



# Nanostructure of TiO<sub>2</sub> and WO<sub>3</sub> multilayer films deposited on ITO glass for electrochromic enhanced photocatalytic activity

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## Abstract

The photocatalytic activity (PA) by electrochromic (EC) enhancement of single and multilayer films of TiO<sub>2</sub>, WO<sub>3</sub>, TiO<sub>2</sub>/WO<sub>3</sub>, and WO<sub>3</sub>/TiO<sub>2</sub> was investigated. All films were deposited from metal on an ITO glass substrate using direct current (DC) magnetron sputtering via an oblique angle deposition (OAD) technique at 85°. Subsequently, a thermal oxidation (TO) process at 500°C was applied for the samples to form metal oxide films. The morphology, elemental composition, crystal structure, and optical properties were studied by using field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffractometry (XRD), and UV-vis spectroscopy, respectively. The photocatalytic properties were investigated by showing the degradation rate of methylene blue (MB) solution as an organic pollutant that was examined under ultraviolet irradiation of 300 μW·cm<sup>-2</sup>. The film samples were investigated by comparing the pre-color and colored states that were achieved through the EC process. The EC properties of WO<sub>3</sub> led to increased charge insertion on the film surface. This observation was further supported by cyclic voltammetry (CV) testing, which revealed a higher current density for the thin film samples. The photodegradation results showed that the samples in the colored state exhibited a significantly higher degradation rate of MB compared to the pre-color state.

## 1. Introduction

In the past few years, titanium dioxide (TiO<sub>2</sub>) nanostructures have gained popularity in a variety of applications, including sensors, self-cleaning, and the degradation of organic pollutants [1]. TiO<sub>2</sub> is widely recognized as an effective photocatalyst, especially at UV and NIR range. It was chosen as the preferred catalyst for photodegradation applications over other metal oxides. However, the photocatalytic efficiency of TiO<sub>2</sub> is limited by its band gap (E<sub>g</sub>) of approximately 3.0 eV to 3.2 eV, but there are several ways to enhance this efficiency, including reducing e<sup>-</sup>-hole recombination [2], increasing e<sup>-</sup>-hole pair generation, and increasing charge separation and surface area [3]. The most common method for improving performance is to combine TiO<sub>2</sub> with other metal nanoparticles and coat them on top of TiO<sub>2</sub> [4,5]. However, this may reduce the active surface area between TiO<sub>2</sub> and the liquid pollutants, resulting in a decrease in catalyst efficiency. To address this problem, modifying TiO<sub>2</sub> with tungsten trioxide (WO<sub>3</sub>) improves the charge separation efficiency, as WO<sub>3</sub> has a band gap of approximately 2.8 eV and a similar conduction band level to TiO<sub>2</sub> [6]. The primary function of WO<sub>3</sub> is to give and receive charges from the TiO<sub>2</sub> band and maintain them in an excited state for a certain period to reduce the recombination rate, also known as a heterojunction [7-9]. Furthermore, WO<sub>3</sub> is used in a variety of technological applications

including EC devices and smart windows [10-12]. The electrochemical coloration is combined with intercalation of lighter ions such as H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> [13,14], which can increase the charge density on the film surface [15,16] and is related to the oxidation-reduction rate of degrading organic pollutants.

In this study, the two materials, Ti and W, were deposited on an indium-doped tin oxide (ITO) substrate with a nanorod structure to allow the multiple layers to synergistically increase the surface area, using the DC magnetron sputtering technique combined with OAD to increase the surface area of the films beyond that which dense film can achieve [17,18]. During the deposition process, the particles form an aligned nanorod array on the surface, which causes the shadowing effect. In addition, the deposition rate has a direct impact on film nucleation and growth. A higher deposition rate would cause adatoms on the surface to form an ordered alignment [19]. In this study, we intend to form the Ti thin film layer at a high deposition rate to achieve higher crystallinity with fewer defects, which is beneficial for minimizing the recombination of photogenerated e<sup>-</sup> and holes [20]. Furthermore, we aim to achieve a W thin film layer at a low deposition rate to create a porous structure, which improves EC performance by allowing e<sup>-</sup> and cations to pass through more easily [21-26]. Furthermore, the TO technique was used to create metal oxide films of TiO<sub>2</sub> and WO<sub>3</sub> on an ITO glass substrate. External heat is used to create reactions inside

an open pipe, such as  $\text{Ti}^{4+} + 2\text{O}^{2-} \rightarrow \text{TiO}_2$  and  $\text{W}^{6+} + 3\text{O}^{2-} \rightarrow \text{WO}_3$ . We demonstrated and compared the photocatalytic performance of 1-layer and 2-layer samples in their pre-colored and colored states by monitoring the degradation rate of MB solution under UV irradiance. The colored state, achieved through the EC process, involves the injection of  $e^-$  and cations into the film's structure (see Figure 1) [27]. This results in a high carrier density on the film's surfaces, thereby improving the PA performance, as shown in Figure 2.

## 2. Materials and methods

### 2.1 Preparation of thin films

The 100 nm thick ITO films coated on glass ( $1 \text{ cm}^2 \times 1.5 \text{ cm}^2$ ) were used as a transparent conducting oxide substrate. The ITO glass substrates were cleaned under an ultrasonic process with acetone, methanol, and DI water, each for 15 min, respectively. After that, 1-layer films with 100 nm thick metallic Ti and W layers were deposited on the ITO glass substrate using DC magnetron sputtering and OAD at  $85^\circ$ , as shown in Figure 3(a). The 2-inch Ti disc (99.995% purity) and W disc (99.95% purity) (Kurt J. Lesker Company) were used as the targets. Argon (99.999% purity) at a flow rate of 15 sccm was used as the sputtering gas in a high vacuum chamber system. The system had a base pressure of  $5.0 \times 10^{-5}$  mbar, maintained by a rotary pump coupled with a diffusion pump, and an operating pressure of  $2.5 \times 10^{-2}$  mbar for all deposited films. Moreover, 2-layer films (ITO/Ti/W and ITO/W/Ti) were deposited with a total thickness of 100 nm, each layer being 50 nm thick. Finally, all films were oxidized by the TO in air at  $500^\circ\text{C}$  for 1 h within a furnace, as shown in Figure 3(b). These samples are summarized in Table 1. Photographs of the as-deposited Ti, W, Ti/W, and W/Ti films, and after the TO process at  $500^\circ\text{C}$  for 1 h, are shown in Figure 4.

### 2.2 Characterization of thin films

The top and cross-sectional views before and after the TO were observed by FE-SEM (Tescan Mira3, Czech Republic). Elemental composition was analyzed by EDS. Crystal structures were determined by XRD (D2 PHASER, Bruker) with  $\text{Cu K}\alpha$  radiation at  $1.54 \text{ \AA}$ , scanning from  $20^\circ$  to  $80^\circ$  with a time per step of 0.2 s and increments of  $0.02^\circ$ . Transmittance (T%) in the range of 200 nm to 1000 nm was measured by UV-Vis spectrophotometer (Genesys S10, Thermo Scientific). Furthermore, the colored films were achieved through EC by applying a 2.0 V DC supply, connecting the films as the cathode, Pb as the anode, and immersing them in 0.1 M  $\text{H}_2\text{SO}_4$  for 1 min.

After that, the PA performance of the films in the pre-color and colored states was tested by monitoring the relative absorbance of MB

at 664 nm with a base concentration of 0.05 mM under UV irradiance ( $300 \mu\text{W}\cdot\text{cm}^{-2}$ , Silver light 10W/T8/BL Blacklight). Finally, the current density was measured by CV testing (Wuhan Corrtest Instruments Corp., Ltd.). A 3-electrode setup was used, with films serving as working electrodes, Ag/AgCl as reference electrodes, and Pt as counter electrodes. DC voltage  $\pm 2.0 \text{ V}$  was applied at a constant scanning rate of  $100 \text{ mV}\cdot\text{s}^{-1}$  in the  $\text{H}_2\text{SO}_4$ . Figure 5 illustrates the schematic setup for CV and PA testing.

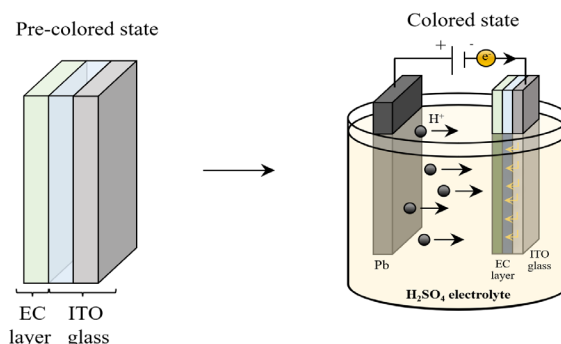


Figure 1. Schematic of EC process.

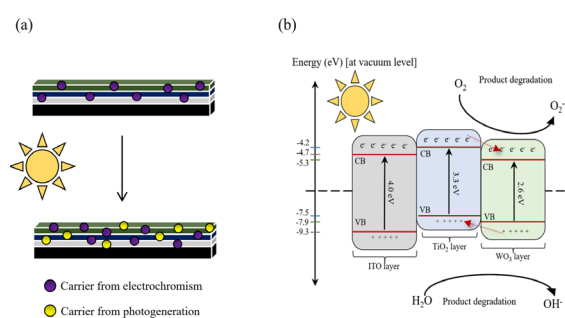


Figure 2. Mechanism of (a) carrier presence on the film surface in the colored state during irradiance light and (b) the PA of ITO/Ti/W films.

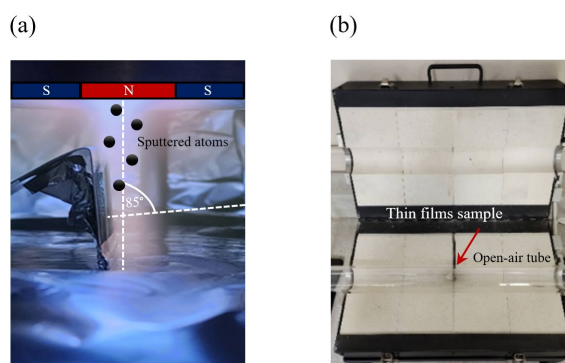
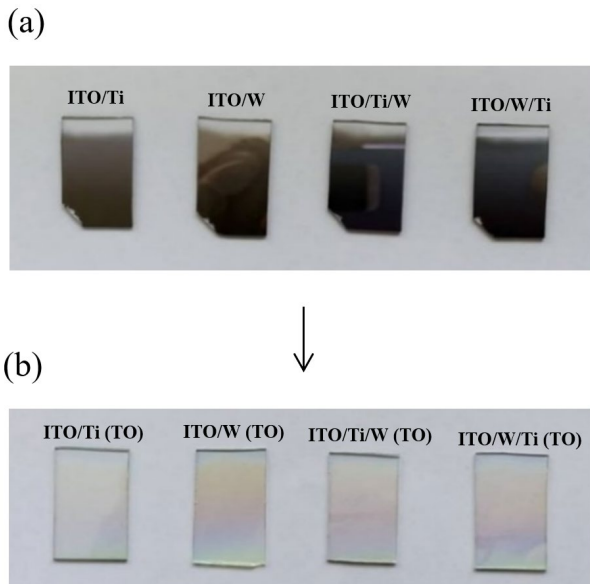


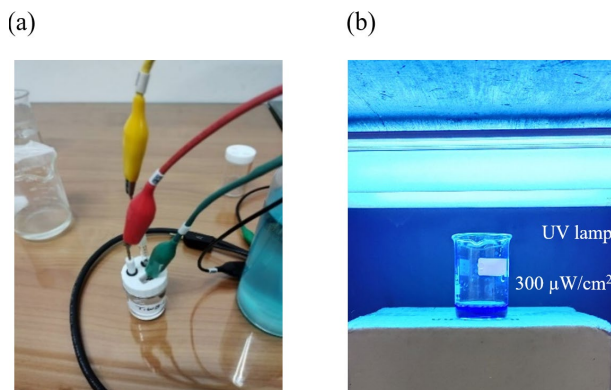
Figure 3. Schematic of experimental for (a) sputtering process with OAD, and (b) TO at  $500^\circ\text{C}$  for 1 h.

Table 1. Summary of preparation of ITO/Ti, ITO/W, ITO/Ti/W, and ITO/W/Ti films.

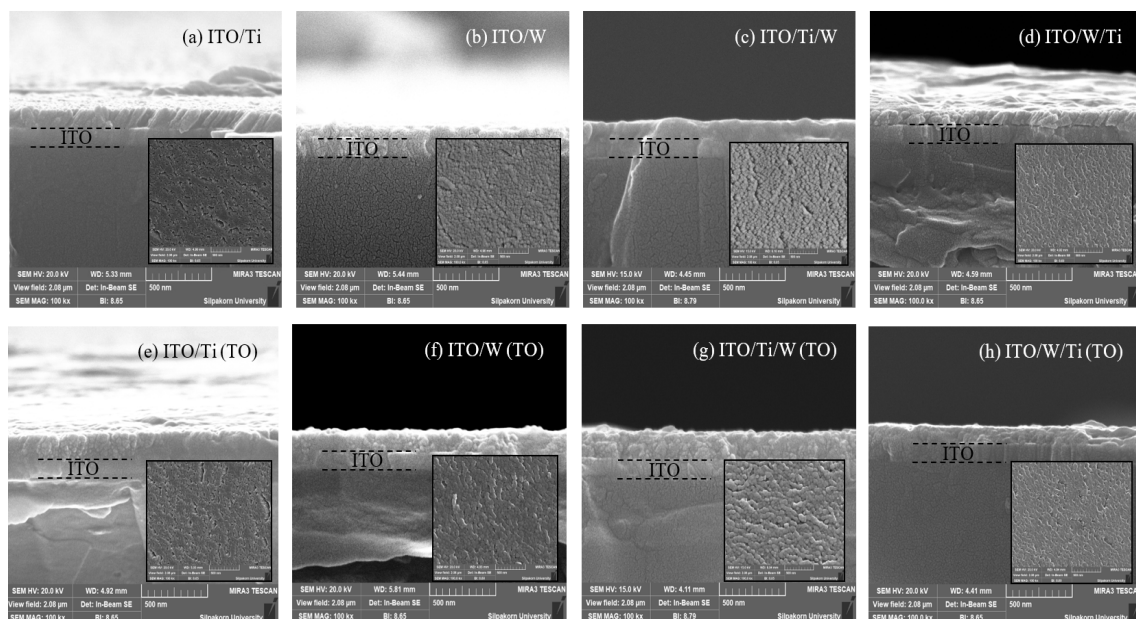
Samples	Sputtering power (Watts)		Total thickness (nm)	TO temperature and timen ( $^\circ\text{C}$ , h)
	Ti	W		
ITO/Ti (TO)	100	-	100	500, 1
ITO/W (TO)	-	20	100	500, 1
ITO/Ti/W (TO)	100	20	50+50	500, 1
ITO/W/Ti (TO)	100	20	50+50	500, 1



**Figure 4.** Photograph of (a) as-deposited metal Ti, W, Ti/W, and W/Ti films, and (b) after TO at 500°C for 1 h.



**Figure 5.** Experimental setup for (a) CV and (b) PA testing.



**Figure 6.** Top and cross-sectional views of FE-SEM images of as-deposited (a) Ti, (b) W, (c) Ti/W, and (d) W/Ti and after TO at 500°C for 1 h, (e) Ti, (f) W, (g) Ti/W, and (h) W/Ti.

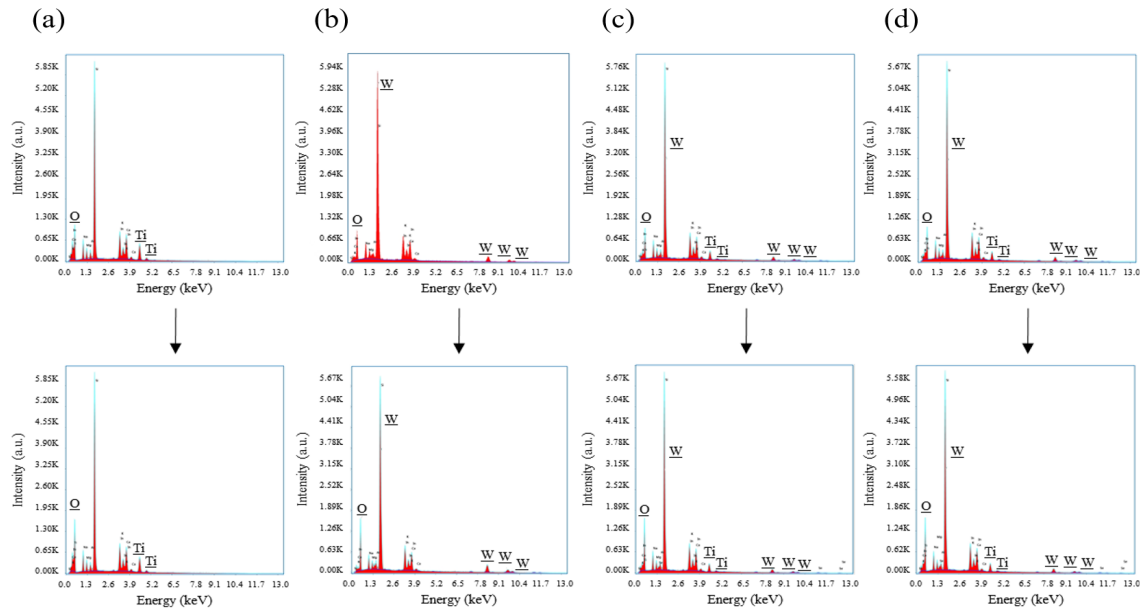
### 3. Results and discussion

#### 3.1 Morphology and elemental composition

The top and cross-sectional views of the as-deposited and TO of ITO/Ti, ITO/W, ITO/Ti/W, and ITO/W/Ti are shown in Figure 6. The OAD techniques produce a nanorod structure according to the shadowing effect and the limitations of atom diffusion [28]. The realignment of nanorod alloys responds to the deposition rates ( $0.273 \text{ nm}\cdot\text{s}^{-1}$  and  $0.115 \text{ nm}\cdot\text{s}^{-1}$  for Ti and W, respectively), with the higher deposition rate resulting in ITO/Ti showing orderly alloys. Conversely, ITO/W forms a porous structure, as observed in previous research [29], and the TO process results in the formation of oxides covering the surface.

The elemental compositions of as-deposited and after TO, represented by the weight percentages (wt%) from the EDS spectra, are shown in Figure 7 and Table 2 and Table 3. The Ti and W layers show a slightly different wt% of O due to the higher mass density of W atoms compared to Ti atoms, resulting in the EDS spectra being more likely to detect the presence of W atoms. In the 2-layer system, the wt% of Ti and W decreased by 50% due to the reduced thickness of the Ti and W layers. After TO, the wt% of O increased because the O atoms bonded with Ti and W atoms to form oxide components as described by the reactions:  $\text{Ti}^{4+} + 2\text{O}^{2-} \rightarrow \text{TiO}_2$  and  $\text{W}^{6+} + 3\text{O}^{2-} \rightarrow \text{WO}_3$ .

In terms of elemental ratio, the 2-layer samples showed a slight difference in the Ti/W ratio. This can be attributed to the quantity of metal oxides in the samples. The porous surface of ITO/Ti/W allows O atoms to penetrate the film easily, leading to the strong formation of metal oxides, which is reflected in the reduced Ti and W wt%. On the other hand, the ITO/W/Ti sample has a more compact surface, resulting in a similar O wt% compared to ITO/Ti/W but higher Ti and W wt% [30]. Additionally, the other observed peaks correspond to components in the ITO glass (Si, In, Sn, Na, etc.).



**Figure 7.** EDS spectra of (a) ITO/Ti, (b) ITO/W, (c) ITO/Ti/W, (d) ITO/W/Ti as-deposited (above) and after TO at 500°C for 1 h (below).

**Table 2.** Elemental composition of film samples as-deposited and after TO at 500°C for 1 h.

Samples	Elemental composition (wt%)					
	Ti		O		W	
	As-deposited	TO	As-deposited	TO	As-deposited	TO
ITO/Ti	7.63	6.34	23.77	30.46	-	-
ITO/W	-	-	12.99	24.62	28.86	25.24
ITO/Ti/W	4.02	3.21	19.02	26.31	14.67	11.94
ITO/W/Ti	3.82	3.22	19.40	26.40	15.54	13.05

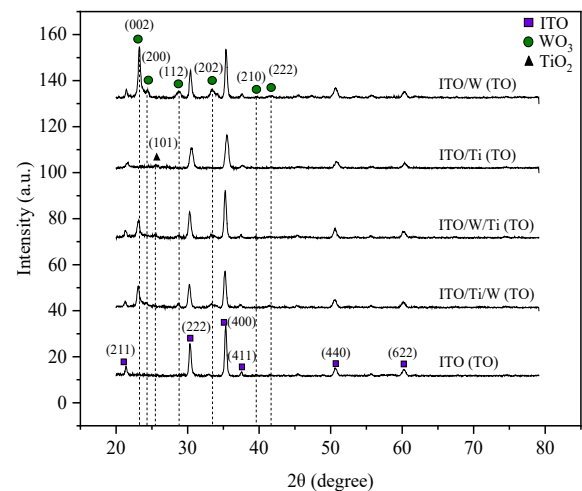
**Table 3.** Elemental ratio of film samples as-deposited and after TO at 500°C for 1 h.

Samples	Elemental ratio					
	Ti/O		W/O		Ti/W	
	As-deposited	TO	As-deposited	TO	As-deposited	TO
ITO/Ti	0.32	0.21	-	-	-	-
ITO/W	-	-	2.22	1.03	-	-
ITO/Ti/W	0.21	0.12	0.77	0.45	0.27	0.27
ITO/W/Ti	0.20	0.12	0.80	0.49	0.25	0.25

### 3.2 Crystal structure

The crystal structures after TO at 500°C for 1 h were characterized by XRD, as shown in Figure 8. The small reflection at  $2\theta$  of 25.52° corresponded to the Miller indices (hkl) at the (101) plane of the TiO<sub>2</sub> anatase phase (JCPDS PDF no. 21-1272). The strong signals correspond to the primary reflections of WO<sub>3</sub> at 23.28°, 24.41°, 28.79°, 33.41°, 39.58°, and 41.67° corresponding to (002), (200), (112), (202), (210), and (222), respectively, with crystal orientations of the WO<sub>3</sub> orthorhombic phase (JCPDS PDF no. 83-0951).

In the case of the 2-layer samples (ITO/Ti/W and ITO/W/Ti) after TO, the anatase and orthorhombic phases were observed, similar to the 1-layer samples. This confirms that the crystal orientations did not change in the 2-layer system, regardless of whether the Ti or W layer was on top. However, the 2-layer samples showed evidence of lower peak intensity compared to the 1-layer samples because the ratio of the layers had decreased.



**Figure 8.** XRD patterns of the Ti and W sputtered with OAD 85° and after TO at 500°C for 1 h.

### 3.3 Optical properties

The optical transmittance spectra (T%) of the 1-layer and 2-layer film samples in the wavelength range of 200 nm to 1100 nm are shown in Figure 9 and used to determine the E<sub>g</sub> values by Tauc's relation, as shown in Equation (1), where α is the absorption coefficient, hv is the incident photon energy, and E<sub>g</sub> is the optical band gap energy.

$$\alpha hv = (hv - E_g)^n \quad (1)$$

where n = 2 for indirect transition of the E<sub>g</sub> and intercepts of the tangent drawn at the absorption function to the energy axis at zero absorption are evaluated to get the E<sub>g</sub> values.

After the TO, the film samples exhibited high transparency, and the E<sub>g</sub> values were found to be 3.64, 3.67, 3.76, and 3.78 eV for ITO/Ti (TO), ITO/Ti/W (TO), ITO/W (TO), and ITO/W/Ti (TO), respectively. The results of the E<sub>g</sub> values provide evidence of charge transfer between the Ti and W layers, especially in the W layer, where there is a change to the WO<sub>3</sub> orthorhombic phase. This phase change results in a reduced band alignment strategy in the 2-layer system [31,32].

### 3.4 Photocatalytic performance

In this study, the 1-layer and 2-layer films are divided into two states: i) pre-color state and ii) colored state. The colored state is achieved by applying a 2.0 V DC, connecting film as the cathode, and Pb as the anode, before immersion in H<sub>2</sub>SO<sub>4</sub> as the electrolyte for 1 min, followed by the EC process.

The PA performance was evaluated through 4 iterations of tests by monitoring the degradation of 0.05 mM MB as an organic pollutant. The relative absorbance at 664 nm was measured and plotted against time to investigate the degradation over a total of 250 min. For the first 50 min, we observed the adsorption-desorption on the surface by sealing the samples in the dark. The remaining 200 min were conducted under UV irradiation at an intensity of 300 μW·cm<sup>-2</sup> with recordings taken every 50 min. The chemical kinetics can be used to describe the behavior of the MB degradation rate, which follows a first-order reaction as described in Equation (2) [33].

$$\ln\left(\frac{C}{C_0}\right) = kt \quad (2)$$

where C is the MB concentration, C<sub>0</sub> is the initial MB concentration (0.05 mM), k is the first-order rate constant, and t is time.

#### 3.4.1 PA in the pre-color state

The first step of observation takes place in the pre-color state. The results are presented in Figure 10 and Figure 11. The first 50 min in darkness revealed absorption and fast activity by the catalyst surface. After the UV irradiation, the MB concentration clearly decreased due to the redox reaction. For the 1-layer samples, ITO/Ti (TO) showed a high photodegradation performance, benefiting from the catalytic properties of Ti compared to ITO/W (TO).

For the 2-layer films, the position of the layers significantly affected their PA performance. In the case of ITO/Ti/W (TO), the photodegradation performance was comparable to ITO/Ti (TO), despite the reduced thickness of the Ti layer. This indicates that the Ti layer plays the role of catalyst, and the W layer contributes to initial absorption [34,35], aiding the generation of e<sup>-</sup>-hole pairs and reducing the recombination rate due to e<sup>-</sup> acceptance efficiency [36-39]. However, ITO/W/Ti (TO) did not perform effectively in photodegradation, showing a slower degradation rate because the ITO and Ti layers acted as barriers, obstructing the redox reaction by trapping e<sup>-</sup> in the W layer [40], as shown in Figure 12.

Regarding durability, after cycling tests, ITO/Ti (TO) showed a decrease in performance, trending towards the performance of ITO/Ti/W (TO) after 4 tests of photodegradation under UV irradiation. Nonetheless, both ITO/Ti (TO) and ITO/Ti/W (TO) showed strong degradation performance and were chosen for photodegradation testing in the colored state.

#### 3.4.2 PA in the colored state

After the first observation step, the 1-layer and 2-layer ITO/Ti and ITO/Ti/W samples were chosen based on their PA performance in the pre-color state. The next step of PA testing was conducted in the colored state by applying 2 V DC to the film, with the film as the cathode and Pb as the anode, and immersing it in H<sub>2</sub>SO<sub>4</sub> for 1 min. The testing conditions were the same as in the pre-color state. Additionally, we studied the mechanism and stability of the film in the colored state during PA testing by measuring T% and calculating E<sub>g</sub> before and after the EC process. We also collected T% at each step and observed photodegradation during the 1<sup>st</sup> test.

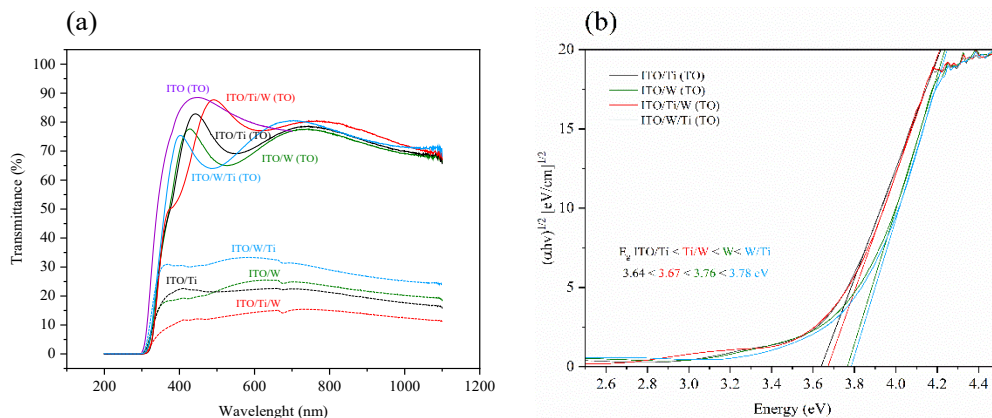
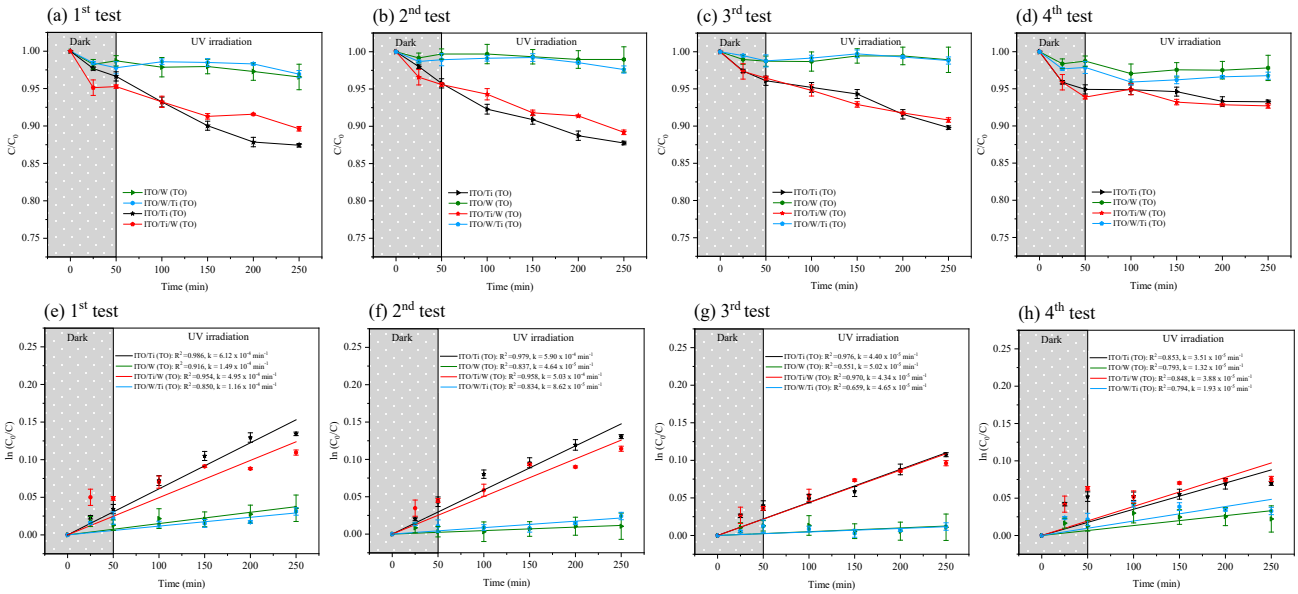
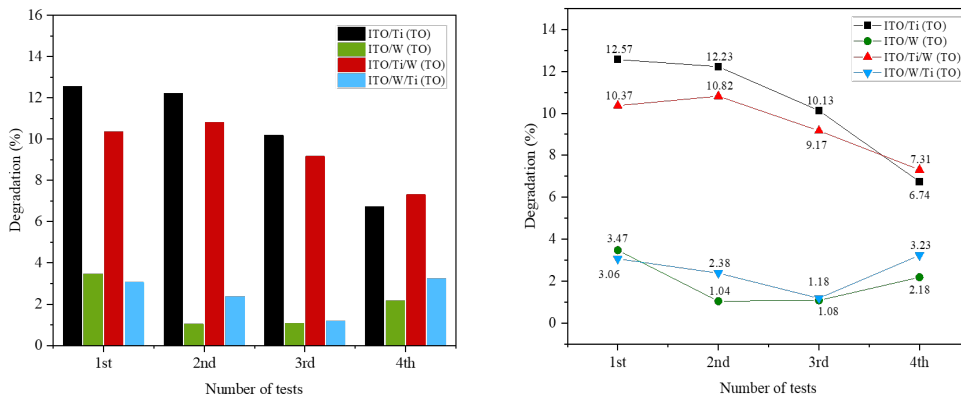


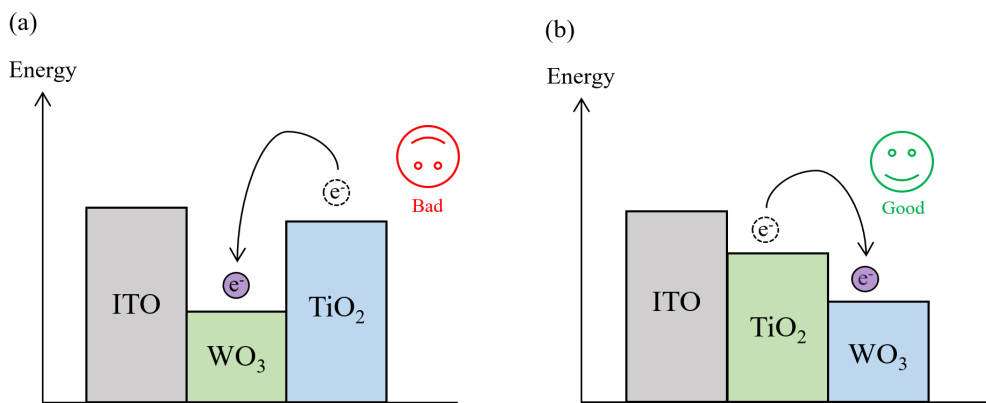
Figure 9. (a) T% and (b) E<sub>g</sub> values from Tauc's plot of the film sample as-deposited and after TO at 500°C for 1 h.



**Figure 10.** (a-d) Degradation of MB by measuring relative absorbance at 664 nm versus testing time and (e-h) the first-order rate constants for TO samples from 4 tests.



**Figure 11.** Comparison of the degradation % of thin films after TO at 500°C for 1 h based on data from 4 tests.



**Figure 12.** Effects of  $e^-$  transfer from layer arrangement of (a) ITO/W/Ti (TO), and (b) ITO/Ti/W (TO).

The results of T% and  $E_g$  of the films in both the pre-color and colored states are represented by dashed and solid lines, respectively, as shown in Figure 13. In the colored state, C-ITO/Ti (TO) exhibits only slight changes compared to C-ITO/Ti/W (TO), which shows significant absorption in the green spectrum and appears as a deep blue color. This is because the W layer, being a strong EC material, facilitates the quantity

of ions and  $e^-$  into the structure, thereby enhancing the change in optical properties [41].

In terms of  $E_g$ , we found that for C-ITO/Ti/W (TO), right after the EC process, the  $E_g$  slightly increased to 3.71 eV and then decreased back to 3.77 eV as the film started bleaching after immersion in MB in a dark location for 25 min, and it was completely bleached after

100 min. In contrast, the C-ITO/Ti (TO) did not show a significant change in E<sub>g</sub> and remained at 3.60 eV for 250 min. This behavior may be explained by the charge quantity and coloration efficiency in the EC effect.

The PA performance was observed using the same method as in the pre-color state, as shown in Figure 14 and summarized in Figure 15. After the EC process, the degradation of C-ITO/Ti/W (TO) increased from 12.78% to 15.46%, and C-ITO/Ti (TO) from 21.69% to 22.37%. This clearly demonstrates the effect of EC properties on increasing degradation efficiency, providing the evidence that the colored state

does affect PA performance. The EC effect allows charge insertion and storage/trapping in the film's structure by forming specific compounds (H<sub>x</sub>WO<sub>3</sub> and H<sub>x</sub>TiO<sub>x</sub>), which induce absorption in specific spectra. We investigated the surface charge by monitoring the current density during the EC process using CV testing, as shown in Figure 16. The results show that C-ITO/Ti/W (TO) has a charge density of -0.0139 A·cm<sup>-2</sup>, higher than C-ITO/Ti (TO) at -0.0112 A·cm<sup>-2</sup>. This indicates that the films with more color formation had a greater number of carriers on the surface, leading to an increased oxidation-reduction rate of MB degradation [42-44].

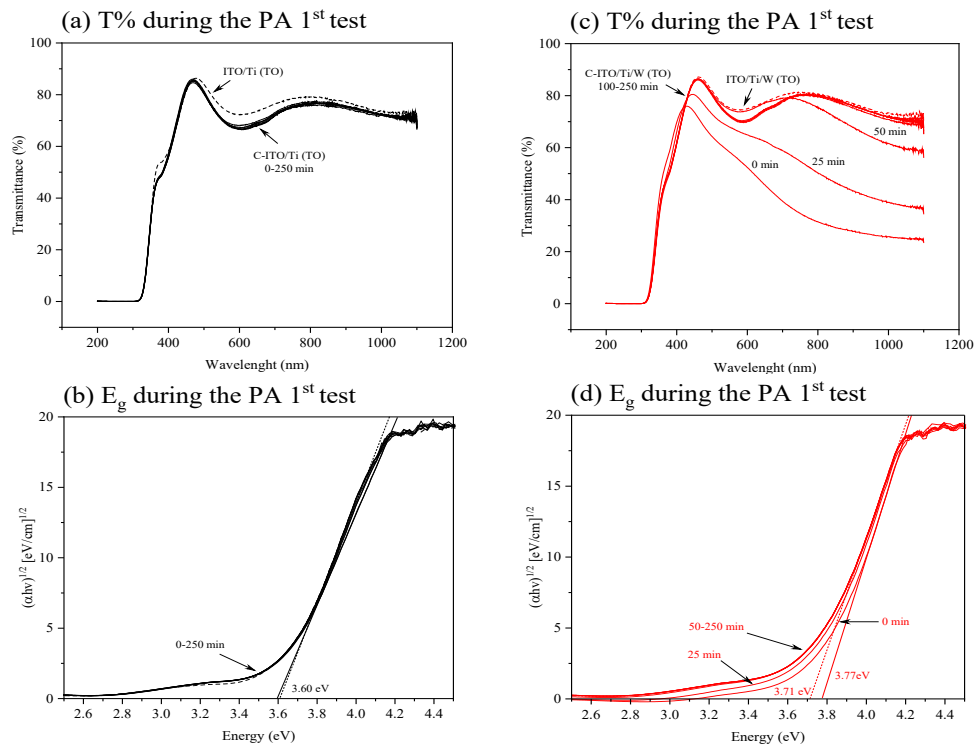


Figure 13. T% and before and after colored state and Tauc's plot relation of (a,b) ITO/Ti (c,d) and ITO/Ti/W during PA 1<sup>st</sup> test.

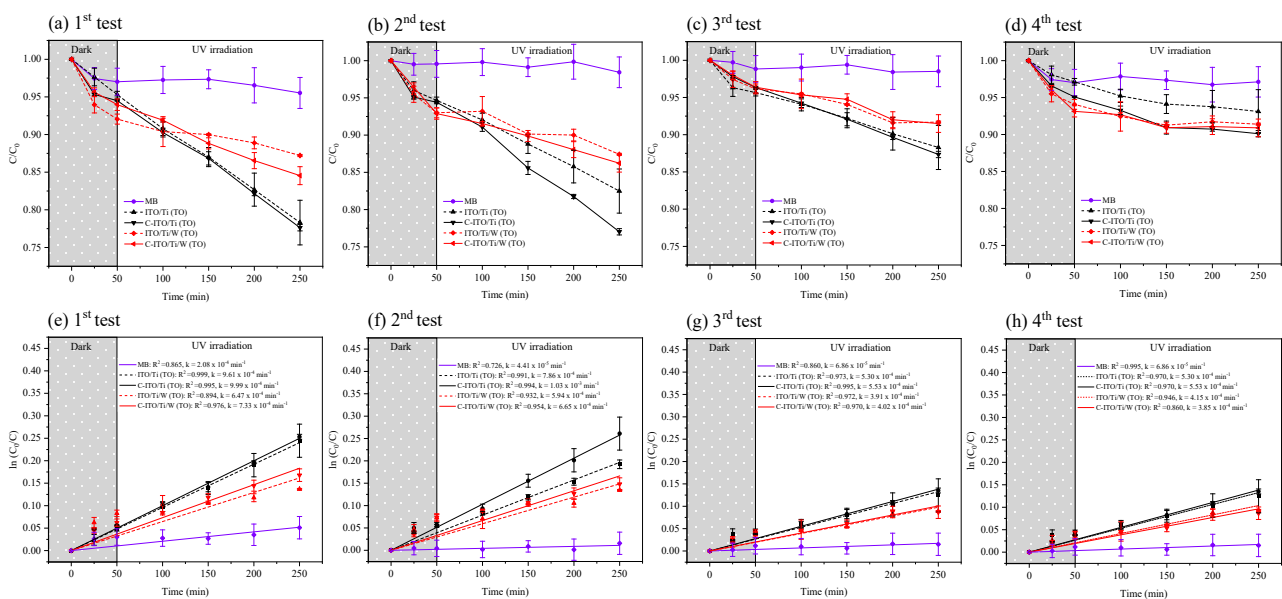
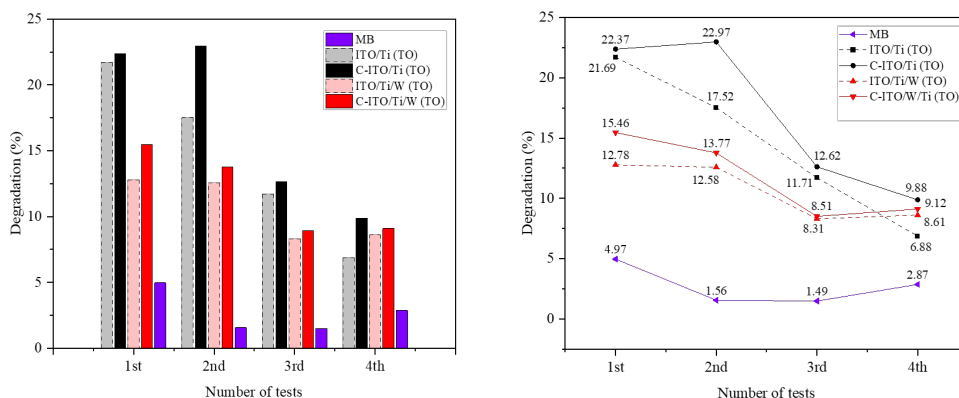
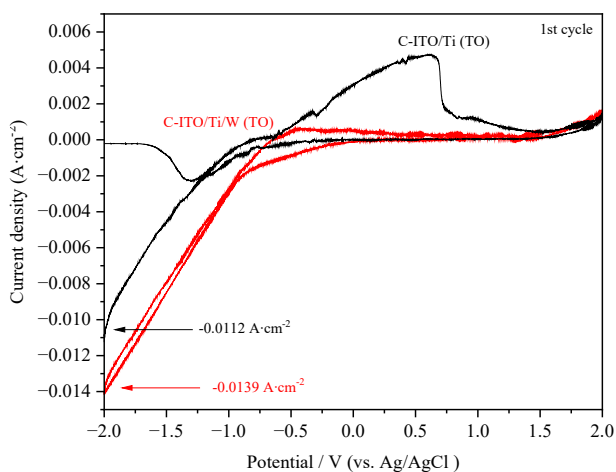


Figure 14. (a-d) Degradation of MB by measuring relative absorbance at 664 nm versus testing time and (e-h) the first-order rate constants for pre-color and colored states from 4 tests.



**Figure 15.** Comparison of the degradation % of pre-color and colored states for 1 h based on data from 4 tests.



**Figure 16.** Cyclic voltammetry for the 1<sup>st</sup> cycle of C-ITO/Ti (TO) and C-ITO/Ti/W (TO).

Additionally, there are some interesting parts in C-ITO/Ti/W (TO) samples. Unfortunately, under our testing conditions, the colored state began to bleach after immersion in MB for 25 min, even without UV irradiation. We propose that if the colored state can be maintained long enough to be active in the UV region, the film may increase degradation by allowing activation in the visible spectrum.

#### 4. Conclusions

The 1-layer and 2-layer Ti and W films were deposited using DC magnetron sputtering combined with an OAD technique, and the TO process was applied to form metal oxide films at 500°C for 1 h. The Ti layer exhibited an ordered tilted nanorod and the W layer exhibited a dense and porous surface due to the limitations of atom diffusion. XRD analysis revealed the crystalline structure of the anatase phase of TiO<sub>2</sub> and the orthorhombic phase of WO<sub>3</sub>. The first step of observation of PA performance revealed that ITO/Ti (TO) and ITO/Ti/W (TO) exhibited higher degradation rates compared to ITO/W (TO) and ITO/W/Ti (TO), according to the charge transfer in band alignments of the heterojunction.

The ITO/Ti (TO) and ITO/Ti/W (TO) were chosen to test the PA performance in the colored state based on their degradation %, and the colored state achieved though the EC process revealed that C-ITO/Ti/W (TO) has higher coloration efficiency compared to C-ITO/Ti (TO) because the W layer plays a significant role as EC material which

facilitates the charge into the structure confirmed by the current density in CV testing ( $-0.0139$  and  $-0.0112$  A·cm<sup>-2</sup> for C-ITO/Ti/W (TO) and C-ITO/Ti (TO), respectively).

In terms of MB degradation under UV irradiance, both ITO/Ti and ITO/Ti/W in the colored state show higher degradation rates than in the pre-color state, and the degradation rate was enhanced by the double injection of e<sup>-</sup> and ions by the EC effect.

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