethanol and a drop of the suspension was placed on a holey carbon covered Cu grid. HR-TEM analysis was performed using a JEOL 2010F transmission electron microscope at an accelerating voltage of 200 kV. The chemical composition of the  $\text{WO}_3$  thin films was measured by XPS ESCALAB 250 using Al- $K\alpha$  radiation source.

Photocurrent densities of the samples were measured at room temperature in a dark box using the PGSTAT2014 Applied Potentiostat, where in this instance, the FTO glass slide was used as the WE. Also the peroxy-tungstic acid (PTA) electrolyte solution was replaced by 0.1 mol/L sodium acetate ( $\text{CH}_3\text{COONa}$ ) aqueous solution during the photocurrent density measurements. During the photocurrent density measurements, illumination from a 100 W halogen lamp restricted at a frequency of 0.05 Hz was used as the light source with a light source-to-sample distance of 10 cm. The

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