

Characterization and Comparison of WO₃ with Hybrid WO₃-MoO₃ and TiO₂ with Hybrid TiO₂-ZnO Nanostructures as Photoanodes [†]

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[†] Presented at the 4th International Online Conference on Nanomaterials, 5–19 May 2023; Available online: <https://iocn2023.sciforum.net>.

Abstract: Tungsten oxide (WO₃) and zinc oxide (ZnO) are n-type semiconductors with numerous applications in photocatalysis. The objective of this study was to synthesize and characterize different types of nanostructures (WO₃, WO₃-Mo, TiO₂, and TiO₂-ZnO) for a comparison of hybrid and pure nanostructures to use them as a photoanodes for hydrogen production. With the aim of comparing the properties of both samples, field emission scanning electron microscopy (FE-SEM) and confocal laser-Raman spectroscopy have been employed to study the morphology and composition and crystallinity, respectively. Finally, water splitting tests were conducted to compare the photoelectrochemical properties of the photoanodes.

Keywords: nanostructures; hybrid nanostructures; WO₃; TiO₂; water splitting; emerging contaminants



Citation: Cifre-Herrando, M.; Roselló-Márquez, G.; Navarro-Gázquez, P.J.; Muñoz-Portero, M.J.; Blasco-Tamarit, E.; García-Antón, J. Characterization and Comparison of WO₃ with Hybrid WO₃-MoO₃ and TiO₂ with Hybrid TiO₂-ZnO Nanostructures as Photoanodes. *Mater. Proc.* **2023**, *14*, 69. <https://doi.org/10.3390/IOC2023-14487>

Academic Editor: Jian-Gan Wang

Published: 5 May 2023



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1. Introduction

The severity of environmental problems caused by the increase of CO₂ in the atmosphere has increased the scientific research into new and renewable energy sources. Hydrogen is regarded as one of the most promising alternative energy sources to replace fossil fuels. Photoelectrochemical (PEC) water splitting using solar light is a novel method to produce clean and sustainable hydrogen from water and sunlight. For an efficient PEC process, it is necessary to find a suitable semiconductor photoelectrode. Oxide semiconductors are the most common materials; in particular, those with a high visible-light absorption, efficient charge carrier separation, and chemical stability, which could be TiO₂ or WO₃ [1].

On one hand, WO₃ is claimed to be a suitable material for PEC water splitting applications due to its high resistance to photocorrosion, stability in acidic media, good electron transport properties, and its bandgap (E_g = 2.6-eV). As its bandgap is only capable of capturing 12% of the incident light of the solar spectrum, several approaches have been tried to enhance PEC water splitting of WO₃ by band-gap modifications [2]. Doping of WO₃ with Mo can narrow the bandgap of WO₃ and consequently, improve the photocatalytic properties [3]. Therefore, a simple method for the synthesis of hybrid WO₃-MoO₃ nanostructures is proposed.

On the other hand, TiO₂ is one of the most extensively studied materials for PEC water splitting [4]. This is because it is a non-toxic semiconductor, has high chemical stability, excellent photocatalytic activity, profitability, and the ability to generate electron/hole pairs [5]. However, its photocatalytic applications are limited to ultraviolet light due to its wide-value of bandgap (3.2 eV) [6]. In order to reduce its bandgap, different elements

could be added to TiO₂ nanostructures. In this study, hybrid nanostructures of TiO₂ with ZnO are synthesized to increase the TiO₂ efficiency in water splitting PEC.

Thus, the objective of this work is to synthesize and characterize different types of nanostructures (WO₃, hybrid WO₃-MoO₃, TiO₂, and TiO₂-ZnO) for a comparison of hybrid and pure nanostructures. Then, they will be used as a photoanodes for PEC water splitting to produce hydrogen.

2. Materials and Methods

2.1. Synthesis of Nanostructures

The procedure to synthesize nanostructures was conducted by electrochemical anodization under hydrodynamic conditions using a rotatory disk electrode (RDE). The process was optimized by the authors in previous works [7,8].

For the WO₃ nanostructures, anodization of W was carried out at a velocity of 375 rpm, applying 20 V for 4 h. The electrolyte consisted of 1.5 M methanesulfonic acid and 0.01 M citric acid at 50 °C. After anodization, WO₃ nanostructures were annealed for 4 h at 600 °C in an air atmosphere.

For synthesizing hybrid nanostructures of WO₃-MoO₃, the same anodization was carried out but different concentrations of Na₂MoO₄·2H₂O (Mob) were added to the electrolyte.

For the TiO₂, the electrochemical anodization of Ti was carried out at room temperature under 3000 rpm applying 30 V during 3 h. The electrolyte consisted of glycerol (60% vol.), water (40% vol.), and 0.27 M NH₄F. Finally, the samples were heated at a temperature of 450 °C during 1 h in air atmosphere to transform TiO₂ nanostructures to the anatase phase.

For the TiO₂-ZnO hybrid nanostructures, after forming TiO₂ nanosponges, the ZnO electrodeposition technique was performed from a Zn(NO₃)₂ solution at 75 °C using a potential of −0.86 V_{Ag/AgCl} for 15 min in an Autolab PGSTAT302N potentiostat. A quartz reactor with a three-electrode configuration was used: the working electrode was the nanostructure synthesized, the reference electrode was an Ag/AgCl (3 M KCl) electrode, and the counter electrode was a platinum wire. The effect of Zn(NO₃)₂ concentration (1–10 mM) on the photoelectrochemical properties of the photoelectrode was analyzed.

2.2. Morphological and Crystalline Characterization

Field emission scanning electron microscopy (FE-SEM) with energy-dispersive X-ray spectroscopy (EDX) enabled the study of the morphology and the identification of the elements present in the synthesized nanostructures. The equipment used was a Zeiss Ultra-55 scanning electron microscope applying 20 kV. Furthermore, the crystallinity of the nanostructure was analyzed via Raman confocal laser spectroscopy (Witec alpha300R) with a neon laser of 488 nm at 420 μW.

2.3. Photoelectrochemical Properties

A potentiostat (Autolab PGSTAT302N) and a solar simulator (500 W xenon lamp) were used to study the photoelectrochemical properties of the samples. The reactor and configuration used were the same as for the ZnO deposition. A potential sweep with a scan speed of 2 mV·s^{−1} was carried out applying dark (30 s) and light (10 s) cycles.

3. Results and Discussion

3.1. FE-SEM

Figure 1 present the FE-SEM images of the synthesized nanostructures. Observing the images of Figure 1a,b the effect of doping the WO₃ nanostructures with MoO₃ can be observed. In both cases, defined small-sized nanoparticles with a mountain-shape were obtained. In contrast, Figure 1c,d allows to compare the effect of adding ZnO into the TiO₂ nanostructures. Figure 1c shows nanostructures with a rough surface and high specific area, typical from a nanosponge-like morphology [9]. Figure 1d shows the overall appearance of the hybrid nanostructures TiO₂-ZnO, where a nanosponge-shaped nanostructure without the presence of different particles on its surface can also be observed. Consequently, the

morphology is the same for the pure nanostructure than for the hybrid. This shows that no MoO_3 or ZnO agglomerations occurred during the doping procedure [5].

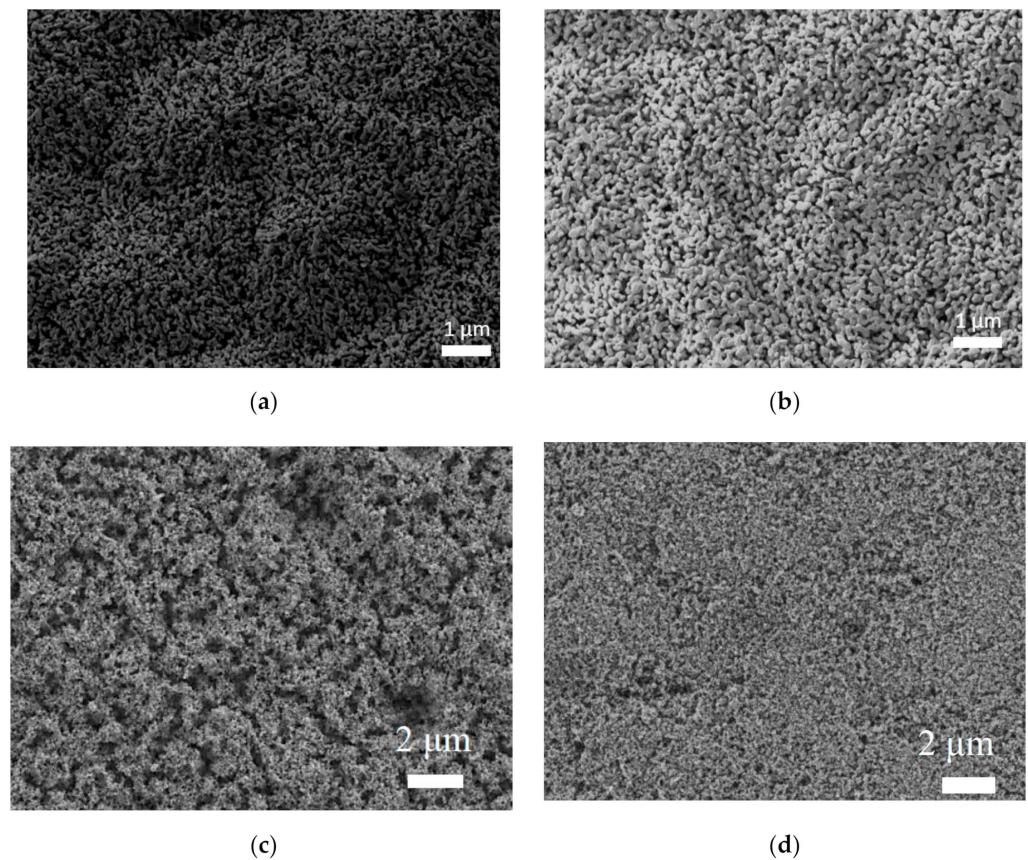


Figure 1. FE-SEM images of the different nanostructures (a) WO_3 ; (b) $\text{WO}_3 + 0.01 \text{ M Mob}$; (c) TiO_2 ; and (d) $\text{TiO}_2 + 0.01 \text{ M ZnO}$.

EDX analysis has been carried out to demonstrate the occurrence of MoO_3 and ZnO in the nanostructures and to quantify the elements. Table 1 shows the results of the EDX analysis for both hybrid nanostructures. In the case of MoO_3 addition, the percentage of MoO_3 increases when increasing the concentration in the electrolyte. Similarly, for the ZnO deposition, the quantity of Zn in the samples increases when increasing the concentration of ZnO in the electrodeposition. Consequently, it can be confirmed that MoO_3 and ZnO are deposited over the pure nanostructure.

Table 1. Results of the EDX analysis shown as percentage, in weight and atomic, for the various elements present in the samples.

Concentration of Mob (M)	% (Weight)			% (Atomic)			Concentration of $\text{Zn}(\text{NO}_3)_2$ (M)	% Weight			% Atomic		
	O	W	M	O	W	M		O	Ti	Zn	O	Ti	Zn
0	18.02	81.98	0.00	71.66	28.33	0.00	0	34.51	65.49	0.00	61.21	38.79	0.00
0.001	28.77	70.32	0.92	82.10	17.46	0.44	0.001 M	38.11	57.56	4.33	65.26	32.92	1.82
0.005	19.40	78.88	1.71	73.07	25.85	1.08	0.005 M	36.07	58.08	5.85	63.39	34.10	2.51
0.01	18.01	80.02	1.97	71.18	27.53	1.30	0.01 M	35.04	57.81	7.15	62.45	34.43	3.12

3.2. Raman

The Raman spectra of the different nanostructures are presented in Figure 2. Figure 2a shows the Raman spectra of the WO_3 nanostructure and the hybrid $\text{WO}_3\text{-MoO}_3$ nanostructures after a heat treatment of 600°C for 4 h, where peaks located at 135, 270, 714, 805,

and 955 cm^{-1} can be seen, which are those corresponding to monoclinic WO_3 . As seen in Figure 2a, the relative intensity of the bands diminishes when increasing the percentage of Mob in the electrolyte. Furthermore, the Raman spectra show the principal bands of MoO_3 : $190, 647, 867, 955\text{ cm}^{-1}$ [10]. Figure 2b shows the spectra of the TiO_2 nanostructures after a heat treatment at $450\text{ }^\circ\text{C}$ for 1 h. For the pure nanostructure, the peaks associated with the anatase phase of TiO_2 are observed ($145, 397, 520$ and 635 cm^{-1}). However, for the hybrid nanostructure with ZnO , the peaks are not observed due to the high fluorescence of ZnO . Therefore, this allows us to reaffirm that ZnO is indeed deposited on the TiO_2 nanostructure.

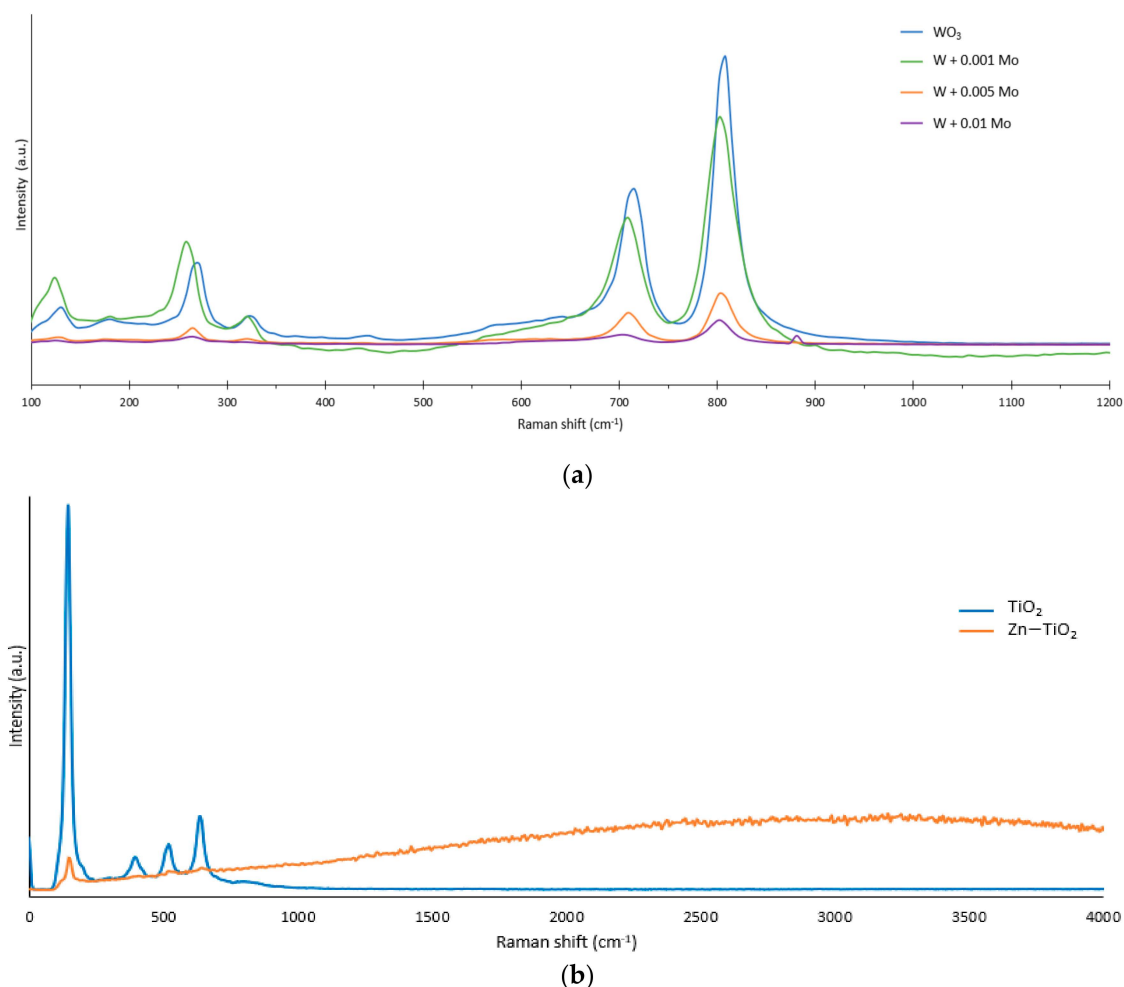


Figure 2. Raman spectra of the nanostructures (a) WO_3 + different Mob concentrations; (b) TiO_2 ; and $\text{TiO}_2 + \text{ZnO}$.

3.3. Water Splitting Tests

The influence of the doping element concentration in the electrolyte on the photoelectrochemical (PEC) behavior of the samples was also analyzed by water splitting tests, shown in Figure 3. For Mob, it can be seen from Figure 3a, that the sample with higher photoresponse is the one without Mob. Furthermore, as the concentration of Mob increases the photocurrent decreases, indicating worse photoelectrochemical properties. The worsening of the nanostructure after the addition of MoO_3 could be explained by the fact that MoO_3 is deposited on the surface of the nanostructure and prevents electron transfer.

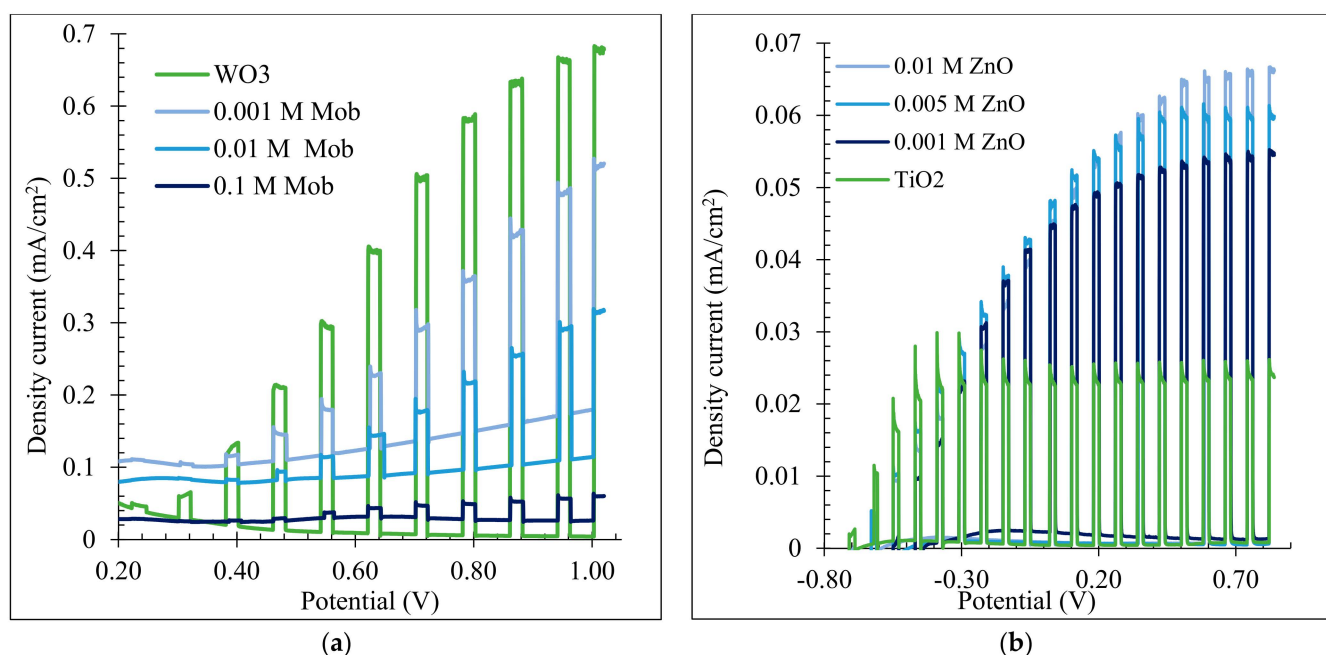


Figure 3. Water splitting curves of the (a) WO₃ nanostructures synthesized with different Mob concentrations and (b) TiO₂ nanostructures synthesized with different ZnO concentrations.

On the other hand, from Figure 3b it can be seen that the sample with higher photocurrent is that one with 0.01 M ZnO. Furthermore, by increasing the ZnO concentration, the photoelectrochemical efficiency of the nanostructures is enhanced. This demonstrates that ZnO crystals delay the recombination of the electron/hole pairs generated, increasing the lifetime of the excited electrons and thus, enhancing the photocatalytic activity of the nanostructures.

4. Conclusions

In this study, various types of nanostructure (WO₃ and TiO₂) have been synthesized by anodization of W and Ti, respectively, under hydrodynamic conditions. Hybrid nanostructures have also been synthesized with WO₃-MoO₃ and TiO₂-ZnO to improve the original nanostructures. In the case of WO₃-MoO₃, the photocatalytic activity of the nanostructures could not be increased via electrodeposition of MoO₃ on the surface of the WO₃ nanostructures. In contrast, the photocatalytic activity of the TiO₂-ZnO was significantly enhanced compared to TiO₂ nanosponges. The optimum nanostructure was achieved when performing the ZnO electrodeposition with a 0.01 M Zn(NO₃)₂ concentration, obtaining a photoelectrochemical response 141% higher than the crystalline TiO₂ nanosponges.

Author Contributions: Conceptualization, M.C.-H. and G.R.-M.; methodology, M.C.-H., P.J.N.-G. and G.R.-M.; investigation, M.C.-H. and P.J.N.-G.; resources, G.R.-M.; writing M.C.-H. and G.R.-M.; supervision, E.B.-T., M.J.M.-P. and J.G.-A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to express their gratitude to AEI (PID2019-105844RB-I00/AEI/10.13039/501100011033) for the financial support. M. Cifre-Herrando thanks Ministerio de Universidades for the concession of the pre-doctoral grant (FPU19/02466). G. Roselló-Márquez thanks the UPV for the concession of a post-doctoral grant (PAID-10-21). P.J. Navarro-Gázquez also thanks the Grant PEJ2018-003596-A-AR funded by MCIN/AEI/10.13039/501100011033. Finally, the project co-funded by FEDER operational programme 2014-2020 of Comunitat Valenciana (IDIFEDER/18/044) is acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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