**Characterization and Comparison of WO_3 with Hybrid WO_3-MoO_3 and TiO_2 with Hybrid TiO_2-ZnO Nanostructures as Photoanodes** †

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**Abstract:** Tungsten oxide (WO_3) 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 (WO_3, WO_3-Mo, TiO_2, and TiO_2-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; WO_3; TiO_2; water splitting; emerging contaminants

**1. Introduction**

The severity of environmental problems caused by the increase of CO_2 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 TiO_2 or WO_3 [1].

On one hand, WO_3 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 WO_3 by band-gap modifications [2]. Doping of WO_3 with Mo can narrow the bandgap of WO_3 and consequently, improve the photocatalytic properties [3]. Therefore, a simple method for the synthesis of hybrid WO_3-MoO_3 nanostructures is proposed.

On the other hand, TiO_2 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 TiO$_2$ nanostructures. In this study, hybrid nanostructures of TiO$_2$ with ZnO are synthesized to increase the TiO$_2$ efficiency in water splitting PEC.

Thus, the objective of this work is to synthesize and characterize different types of nanostructures (WO$_3$, hybrid WO$_3$-MoO$_3$, TiO$_2$, and TiO$_2$-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 WO$_3$ 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 methanosulfonic acid and 0.01 M citric acid at 50 °C. After anodization, WO$_3$ nanostructures were annealed for 4 h at 600 °C in an air atmosphere.

For synthesizing hybrid nanostructures of WO$_3$-MoO$_3$, the same anodization was carried out but different concentrations of Na$_2$MoO$_4$·2H$_2$O (Mob) were added to the electrolyte.

For the TiO$_2$, 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 NH$_4$F. Finally, the samples were heated at a temperature of 450 °C during 1 h in air atmosphere to transform TiO$_2$ nanostructures to the anatase phase.

For the TiO$_2$-ZnO hybrid nanostructures, after forming TiO$_2$ nanosponges, the ZnO electrodeposition technique was performed from a Zn(NO$_3$)$_2$ 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(NO$_3$)$_2$ 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 WO$_3$ nanostructures with MoO$_3$ 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 TiO$_2$ 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 TiO$_2$-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) WO$_3$ + 0.01 M Mob; (c) TiO$_2$; and (d) TiO$_2$ + 0.01 M ZnO.](image)

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.

<table>
<thead>
<tr>
<th>Concentration of Mob (M)</th>
<th>% (Weight)</th>
<th>% (Atomic)</th>
<th>Concentration of Zn(NO$_3$)$_2$ (M)</th>
<th>% Weight</th>
<th>% Atomic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
<td>W</td>
<td>M</td>
<td>O</td>
<td>W</td>
</tr>
<tr>
<td>0</td>
<td>18.02</td>
<td>81.98</td>
<td>0.00</td>
<td>71.66</td>
<td>28.33</td>
</tr>
<tr>
<td>0.001</td>
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<td>70.32</td>
<td>0.92</td>
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</tr>
<tr>
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<td>1.71</td>
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<tr>
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<td>18.01</td>
<td>80.02</td>
<td>1.97</td>
<td>71.18</td>
<td>27.53</td>
</tr>
</tbody>
</table>

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 WO$_3$-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 cm\(^{-1}\) [10]. Figure 2b shows the spectra of the TiO\(_2\) nanostructures after a heat treatment at 450 °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\(_3\) with different Mob concentrations; (b) TiO\(_2\); and TiO\(_2\)+ZnO.](image)

3.3. Water Splitting Tests

The influence of the doping element concentration in the electrolyte on the photocurrent 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) WO$_3$ nanostructures synthesized with different Mob concentrations and (b) TiO$_2$ 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 (WO$_3$ and TiO$_2$) have been synthesized by anodization of W and Ti, respectively, under hydrodynamic conditions. Hybrid nanostructures have also been synthesized with WO$_3$-MoO$_3$ and TiO$_2$-ZnO to improve the original nanostructures. In the case of WO$_3$-MoO$_3$, the photocatalytic activity of the nanostructures could not be increased via electrodeposition of MoO$_3$ on the surface of the WO$_3$ nanostructures. In contrast, the photocatalytic activity of the TiO$_2$-ZnO was significantly enhanced compared to TiO$_2$ nanosponges. The optimum nanostructure was achieved when performing the ZnO electrodeposition with a 0.01 M Zn(NO$_3$)$_2$ concentration, obtaining a photoelectrochemical response 141% higher than the crystalline TiO$_2$ nanosponges.


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

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