

## Research Article

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## Fabrication of a $\text{WO}_3\text{-Bi}_2\text{WO}_6$ Composite Electrode by Electrodeposition and its Application for Microbial Degradation

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### Abstract

Photoelectrocatalytic (PEC) techniques are an innovative and promising method for eliminating microorganisms. Developing and applying such advanced technologies is essential for protecting public health and the environment. Semiconductor electrode development is a major issue in the advancement of such methods. We have developed a technique for fabricating  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes using cyclic voltammetry (CV), focusing on the efficiency of the reaction and investigating key aspects for its use in microbial degradation. The optimization of the CV method parameter and calcination temperature was conducted in order to enhance the characteristics of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes for the aqueous oxidation process. The properties of the fabricated composited  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode were analyzed by several techniques, including UV-visible spectrophotometry, scanning electron microscopy, X-ray diffraction, Energy Dispersive X-ray Spectroscopy, X-ray photoelectron spectroscopy, and electrochemical impedance spectroscopy. The PEC water oxidation and total microorganism elimination efficiencies were investigated to validate the application of the developed composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode properties. The characteristics of the prepared composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes are significantly influenced by the calcination temperature. We were able to satisfactorily verify the electrodes' properties in a reaction involving different calcining temperatures. At a calcining temperature of 450 °C,  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes exhibited excellent PEC activity in water oxidation and electron transfer rate at the electrode surface. The composited  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode can effectively remove 96% of total microorganisms under the PEC process within 15 minutes. This study provides important background information for future work on composite semiconductor thin film preparations with potential applications in microbe eradication and environmental protection.

**Keywords:** Photoelectrocatalytic Method, Microorganisms Elimination, Composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$

### 1. Introduction

Microbial contamination in water sources is a big issue that has an impact on the quality of life of those who rely on that water for survival. As a result, a highly effective technique must be devised to eradicate such toxins as soon as possible before releasing them into the

environment. The photoelectrocatalytic (PEC) oxidation process is an alternate technological approach to addressing water pollution, which includes the eradication of microorganisms in natural water sources (1-6). The advancement of this approach has aided in the selection of appropriate semiconductors as well as the

different electrode properties (5-7). The effect of calcination temperature on the morphology, optical properties, chemical composition, and crystal structure of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  thin films synthesized by the CV technique for water oxidation and total microbial elimination in water is described. This research could potentially be helpful in the development of semiconductor thin film preparations using electrochemical methods, as well as in utilizing those preparations for the purpose of PEC cells aimed at the degradation of microorganisms.

## 2. Materials and Experiment

### 2.1 Materials

All chemicals in the analytical grade and all solutions throughout the experiments were prepared using deionized water. Diethylenetriamine pentaacetic acid; DTPA (Sigma Aldrich), Ammonium hydroxide;  $\text{NH}_4\text{OH}$  (J.T.Baker), Bismuth(III)oxide;  $\text{Bi}_2\text{O}_3$  (Sigma Aldrich), Ammonium metatungstate hydrate;  $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot\text{H}_2\text{O}$  (Sigma Aldrich), Nitric acid;  $\text{HNO}_3$  (Univar), Hydrogen peroxide;  $\text{H}_2\text{O}_2$  (Chem-supply), Ethanol;  $\text{C}_2\text{H}_5\text{OH}$  (Rcl Labscan), Sodium chorine;  $\text{NaCl}$  (Kemaus), Methylene blue;  $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$  (KEMAUS) Sodium hydroxide;  $\text{NaOH}$  (Univar) and Fluorine doped tin oxide; (FTO with dimension of  $2\text{x}2\text{ cm}^2$ ; Bangkok solar co.ltd., THAILAND).

### 2.2 Composite $\text{WO}_3\text{-Bi}_2\text{WO}_6$ electrode preparation

The conductive glass fluorine doped tin oxide (FTO) base was cleaned by sonicating it for 10 minutes in a solution of detergent, 3 M  $\text{NaOH}$ , ethanol, and deionized water, respectively. To make the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  precursor solution, 0.83 g of diethylenetriamine pentaacetic acid (DTPA) was dissolved in 2.5 ml of 30% ammonia solution ( $\text{NH}_4\text{OH}$ ), and the end amount was brought up to 50 ml by adding deionization water. The solution was stirred, and then 0.4 g of bismuth (III) oxide ( $\text{Bi}_2\text{O}_3$ ) and 0.15 g of ammonium metatungstate hydrate ( $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot\text{H}_2\text{O}$ ) were added. The solution was stirred at 80 °C until it was uniform. The solution was then mixed efficiency of fabricating a thin layer of semiconductors on an electrode substrate. Bismuth-tungstate ( $\text{Bi}_2\text{WO}_6$ ) and tungsten oxide ( $\text{WO}_3$ ) are a promising semiconductor material for the PEC water oxidation due to its narrow band gap energy and

high positive potential of its valence band (8-10). Furthermore, the fabrication process of  $\text{WO}_3$  and  $\text{Bi}_2\text{WO}_6$  semiconductor thin films has significant importance in the advancement of PEC techniques, aiming to achieve electrodes that exhibit high reaction efficiency, long-term durability, and simplified processing methods. The most used technique is hydrothermal, but it also involves a challenging procedure that involves great heat and pressure (11, 12). The sol-gel method is widely used for the fabrication of  $\text{Bi}_2\text{WO}_6$  and  $\text{WO}_3$  films on substrates, owing to its straightforward and cost-effective nature (13, 14). However, this method has a disadvantage in that the film creation process may be time-consuming, and the resulting films may have considerable porosity, decreasing their photocatalytic activity. To overcome the drawbacks of the aforementioned approaches while maintaining semiconductor performance, it is essential to create a process for  $\text{WO}_3$  and  $\text{Bi}_2\text{WO}_6$  film preparation.  $\text{Bi}_2\text{WO}_6$  and  $\text{WO}_3$  film preparation using the electrochemical approach is a viable option because of its precision, scalability, affordability, and low energy requirements (14-17). Therefore, this study has devised an electrochemical method for fabricating composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  films using cyclic voltammetry (CV), which allows for the quality of the films to be controlled by varying parameter settings. There are several benefits to using CV techniques for semiconductor film preparation, such as accurate electrochemical regulation, controllable film thickness, consistent deposition, and high purity levels. However, the application of CV technique for composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film preparation has not yet been reported, confirming the novelty of this research. We have also investigated the effect of electrode sintering on reaction efficiency and the impact of temperature on with 1,190  $\mu\text{l}$  of nitric acid ( $\text{HNO}_3$ ) and 77  $\mu\text{l}$  of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) for 15 minutes at 80 °C.  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  precursor solution was deposited on a cleansed FTO substrate using cyclic voltammetry with a Versa STAT 3 (Princeton Applied Research, Inc.) under the optimized potential range of -0.6 to 0.8 V and scan rate of 50 mV/s for 30 cycles at 80 °C. A common three-electrode system consisted of an FTO working electrode, an  $\text{Ag}/\text{AgCl}$  (3 M  $\text{KCl}$ ) reference electrode, and a platinum wire counter electrode. The composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film on the FTO substrate was taken out, rinsed with

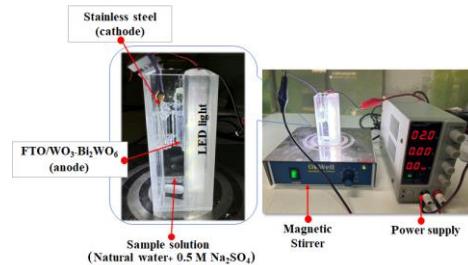
deionized water, and then calcined at 25°C, 300°C, 400°C, 450°C, 500°C, and 600°C in the air for 1 hour to study the effects of different calcination temperatures. The optimal condition with the highest photocurrent from the PEC water oxidation process in relation to the distinguishing characteristics electrode were evaluated.

### 2.3 Characterization and PEC properties study

A UV-VIS spectrophotometer (Shimadzu, UV-2401PC) was used to examine the absorption characteristics of the fabricated  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode. A scanning electron microscope (SEM; JEOL, JSM-6510) was used to investigate the morphology in top views. The chemical state, chemical composition, and crystalline structure were investigated using an X-ray photoelectron spectrometer (JPS-9010TR), an Energy Dispersive X-ray Spectrometer (EDX), and an X-ray diffraction (XRD) (JEOL, JDX-3530). In order to validate the presence and characteristics of the produced electrodes, a comparison was conducted between the characteristics of FTO and modified FTO with  $\text{WO}_3\text{-Bi}_2\text{WO}_6$ . The proposed  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes' photoelectrocatalytic water oxidation performance and charge transfer efficiency were studied in 0.5 M  $\text{Na}_2\text{SO}_4$  electrolyte solution utilizing a potentiostat and electrochemical impedance spectroscopy (METEK, Versa STAT 3).

### 2.4 PEC microbial elimination efficiency study

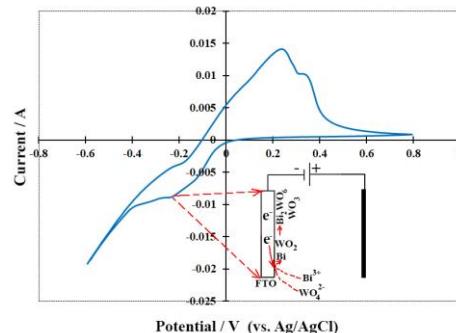
As shown in the experimental setup in Figure 1, natural water was used as an actual sample for microbial contamination in water to evaluate the efficiency of the developed PEC cell. The microbial culture medium was prepared using 0.8 g of nutrient bouillon diluted in 100 mL of distilled water, which was then autoclaved at 121°C at 15 bar pressure for 15 minutes and disposed of in the PEC cell. A 1 mL sample of the solution was collected at 5-minute intervals throughout a 15-minute period. The sample was then placed onto a sterile dish containing agar medium and incubated at a temperature of 37°C for a duration of 24 hours. The number of microorganisms present on the sterile dish was afterwards determined.



**Figure 1** Experimental setup for investigating the degradation of microorganisms utilizing the developed PEC cell.

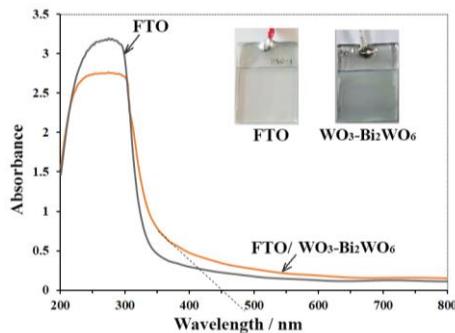
## 3. Results and Discussion

### 3.1 Cyclic Voltammetry Technique for composite $\text{WO}_3\text{-Bi}_2\text{WO}_6$ Film Preparation



**Figure 2** Cyclic voltammogram of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  deposition on FTO substrate and inset of schematic reaction of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film formation.

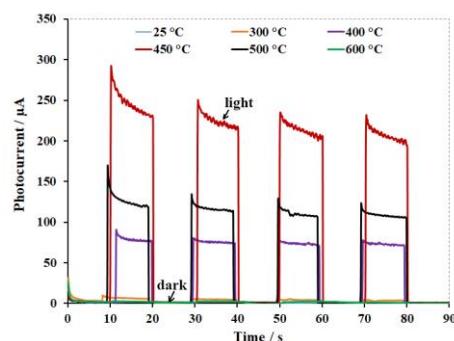
Figure 2 depicts the reduction reaction of the precursor solution while varying the voltage from 0.8 to -0.6 V to cause the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  layer to adhere to the FTO electrode surface. The schematic reaction at the FTO substrate is shown in the inset of Figure 2. When a negative potential is introduced,  $\text{Bi}^{3+}$  and  $\text{WO}_4^{2-}$  ions agglomerate to create a composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  layer that adheres to the FTO surface. The reduction current occurred in the range of -0.2 V on the cyclic voltammogram, indicating the value of the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film-forming current at the electrode surface.



**Figure 3** The absorbance properties of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  immobilized on FTO substrate, as well as images of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film compared to FTO substrate, are shown in the inset.

Figure 3 shows the absorption edge of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  starting at 450 nm, which is consistent with the absorption characteristics of  $\text{WO}_3$  and  $\text{Bi}_2\text{WO}_6$  with a band energy of 2.80 eV (16). The inset of Figure 3 reveals a bright yellow hue of  $\text{WO}_3$  and  $\text{Bi}_2\text{WO}_6$ , which corresponds to the electrode's absorption capabilities in the visible range(18). The findings of the aforementioned investigation indicate the ability of the CV approach to immobilize composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  film, which is a simple, practical, and rapid technology that has been studied extensively.

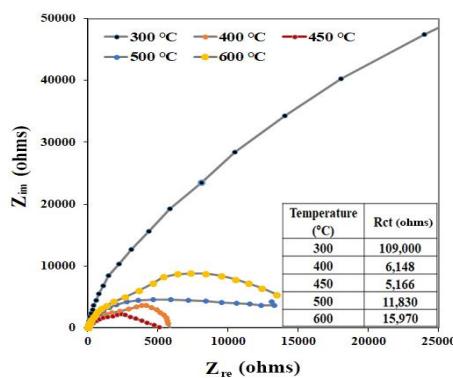
### 3.2 Effect of calcination temperature on the fabrication of composite $\text{WO}_3\text{-Bi}_2\text{WO}_6$ electrodes



**Figure 4** Effect of calcination temperature with photocurrent reaction from water oxidation on the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode developed using the CV method.

Calcination is a thermal treatment process that entails heating the precursor materials to a particular temperature to facilitate the formation of the desired phase and enhance the structural, morphological, and electronic properties of the resulting composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  films. Figure 4 shows how the calcination temperature affects the PEC performance of the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode. This was done by measuring the photocurrent from the water oxidation process under the chopped visible-light illumination at an applied voltage of 1.0 V (versus  $\text{Ag}/\text{AgCl}$ ).

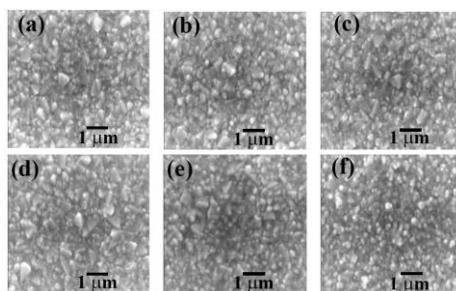
PEC activities characteristics were not seen in composited  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes calcined at temperatures lower than 400°C. We discovered that the electrodes had good reactive characteristics at rising sintering temperatures ranging from 400°C to 450°C, and that the reactive qualities decreased with increasing temperatures up to 500°C. The aforementioned findings show the unique influence of the sintering temperature on the characteristics of the composited  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes in their as-prepared state in relation to thin film characteristics at various sintering temperatures.



**Figure 5** Nyquist diagrams and  $\text{R}_{\text{ct}}$  value of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  prepared by the different calcination temperatures of 300°C, 400°C, 450°C, 500°C, and 600°C.

Electrochemical Impedance Spectroscopy (EIS) is a useful method for investigating the charge transfer mechanisms and interfacial properties of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  and gaining insight into its PEC behavior. Figure 5 illustrates the considerable changes in the Nyquist diagram of composite

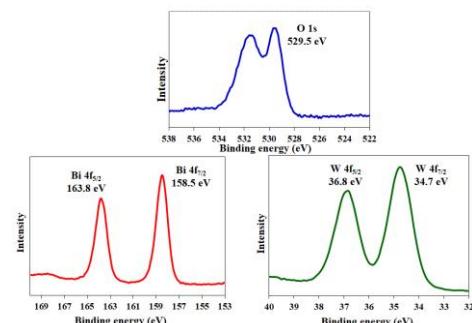
WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> thin films recorded at different calcination temperatures. The composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrode that was heated to 450°C had the smallest hemispherical radius Nyquist plot, which means it had the least charge transfer resistant (R<sub>ct</sub>) properties at the electrode/electrolyte interface. Figure 5's inset shows that an electrode with the lowest R<sub>ct</sub> value had the maximum photocurrent value at 450°C, which may help to explain how the best electron transfer process is affected by proper sintering.



**Figure 6** SEM micrographs of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrodes prepared at various annealing temperatures: (a) 25°C, (b) 300°C, (c) 400°C, (d) 450°C, (e) 500°C, and (f) 600°C.

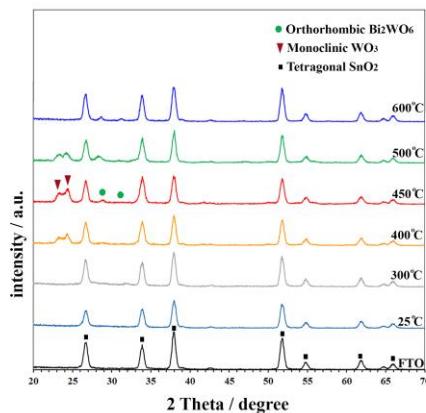
Figure 6 shows that morphological changes are dependent on increasing calcination temperature from 25°C to 600°C, whereas surface roughness and porosity of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> thin films do not change significantly from 25°C to 400°C. At 450°C, the arrangement of particles becomes uniform, resulting in an efficient electron transfer process. However, as temperatures rise to 500°C and 600°C, the particles begin to rearrange due to excessive high-temperature fusing and the influence of electron transfer. This result demonstrates that calcination at a high temperature of approximately 500°C induces observable morphological changes, which influence the physical properties of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> thin films. The optimal calcination temperature for porosity and roughness was determined to be 450°C.

WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> photoanodes that were calcined at 450°C exhibited good photoelectrocatalytic activity and electron transfer due to the fact that at that temperature there was a good crystal structure and appropriate morphology, resulting in a higher current value resulting from oxidation reactions at the electrode surface. Energy Dispersive X-ray Spectrometer (EDX) was used to determine the quantitative elemental analysis of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrodes fabricated by cyclic voltammetry. It confirmed the adhesion of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> to the electrode surface and quantified the elements present on the electrode surface. The elements W, Bi, and O were discovered to be placed to the electrode surface.



**Figure 7** XPS spectra of composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrodes prepared by cyclic voltammetry.

X-ray photoelectron spectroscopy (XPS) was employed to validate the oxidation states of individual elements present at the surface of the composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrode. Figure 7 illustrates the binding energies of several chemical compositions, namely element O1s at 529.5 eV, elements Bi 4f<sub>5/2</sub> at 163.8 eV and Bi 4f<sub>7/2</sub> at 158.5 eV, as well as elements W 4f<sub>5/2</sub> at 36.8 eV and W 4f<sub>7/2</sub> at 34.7 eV. The O<sup>2-</sup>, Bi<sup>3+</sup>, and W<sup>6+</sup> oxidation numbers in the composite WO<sub>3</sub>-Bi<sub>2</sub>WO<sub>6</sub> electrode were confirmed (19).

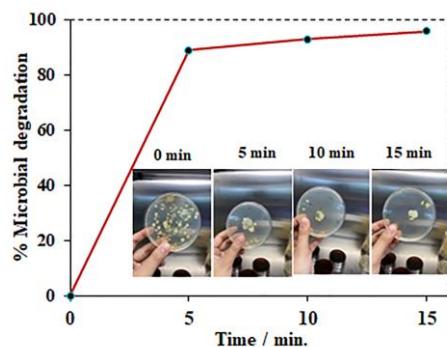


**Figure 8** X-ray diffraction patterns of FTO and the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  with various calcination temperatures of 25°C, 300°C, 400°C, 450°C, 500°C, and 600°C.

Figure 8 illustrates the XRD patterns of  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  composites prepared at various calcination temperatures. The result demonstrates that the XRD peak at 20 of 23.2° and 24.5°, related to the monoclinic  $\text{WO}_3$  crystal structure, was detected at the calcination temperature of the electrode between 400 and 500 °C (20). At the same calcination temperature range, we also observed XRD peaks at 29.0° and 31.0°, confirming the orthorhombic character of  $\text{Bi}_2\text{WO}_6$  (21). This XRD result confirms that calcination processes at temperatures between 400°C and 500°C can contribute to the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$ 's high photoelectrocatalytic properties.

### 3.3 Microbial elimination efficiency

Figure 9 shows the efficiency of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  photoanode performance for microbial elimination by PEC cell. It was found that the developed PEC cell can eliminate 96% of total microorganisms within 15 min. These investigations' findings support the performance of the produced electrodes in applications involving the removal of microorganisms from samples, and also show that they can be improved for use in water treatment.



**Figure 9** Efficiency of total microbial degradation utilizing a composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode and the PEC process.

### 4. Conclusions

This study demonstrates the successful fabrication of composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  coatings on FTO substrates using a cyclic voltammetry method. We were able to confirm the developed electrode characteristics along with the PEC properties for water oxidation. The temperature of calcination has a considerable effect on the characteristic and PEC properties of the developed composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrode. The composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes sintered at 450 °C have the highest PEC activity for water oxidation due to their superior crystalline structure and morphology. In accordance with the PEC mechanism, the composite  $\text{WO}_3\text{-Bi}_2\text{WO}_6$  electrodes demonstrated a total microorganism degradation efficiency of 96%. This research is beneficial for the continued development of semiconductor electrodes for use in PEC cells for environmental and public health applications.

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### Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

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