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# Nanostructured Magnéli-Phase W<sub>18</sub>O<sub>49</sub> Thin Films for Photoelectrochemical Water Splitting

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**Abstract:** Converting water into hydrogen through the photo-electrochemical (PEC) process is one of the most exciting approaches in this field, and there is a quest to design or search for new electro-photo-catalytic materials. In this work, simple steps for fabrication and transformation of metallic tungsten thin film into the photo-active Magnéli-phase ( $W_{18}O_{49}$ ) of tungsten oxide thin film is demonstrated. The post-annealing temperature has a significant impact on the phase evolution of tungsten film into  $W_{18}O_{49}$ . The film thickness of  $W_{18}O_{49}$  is controlled by controlling the sputtering time (or deposition time) of W film. The PEC performance of the as-prepared electrodes is evaluated by monitoring the water oxidation reaction under visible radiation. The PEC findings reveal a correlation between PEC performance and phase, morphology, and thickness of the film. The as-derived  $W_{18}O_{49}$  can efficiently catalyze the water oxidation reaction at neutral solution pH, generating 0.6 and 1.4 mA cm<sup>-1</sup> photo-current at 0.6 and 0.8 V vs. Saturated calomel electrode (SCE), respectively, in addition to excellent stability. The electrical conductivity and the charge transfer kinetics are investigated employing the electrochemical impedance spectroscopic (EIS) technique.

Keywords: photo-electrochemical; water spitting; thin films; tungsten oxide

# 1. Introduction

Strong overuse and dependence of fossil fuels (coal, oil, and natural gas) are intensifying air pollution and climate change. Water splitting is one of the most promising methods to generate clean energy through hydrogen and oxygen evolution reactions using a clean and sustainable approach. However, developing low-cost water-splitting catalysts is still a scientific challenge to generating chemicals and renewable fuels from different renewable feedstocks [1–3]. Photo-electrochemical (PEC) is a process of splitting water into its two constituents, oxygen and hydrogen, using solar power [4–6].

To date, several different semiconductor metal oxides such as ZnO, TiO<sub>2</sub>, CuO, Bi<sub>2</sub>WO<sub>6</sub>, and MoO<sub>3</sub> have been developed for water splitting [7–11]. Among them, tungsten oxide is one of the most common semiconductor oxides used in PEC cells due to its ability to absorb the visible light spectrum, high stability in the electrolyte solutions, and the ability to exist in various compositional forms such as WO<sub>2</sub>, WO<sub>3</sub>, and W<sub>18</sub>O<sub>49</sub> [12–14]. Additionally, the tungsten oxide valance band potential edge is much higher (3.2 eV) than the potential required to oxidize the water (1.23 eV) [15,16].

The Magnéli-phase ( $W_{18}O_{49}$ ) [17], which is attracting considerable interest in different applications, such as solar cells, photo-catalysis, and sensors, is a non-stoichiometric tungsten oxide phase that possesses abundant oxygen vacancies [18,19]. The oxygen vacancies present in  $W_{18}O_{49}$  is functionalized as active sites to enhance the adsorption of oxygen molecules from the water [18]. Moreover, the

 $W_{18}O_{49}$  phase is capable of absorbing visible light illumination, without the addition of other dopant materials [20,21].

The photo-catalytic activity of Magnéli-phase  $W_{18}O_{49}$  is dictated by several factors, such as morphology, particle size, and surface area, which are ultimately controlled by the fabrication method. For example, Chongshen et al. [22] demonstrated that the light absorption properties of the  $W_{18}O_{49}$  changed with changing the bulk  $W_{18}O_{49}$  to nanorods, nanograins, nanofibers, and nanoparticles. Guojuan et al. [23] found that the directional growth of  $W_{18}O_{49}$  significantly affected oxygen vacancies, bandgap width, electron/hole separation, and optical attributes.

Herein, we demonstrate the preparation of  $W_{18}O_{49}$  thin films by annealing the metallic films of tungsten prepared by direct current (DC) sputtering. Formation of  $W_{18}O_{49}$  thin films are optimized by changing the sputtering deposition time (and hence the film's thickness), and varying the annealing temperature. The PEC performance of the as-obtained  $W_{18}O_{49}$  thin films is investigated by monitoring the water oxidation reaction. The crystallinity, morphological features, oxidation state, oxygen vacancy, and charge transfer resistance of the fabricated films are determined and correlated to PEC performance.

#### 2. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of the sputtered W film and  $W_{18}O_{49}$  films prepared under different conditions. The diffraction patterns of the  $W_{18}O_{49}$  films synthesized by post-annealing of sputtered W films are presented in Figure 1a. As can be observed, the XRD of films prepared after different deposition time shows sharp reflections at 26.8°, 34.1°, 38.1°, 51.8°, and 54.8°, which are attributed to FTO glass substrate. Furthermore, the diffractions centered at 23.5°, 24.0°, 24.6°, 28.9°, 33.5°, and 34.0° are ascribed to (010), (502), (103), (004), (113), and (505) planes of monoclinic  $W_{18}O_{49}$  with P2/m space group (JCPDS No: 84-1516) [24]. With increasing film thickness (deposition time), the intensity of the characteristic diffractions of  $W_{18}O_{49}$  is increasing. The enhancement of the crystallinity by increasing the thickness of the film might be due to the energy of the impinging nanoparticle [25].



Figure 1. Cont.



**Figure 1.** X-ray diffraction (XRD) patterns of the (**a**)  $W_{18}O_{49}$  films with various thickness fabricated by post-annealing of sputtered W film at 500 °C in air (**b**) metallic W film to  $W_{18}O_{49}$  phase transformation as a function of post-annealing treatment.

Figure 1b shows the phase evolution from W to  $W_{18}O_{49}$  as a function of annealing temperature. As can be seen, the diffractions of the as-fabricated w film and those annealed at 100 °C and 200 °C show the patterns of the FTO substrate only, indicating the amorphous nature of the deposited films at these annealing temperatures. As the temperature was increased to 400 °C, the change of the amorphous to the crystalline phase is demonstrated by the appearance of the diffractions at 35.8°, 40.3°, and 44.1°. These reflections are attributed to (002), (110), and (112) planes of the W<sub>3</sub>O phase with Pm-3n space group (JCPDS No: 41-1230) [26]. Formation of  $W_{18}O_{49}$  was observed at a higher temperature; the diffraction peaks of W film annealed at 500 and 600 °C matches the monoclinic phase of  $W_{18}O_{49}$ , indicating the phase transformation from  $W_3O$  to  $W_{18}O_{49}$  thin film. Thermal treatment of the  $W_3O$  films in the air provides further oxygen molecules that are needed for the formation of  $W_{18}O_{49}$ . It is worth mentioning that no other diffraction peak appeared after the thermal heating procedures.

The surface morphologies of the fabricated films were investigated in detail by field-emission scanning electron microscopy (FE-SEM). FE-SEM images of the  $W_{18}O_{49}$  films obtained after the post-annealing of sputtered W films prepared as a function of deposition time are shown in Figure 2. It can be observed that the thinnest film, deposited for 1 min, has a film thickness of 52 nm (Figure 2a,e), and it is originally grown in the form of packed spherical grains that have an average grain size ranging between 20 and 40 nm, numerous large particles with an average size of 70 nm, and small sheets. The diameter and length of these sheets are measured to be about 20 nm and 1.5  $\mu$ m, respectively. Upon increasing the deposition time to 5 min, Figure 2b,f, the flat and compact surface of the  $W_{18}O_{49}$ 

film evolved into a film with a thickness of 146 nm that attached as various large sheets over several micrometers. This transformation may be due to the formation of planar defects induced by the structural strain caused by heat treatment followed by aggregation process. The film deposited for 10 min has a thickness of 290 nm, as shown in Figure 2c,g. It consists of well-distributed and interconnected nanosized sheets without any significant voids. Meanwhile,  $W_{18}O_{49}$  film deposited for 20 min shows uniform and stacked sheets to form a nanorod-like structure with a thickness of 550 nm, as shown in Figure 2d,h.



**Figure 2.** Field-emission scanning electron microscopy (FE-SEM) images of  $W_{18}O_{49}$  films deposited for (a) 1, (b) 5, (c) 10, and (d) 20 min. and FE-SEM cross-section images of  $W_{18}O_{49}$  films deposited for (e) 1, (f) 5, (g) 10, and (h) 20 min. All the films were annealed at 500 °C in air.

Low and high-magnification FE-SEM images of the sputtered W films annealed at different temperatures are shown in Figure 3. It can be noticed from Figure 3 that the microstructure of the films annealed at 100 °C and 200 °C revealed a compact, voids-free and smooth microstructure with small grains. At 300 °C, the deposited film started to crack, forming a first oxide phase (W<sub>3</sub>O) as a result of particles accumulation. With further heating, the particles built-up to form small sheets as shown in the samples annealed at 400 °C. At 500 °C, all the nanoparticles accumulated in groups to form uniform  $W_{18}O_{49}$  nanosheets. By increasing the annealing temperature to 600 °C, the  $W_{18}O_{49}$  nanosheets grew vertically to form a pillar-like structure as shown in the high-resolution inset image of 600 °C annealed sample.

The optical properties of the fabricated films are presented in Figure 4. Figure 4a shows the influence of  $W_{18}O_{49}$  film's thickness on the ability to absorb the light in the visible and ultraviolet (UV) range. As can be seen, the light absorption increased with increasing the deposition time of the films in both visible and UV range. This behavior is due to the increase in the average particle size caused by the increase of the W mass thickness. Furthermore, the absorption edge of  $W_{18}O_{49}$  films shifted to a shorter wavelength (blue shift) when increasing the deposition time, which can presumably be ascribed to the quantum size effect. The optical band gap of the prepared photo-anodes is calculated using the Tauc relation [27,28]:

$$(\alpha hv)^n = A(hv - E_g)$$

where,  $\alpha$  is the absorption coefficient, ( $E_g$ ) is the optical band gap, h is the Planck's constant, v is the frequency, A is constant, n = 2 for direct bandgap and  $n = \frac{1}{2}$  for indirect bandgap. From Figure 4b, it was noticed that the bandgap decreases, from 3.65 eV (for 1 min film) to 3.18 eV (for 20 min film), as a result of increasing the thickness of the film, hence shifting its behavior from one dimension

material to the bulk material. A similar shift in the bandgap of thin films induced by the variation of the thickness has been reported elsewhere [29]. Furthermore, annealing temperature also affected the optical properties of the  $W_{18}O_{49}$  films. Films annealed at temperatures of 100 °C to 400 °C were opaque, indicating the metallic nature of the films while  $W_{18}O_{49}$  film annealed at 500 °C and 600 °C (Figure 4c) showed a certain level of light absorption in the UV and visible range. Moreover,  $W_{18}O_{49}$ film annealed at 600 °C showed a lower absorption level compared to the film annealed at 500 °C. This can be attributed to variation in the morphology of the two films as indicated by the FE-SEM images. The bandgap measurement plot of the  $W_{18}O_{49}$  films annealed at 500 °C and 600 °C is shown in Figure 4d. The bandgap of  $W_{18}O_{49}$  films annealed at 500 and 600 °C are calculated to be 3.45 and 3.50 eV. The value of bandgap slightly increased with increasing annealing temperature. This can presumably be due to the improvement in the crystallinity that resulted in the decrease of localized states in the bandgap [30].



**Figure 3.** Low and high magnification FE-SEM images of the W films annealed at (**a**) 100, (**b**) 200, (**c**) 300, (**d**) 400, (**e**) 500, and (**f**) 600  $^{\circ}$ C in air.



**Figure 4.** Ultraviolet–visible (UV-Vis) absorption spectra and bandgap of  $W_{18}O_{49}$  films as a function of deposition time (**a**,**b**), and UV-Vis absorption spectra and Tauc's plot of  $W_{18}O_{49}$  films (**c**,**d**) fabricated by post-annealing of sputtered W films at 500 and 600 °C in air.

The bonding and chemical environment of the deposited films was investigated by using X-ray photo-electron spectroscopy (XPS). Figure 5a,b show the XPS survey scans of the as-deposited W film and  $W_{18}O_{49}$  film prepared at 500 °C. The results show the XPS spectra of W and O, confirming the high purity of the fabricated films. Moreover, the change in W 4f and O 1s peak intensities of these two films reveal the transformation of metallic W film to oxide phase. The de-convoluted peaks of W 4f XPS spectra show different chemical binding energies corresponding to different oxidation states, i.e., W° (W4f<sub>7/2</sub> (31.1 eV), W4f<sub>5/2</sub> (32.9 eV)), W<sup>5+</sup> (W4f<sub>7/2</sub> (35.0 eV) W<sup>6+</sup> (W4f<sub>7/2</sub> (35.0 eV), W4f<sub>5/2</sub> (37.1 eV)) and  $W^{x+}$  (W4f<sub>7/2</sub> (eV), W4f<sub>5/2</sub> (eV), which is an intermediate oxidation state between  $W^{\circ}$  and  $W^{4+}$  [31,32]. Figure 5c demonstrates the W 4f spectra of as-grown W film, which shows the doublet peaks W  $4f_{7/2}$ and W 4f<sub>5/2</sub> formed due to the spin-orbit coupling. The presence of the small peaks at 31.6 and 33.8 eV is assigned to  $W^{x+}$  such as  $W_3O$ . The XPS spectrum of the prepared  $W_{18}O_{49}$  thin film is displayed in Figure 5d. The W 4f peaks of the  $W_{18}O_{49}$  films are shifted toward higher binding energy, compared with the W 4f spectra of the as-deposited film, which confirms the formation of the high oxidation state of W ( $5^+$ , and  $6^+$ ) [33,34]. The high-resolution XPS spectra of O 1s peaks of the as-fabricated sputtered W and  $W_{18}O_{49}$  films are demonstrated in Figure 5e,f. The decomposition of the O1s peaks showed two different peaks at 530.5 and 532.3 eV which correspond to the lattice oxygen (O<sub>L</sub>) and oxygen vacancy  $(O_V)$ , respectively [35].



**Figure 5.** X-ray photo-electron spectroscopy (XPS) spectra of (**a**,**b**) the survey spectra, (**c**,**d**) W4f, and (**e**,**f**) O1s of the as-deposited W film and  $W_{18}O_{49}$  film fabricated at 500 °C, respectively.

The PEC performance of the fabricated  $W_{18}O_{49}$  photo-anode films was evaluated in 0.1 M of Na<sub>2</sub>SO<sub>4</sub> electrolyte under the illumination of a 300 W Xenon lamp. Figure 6a shows the photo-current density generated by  $W_{18}O_{49}$  films prepared at different deposition time at a bias 0.6 V. Under dark conditions, these samples did not produce any noticeable current. In the presence of light, photo-current was measured to be 0.10, 0.25, 0.60, and 0.62 mA/cm<sup>2</sup> for  $W_{18}O_{49}$  films deposited for 1, 5, 10, and 20 min, respectively. The weak photo-current recorded in the presence of  $W_{18}O_{49}$  thin films deposited 1 and 2 min could be ascribed to the discontinuity of the film's layer as indicated by FE-SEM images (Figure 2). The interconnected sheets of  $W_{18}O_{49}$  film deposited for 10 min showed a significantly higher current density compared to the films prepared after shorter deposition time. This can be correlated to the lower bandgap (3.45 eV), and hence its ability to generate a larger number of electron/hole pairs.  $W_{18}O_{49}$  deposited for 20 min generated comparable or a slightly higher photo-current than that of the film prepared after 10 min. A probable explanation can be as follows.

All the photo-electrodes were illuminated from the front or coated side. The generated holes oxidize the water, while the electrons are transported to the counter electrode [36]. The photo-generated electrons have to diffuse through the entire film's thickness to reach the FTO/W<sub>18</sub>O<sub>49</sub> interface. In other words, the increase in film thickness after the optimal point enlarges the diffusion path for electrons and thus increases the probability of electron/hole pair recombination [37]. Potential-current curves obtained under intermittent illumination are shown in Figure 6b. The  $W_{18}O_{49}$  films deposited for 10 and 20 min produced higher photo-current as compared to the films prepared after 1 and 5 min. It is noteworthy that no current was recorded under dark conditions even at high potential (0.8 V vs. SCE). The effect of annealing temperature on the PEC performance of  $W_{18}O_{49}$  films is shown in Figure 6c. The potentiostatic measurements were carried out at 0.6 V vs. SCE. Since the as-prepared samples and those heated up to 300 °C (dashed line) were almost metallic, the production of low current was discerned under dark conditions. At 400  $^{\circ}$ C, the formation of W<sub>3</sub>O phase was observed, as confirmed by XRD and XPS. The film consisting of W<sub>3</sub>O layers was found to be photo-active and produced a photo-current of 0.4 mA/cm<sup>2</sup>. However, the generation of relatively high dark current was observed. The film obtained at 500 °C generated 0.6 mA/cm<sup>2</sup>. This film was formed in the shape of an interconnected nanosheet structure, which has high light absorption and high oxygen vacancies as confirmed by ultraviolet-visible (UV-Vis) and XPS results, respectively. These nanosheets were transformed into a nanopillar-like structure in the case of  $W_{18}O_{49}$  prepared at 600 °C, resulting in reducing the absorbed light by the film, and hence, reducing its photo-current density to 0.3 mA/cm<sup>2</sup>. A similar trend was observed in the dark or light when linear sweep voltammetry (LSV) measurements were conducted at a voltage range from 0.25 to 0.80 V vs. SCE, Figure 6d. At low biased voltages, 0.0 to 0.20 V, 400 °C sample generated higher dark current, compared with 500 °C and 600 °C, due to its metallic nature (W<sub>3</sub>O phase).



Figure 6. Cont.



**Figure 6.** Photo-electrochemical (PEC) performance measurements: Potentiostatic (**a**,**c**) and potentiodynamic (**b**,**d**) response of the films obtained at different deposition time and annealing temperatures. Measurements were carried out under intermittent light illumination.

The charge transfer process and electrical conductivity are very important factors in semiconductor photo-anode materials. Figure 7 shows EIS results obtained at 0.6 V vs. SCE at frequency ranging from  $10^5$  to  $10^{-2}$  Hz in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. Figure 7a shows the Nyquist plots (imaginary vs. real impedance) of W<sub>18</sub>O<sub>49</sub> films deposited at different sputtering deposition times and annealing at 500 °C. All the experiments and measurements were carried out under illumination. One time constant circuit was used as equivalent circuit, in which, solution resistance (Rs) is connected in series with a sub-circuit formed of a capacitor connected in parallel with charge transfer resistance ( $R_{ct}$ ) [38]. It can be seen that the arc radiuses of the W<sub>18</sub>O<sub>49</sub> films deposited for 20 min ( $R_{ct} = 135 \Omega$ ) and 10 min ( $R_{ct} = 172 \Omega$ ) were enormously short compared with 1 min ( $R_{ct} = 760 \text{ K}\Omega$ ) and 5 min (165 K $\Omega$ ) W<sub>18</sub>O<sub>49</sub> films, suggesting significantly faster charge transfer kinetics in the first mentioned  $W_{18}O_{49}$  films [39]. This result was in good agreement with the PEC results. Nyquist plots of W films annealed at 300, 400, 500, and 600 °C were recorded under illumination and are shown in Figure 7b. The deposition time for all the film was 10 min. The Rct of photo-active materials prepared at 300, 400, 500, and 600 °C were measured to be 430, 240, 172, and 260  $\Omega$ , respectively. The surface charge resistance decreases with increasing calcination temperature from 300 to 500 °C, followed by an increase for the sample heated at 600 °C. The reduction in charge transfer resistance can be rationalized to the improvement in the crystallinity of the photo-catalysts, which increases with increase in calcination temperature. However, high calcination temperature, such as 600 °C, can also lead to sintering, change in morphology, and surface area of photo-catalytic materials. This notion was corroborated by microscopic analyses; the sheet morphology of the sample prepared at 500 °C was transformed into a nanopillar-like structure when

heated at 600 °C. Such factors can undermine the photo-catalysts' surface quality, which can affect the surface charge transfer negatively. For optimal performance, a balance between the crystallinity and other surface properties should be maintained. Charge transfer resistance of  $W_{18}O_{49}$  film fabricated at 500 °C was also recorded with and without the light, and the results are shown in Figure 7c. It can be seen that in the absence of light, the  $R_{ct}$  of the  $W_{18}O_{49}$  film was significantly high (large semi-circle), which is in good agreement with the dark current shown in Figure 6c,d), and reflects the high photo-catalytic activity of  $W_{18}O_{49}$  film. Figure 7d shows the stability of the photo-current density of  $W_{18}O_{49}$  film deposited for 10 min and annealed at 500 °C at a biased voltage of 0.6 V vs. SCE under illumination. A slow drop was observed at the beginning (first 2000 s) due to the double layer charge capacitance at the  $W_{18}O_{49}$  film/Na<sub>2</sub>SO<sub>4</sub> interface [40]. After that, the photo-current density stabilizes at 0.56 mA/cm<sup>2</sup>, and it maintained 100% of this value for the 5200 s, which indicates the excellent stability of the photo-anode film.



**Figure 7.** (a) Nyquist plots of  $W_{18}O_{49}$  films deposited for 1, 5, 10, and 20 min under light. (b) Nyquist plots of W films annealed at 300, 400, 500, and 600 °C under light. (c) Nyquist plots of  $W_{18}O_{49}$  films deposited for 10 min and annealed at 500 °C under dark and light. (d) Stability test of  $W_{18}O_{49}$  films deposited for 10 min and annealed at 500 °C under light for 7200 s.

Table 1 compares the photo-current density of the  $W_{18}O_{49}$  film fabricated at 500 °C with those of other tungsten oxide photo-anodes, prepared by different methods. In this work, the fabricated photo-anode shows high photo-catalytic performance as compared to the most reported works in the table, indicating the high photo-catalytic activity of this phase and the effectiveness of the designed fabrication method.

**Table 1.** A comparison between the optimized  $W_{18}O_{49}$  film fabricated at 500 °C in air and different tungsten oxide photo-anodes reported in the literature.

| Preparation<br>Method        | Structure           | Photo-Current<br>mA/cm <sup>2</sup> | Bias Voltage         | Electrolyte                                 | Light Source  | Ref.         |
|------------------------------|---------------------|-------------------------------------|----------------------|---|---|--------------|
| solvothermal                 | plates-like         | 0.20                                | 0.6 V vs.<br>Ag/AgCl | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | solar simulation<br>A.M. 1.5 G spectrum<br>with the intensity of<br>100 mW·cm <sup>-2</sup> | [41]         |
| solvothermal                 | spindle-like        | 0.20                                | Ag/AgCl              | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | -   | [42]         |
| tungsten foil<br>anodization | nanoporous<br>layer | 0.40                                | 0.6 V vs.<br>Ag/AgCl | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | 300 W Xe lamp   | [43]         |
| Spin coating                 | Nano<br>particles   | 0.25                                | 1.25 V vs.<br>RHE    | 0.1 M<br>Na <sub>2</sub> SO <sub>4</sub>    | 300 W Xenon lamp  | [38]         |
| electrodeposition            | Nano-islands        | 0.02                                | 0.7 V vs.<br>Ag/AgCl | 0.5 M H <sub>2</sub> SO <sub>4</sub>        | Xenon solar simulator<br>(AM 1.5 G, 100 mW/cm <sup>2</sup> )                                | [44]         |
| hydrothermal<br>method       | Nanosheets          | 0.9                                 | 1.2 V vs.<br>RHE     | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | LED lamp coupled with<br>an AM 1.5 G filter<br>(100 mW cm <sup>-2</sup> ,<br>CEL-LED 100)   | [45]         |
| hydrothermal<br>method       | Nanosheets          | 0.3                                 | 1.2 V vs.<br>RHE     | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | 1000 W xenon arc lamp   | [46]         |
| RF-sputtering                | Rough film          | 0.01                                | 1 V vs.<br>Ag/AgCl   | 1 M HClO <sub>4</sub>                       | 400 W ozone-free Xe arc<br>lamp (AM 1.5 G filter)   | [47]         |
| RF-sputtering                | film                | 0.9                                 | 0.6 V vs.<br>SCE     | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | mercury arc lamp<br>350 nm < λ < 450 nm   | [48]         |
| RF-sputtering                | film                | 0.3                                 | 0.6 V vs.<br>SCE     | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | 300 W LOT-qd Xe lamp,<br>equipped with an AM<br>1.5 G filter                                | [49]         |
| RF-sputtering                | Nanosheets          | <0.5                                | 0.6 V vs.<br>SCE     | 0.33 molar<br>H <sub>3</sub> PO             | AM 1.5 G illumination<br>generated by solar<br>simulator                                    | [50]         |
| RF-sputtering                | film                | 0.2                                 | 0.6 V vs.<br>Ag/AgCl | 0.5 mol/L<br>H <sub>2</sub> SO <sub>4</sub> | A 500 W Xe lamp/A<br>400 nm cutoff filter   | [51]         |
| RF-sputtering                | film                | 0                                   | 0.6 V vs.<br>RHE     | 0.1 M<br>Na <sub>2</sub> SO <sub>4</sub>    | Xe lamp<br>(150 W)/wavelengths<br>range from 300 to 570 nm                                  | [52]         |
| DC-sputtering                | film                | 0.05                                | 1.0 V vs.<br>Ag/AgCl | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | visible light irradiation $(\lambda > 420 \text{ nm})$                                      | [53]         |
| DC-sputtering                | Nanosheets          | 0.6                                 | 0.6 V vs.<br>SCE     | 0.5 M<br>Na <sub>2</sub> SO <sub>4</sub>    | 300 W Xenon lamp<br>UV-visible (300–600 nm)   | This<br>work |

RHE: reversible hydrogen electrode, SCE: saturated calomel electrode, LED: light emitting diode.

#### 3. Experimental Details

#### 3.1. Preparation of W<sub>18</sub>O<sub>49</sub> Thin-Film Electrodes

Tungsten oxide ( $W_{18}O_{49}$ ) photo-anode films were fabricated by annealing the film of metallic tungsten prepared by the sputtering system (model NSC-4000, Nanomaster, TX, USA). Tungsten target (99.995% purity) was purchased from ACI alloys INC, (San Jose, CA, USA) and was used to deposit W films on FTO-coated glasses. The deposition was carried out in an argon atmosphere at a power of 100 watts. To investigate and reproduce the PEC performance of the  $W_{18}O_{49}$ , two films of each  $W_{18}O_{49}$  were synthesized with varying thin-film thickness and post-annealing treatment. In both two parameters, the base and deposition pressure inside the sputtering chamber were fixed at  $9 \times 10^{-6}$  and  $3.5 \times 10^{-3}$  torr, respectively. To study the effect of the thin film thickness on the PEC activity of the  $W_{18}O_{49}$ , the sputtered W metallic films were deposited at varying thicknesses (1, 5, 10, and 20 min), while keeping all other parameters constant. To investigate the effect of post-annealing treatment

on the performance of the  $W_{18}O_{49}$ , the sputtered W metallic films were annealed in a tube furnace (OTF-1200X from MTI corp.) at different temperatures in the ambient air. In detail, the deposited film was inserted in the middle of the tube furnace. Then, the furnace was adjusted to heat-up at the rate of 20 °C/min. to reach the targeted temperature (100, 200, 300, 400, 500, and 600 °C). After 2 h annealing, the tube furnace was switched off and the sample was left to cool down, inside the furnace in order to reach room temperature.

### 3.2. Thin Films' Characterization

The fabricated photo-anode films were studded using different characterization techniques. The structural information and crystal phase of the fabricated films was investigated by X-ray diffraction (XRD, Rigaku Miniflex 600 X-ray Diffraction, Tokyo, Japan, with Cu K irradiation at  $\lambda = 1.5406$  Å). The morphological properties were obtained using FE-SEM (Tescan Lyra-3, Brno-Kohoutovice, Czech Republic). The optical bandgap of the prepared films was calculated through ultraviolet and visible light absorption using an UV–Vis spectrophotometer (Jasco V-570, Tokyo, Japan). The subsurface composition was analyzed by X-ray photoelectron spectroscopy (XPS, Model: ESCALAB250Xi, Thermo Fisher, Waltham, MA, USA).

#### 3.3. Evaluation of Photo-Electrochemical (PEC) Activity

The photo-electrochemical performance of the fabricated  $W_{18}O_{49}$  photo-anode was carried out in a three-electrode cell connected to a potentiostat. In this assembly,  $W_{18}O_{49}$  films, saturated calomel electrode (SCE; Hg/Hg<sub>2</sub>Cl<sub>2</sub>), and platinum coil were used as a working, reference, and counter electrodes, respectively. The photo-anodes were illuminated by a 300-watt Xenon lamp (Model: Max-303, Tokyo, Japan). The resistivity measurements of the fabricated electrodes were investigated by electrochemical impedance spectroscopy (EIS) in the frequency range of  $10^{-2}$  to  $10^{5}$  Hz. All the above measurements were undertaken in 0.1 M of sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>).

#### 4. Conclusions

In summary, the study demonstrated the fabrication of tungsten metal film by a DC sputtering magnetron, and its transformation into Magnéli-phase ( $W_{18}O_{49}$ ) thin film of tungsten oxide by post-annealing under an air environment. The thickness (52, 146, 290, and 550 nm) and the morphology (nanoparticles, nanosheets, nanorods, and nanopillars) of the thin films were controlled by adjusting film growth time and post-annealing process. The as-derived  $W_{18}O_{49}$  efficiently catalyzed the water oxidation reaction and produced 0.6 and 1.4 mA cm<sup>-1</sup> photo-current at 0.6 and 0.8 V vs. SCE, respectively. In addition, the photo-electrode showed excellent stability; the performance was stable for ~2 h. The electrical conductivity and the charge transfer kinetics were improved with increasing deposition time and post-annealing temperature. The photo-electrode with the lowest resistance exhibited the highest PEC performance.

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