|  |  |
| --- | --- |
| cetlogo ***CHEMICAL ENGINEERING TRANSACTIONS***  ***VOL. xxx, 2025*** | A publication of  aidiclogo_grande |
| The Italian Association  of Chemical Engineering  Online at www.cetjournal.it |
| Guest Editors: David Bogle, Flavio Manenti, Piero Salatino  Copyright © 2025, AIDIC Servizi S.r.l. **ISBN** 979-12-81206-21-2; **ISSN** 2283-9216 | |

Effect of solvent on the photoelectrochemical performance of WO3 nanostructures for hydrogen evolution

Mireia Cifre-Herrandoa, Gemma Roselló-Márquezb, José García-Antóna \*

aIngeniería Electroquímica y Corrosión (IEC), Instituto Universitario de Seguridad Industrial, Radiofísica y Medioambiental (ISIRYM), Universitat Politècnica de València, C/ Camino de Vera s/n, 46022, Valencia, Spain]

bDepartamento de Ingeniería Química, Universitat de València, Av. de les Universitats, s/n, 46100 Burjassot, Spain

\* [jgarciaa@iqn.upv.es](mailto:jgarciaa@iqn.upv.es)

Hydrogen has emerged as a pivotal energy carrier for a sustainable future, and photoelectrocatalytic (PEC) water splitting presents a promising method for its production using semiconductor materials. Tungsten trioxide (WO₃) is a potential photoanode for PEC water splitting, but its performance is often hindered by poor charge separation, material stability, and low efficiency. This study investigates the effect of solvent additives during the synthesis of WO₃ nanostructures via anodization, focusing on isopropanol and formamide. The impact of these solvents on the morphology and photoelectrochemical properties of the resulting WO₃ films was analyzed. Results indicate that water is the optimal solvent for synthesizing WO₃ nanostructures, yielding the highest photocurrent density (0.629 mA/cm²) and theoretical hydrogen production of 2.87 L H₂/h·m², significantly outperforming samples synthesized with isopropanol and formamide. The introduction of isopropanol and formamide significantly reduced the performance due to morphological and structural changes that hinder charge transport. Although hydrogen evolution was not directly measured, the enhanced photocurrent suggests improved potential for solar water splitting applications. These findings provide insights into optimizing WO₃-based photoanodes for enhanced hydrogen production, contributing to sustainable energy solutions.

* 1. Introduction

Hydrogen has emerged as a key energy carrier in the transition toward a sustainable energy system. Unlike fossil fuels, hydrogen combustion produces only water as a byproduct, making it a clean alternative for power generation, transportation, and industrial applications. However, hydrogen is not a primary energy source but a storage medium that can mitigate the intermittency of renewable energy sources such as solar, wind, and marine energy. By converting excess renewable electricity into hydrogen, energy can be stored and later used when demand increases, contributing to a more stable and reliable energy grid. Additionally, hydrogen offers a flexible solution for mobile and temporary power stations, further expanding its potential applications (Acar et al., 2016).

Among the various hydrogen production methods, photoelectrocatalytic (PEC) water splitting stands out as a promising technology due to its potential to directly convert solar energy into hydrogen using semiconductor materials (Kumar et al., 2022; Wilke et al., 2012). This process, if optimized, could provide a low-cost and sustainable alternative to conventional hydrogen production methods such as steam methane reforming, which relies on fossil fuels and generates CO₂ emissions. However, achieving high conversion efficiencies remains a significant challenge, primarily due to limitations in charge separation, light absorption, and material stability .

Tungsten trioxide (WO₃) is a promising photoanode material due to its favorable bandgap (∼2.6–2.8 eV), good chemical stability, and strong visible-light absorption (Boateng et al., 2022). However, its practical application in PEC water splitting is hindered by several drawbacks, including poor charge separation, low conduction band position, and rapid recombination of photogenerated charge carriers. These limitations significantly reduce its photoelectrochemical performance in water splitting applications. To improve the applicability of WO₃-based photoanodes for solar hydrogen evolution, advanced synthesis strategies are required to optimize their morphology, electronic properties, and interfacial charge dynamics (Zhou et al., 2017).

This study introduces the use of solvent additives with different dielectric constants, such as water (ε = 79), isopropanol (ε = 18) and formamide (ε = 111), during the anodization process of WO₃ to tune the morphology and enhance the photoelectrochemical properties of the resulting nanostructures. While the impact of solvent additives on the synthesis of other semiconductor materials has been explored, their role in optimizing WO₃ for photoelectrocatalytic water splitting is relatively unexplored. By systematically investigating the effect of these solvents on the nanostructure formation, we aim to uncover new approaches to improving the efficiency of WO₃-based photoanodes, providing providing valuable insights into their potential for solar hydrogen generation while addressing material stability and charge separation challenges. The results provide valuable insights into optimizing WO₃-based photoanodes for environmental and energy-related applications.

* 1. Experimental procedure
  2. Synthesis of nanostructures

In this study, different solvents (water, isopropanol and formamide) were added in different proportions (0 %, 25 %, 50 %, 75 %) to the base electrolyte (1.5 M methanesulfonic acid and 0.1 M citric acid) to modify the dielectric properties of the electrolyte and consequently, the properties of the WO3 nanostructures. The electrochemical anodization was conducted at 50 °C, with a rotation speed of 375 rpm, 20 V for 4 hours, followed by a thermal treatment at 600 °C in air to convert the amorphous structures into crystalline ones (Cifre-Herrando et al., 2022).

* 1. Characterization

The morphology of the samples was characterized by field emission scanning electron microscope (FE-SEM). The equipment used was a Zeiss Ultra 55 Scanning Electron Miscroscope at an acceleration potential of 3 kV.

Photoelectrochemical measurements were conducted by performing potential sweeps between 0 V Ag/AgCl and 1 V Ag/AgCl under alternating light and dark cycles to assess the photoelectrochemical behavior of the nanostructures. The current intensity was recorded as a function of the applied potential. The experiments were conducted in a three-electrode electrochemical cell, comprising a working electrode (the synthesized WO3 nanostructures), a reference electrode (an Ag/AgCl electrode with 3 M KCl), and a counter electrode (a platinum tip). The electrolyte used was an aqueous 0.1 M H2SO4 solution. The light source used was a 1000 W Xenon lamp used as a solar simulator (AM 1.5 conditions at 100 mW·cm⁻²).

* 1. Photoelectrocatalytic activity for hydrogen production

Although no direct measurements of hydrogen or oxygen gas evolution were conducted, the photocurrent density obtained from the linear sweep voltammetry experiments was used as an indirect indicator of the photoelectrocatalytic performance. Higher photocurrent values suggest improved charge separation and increased potential for hydrogen generation under illumination.

To provide a comparative metric of the potential hydrogen generation capacity of each sample , the theoretical hydrogen production was estimated from the photocurrent density values obtained during the water-splitting experiments via photoelectrocatalysis. Hydrogen gas generation occurs at the cathode according to Eq (1):

|  |  |
| --- | --- |
|  | (1) |

The amount of hydrogen generation can be approximated by Faraday's laws (Eq. 2):

|  |  |
| --- | --- |
|  | (2) |

Where n is the moles of hydrogen, i is the photocurrent density (A·m⁻²), A is the photoelectrode area (m²), t is the reaction time (s), and F is Faraday’s constant (96485 C·mol⁻¹). The hydrogen volume was then estimated using the ideal gas equation (Eq. 3):

|  |  |
| --- | --- |
|  | (3) |

where P is the system pressure (1 atm), V is the hydrogen volume (L), R is the ideal gas constant (0.082 atm·L·mol⁻¹·K⁻¹), and T is the temperature (298 K). Using these equations, the theoretical hydrogen production was expressed in liters per hour per square meter of photocatalyst.

* 1. Results and discussion
  2. Nanostructures synthesis

The synthesis of nanostructures was investigated by analyzing the transient current density profiles for three different electrolytes (water, isopropanol and formamide) during the electrochemical anodization process. These transients provide crucial insights into the formation mechanism of the nanostructures, which can be divided into three stages: (1) compact WO₃ layer formation, (2) tungsten-citrate complex dissolution., and (3) nanostructure precipitation at supersaturation. Furthermore, citric acid acts as a chelating agent, promoting dissolution-precipitation dynamics. It delays precipitation by forming strong tungsten-citrate complexes, which influence the morphology and porosity of the nanostructures (Fernández-Domene et al., 2021).

Interfaz de usuario gráfica, Gráfico, Gráfico de líneas

Descripción generada automáticamente

*Figure 1: Current density transient obtained during the synthesis of WO3 nanostructures with different electrolytes: (a) Water (b) different proportions of isopropanol and (c) different proportions of formamide.*

Figure 1 (a) shows the current density transient when pure water is used as the solvent. Three distinct stages are observed: stage 1- A rapid decrease in current density occurs due to the formation of a compact WO₃ layer that partially insulates the tungsten surface; stage 2 - Between 0 and 50 minutes, current density increases to a peak as the initial WO₃ layer dissolves, exposing the tungsten surface; stage 3 - The current density stabilizes, marking the precipitation of polytungstate species into insoluble WO₃·H₂O and WO₃·2H₂O nanostructures (Lassner & Schubert, 1999).

Figure 1 (b) illustrates the transient behavior with varying isopropanol proportions (25%, 50%, and 75%). At 25% and 50% isopropanol, the three stages of formation are observed and the stage 2 is extended, favoring the dissolution-precipitation process for nanostructure growth. At 75% isopropanol, the current density remains low, indicating poor formation of WO₃ nanostructures. Figure 1 (c) shows the behaviour of the transient using formamide as dissolvent, at 25% formamide, the transient resembles that of the water, with an extended Stage 2 indicating favorable conditions for WO₃ nanostructure formation. However, at 50% and higher, the current density decreases significantly, suggesting the absence of precipitation and poor nanostructure formation (Reichardt & Welton, 2011).

The solvent composition significantly influences the anodization process. Water, 25%–50% isopropanol, and 25% formamide exhibit optimal conditions for WO₃ nanostructure formation. Further characterization is required to confirm the photoelectrochemical properties of the resulting materials.

* 1. Morphology characterization

All samples were characterized morphologically by FE-SEM. Figure 2 shows different FE-SEM images of the WO3 nanostructures synthesized using different solvents in the electrolyte: water, different proportions of isopropanol (25 %, 50 % and 75 %) and different proportions of formamide (25 % and 50 %).

In Figure 2 (a), corresponding to synthesis with water, a homogeneous layer of well-defined nanostructures is observed, exhibiting a "nanorod" morphology uniformly distributed over the electrode surface.

Figure 2(b), (c) and (d) show the morphological evolution when incorporating different proportions of isopropanol. At low concentration, Figure 2 (b), 25 % isopropanol, the morphology remains similar to that obtained with water, with well-defined nanostructures. However, at 50% isopropanol (Figure 2 (c)), larger particles are deposited on top of the nanotube layer, suggesting changes in the nanostructure growth process. At even higher proportions (75%), figure 2 (d) the nanorod layer begins to disintegrate, leading to a lower quantity of nanostructures and a decrease in compactness. These effects may be attributed to the lower dielectric constant of isopropanol and its impact on ion solubility, which alters the dissolution-precipitation process.

On the other hand, Figure 2 (e) and Figure 2 (f), corresponding to synthesis with formamide, shows a drastic morphological change. Even at low concentrations (25%), the nanostructure layer does not fully develop, and craters appear on the surface. At higher concentrations (≥50%), a homogeneous layer of nanostructures is no longer observed, suggesting that formamide slows down the dissolution stage in the synthesis process. This inhibition prevents the formation of soluble species and/or tungsten dinuclear complexes, which are essential for the growth of WO₃ nanostructures.

Código QR

Descripción generada automáticamente *Figure 2: FE-SEM images of WO3 nanostructures synthesized using different solvents in the electrolyte (a) Water; different proportions of isopropanol (b) 25 % isopropanol, (c) 50 % isopropanol (d) 75 % isopropanol and different proportions of formamide, (e) 25 % formamide and (f) 50 % formamide.*

* 1. Photoelectrochemical characterization

The photoelectrochemical response of WO₃ nanostructures synthesized with different solvents was evaluated through water-splitting tests via photoelectrocatalysis assays. Figure 3 presents the photoelectrochemical response of the WO₃ nanostructures, displaying current density versus potential. The increase and decrease in current density correspond to the switching on and off of the illumination.

When synthesized in water, the nanostructures exhibited clear light/dark cycles, with negligible current in darkness and a pronounced increase under illumination, confirming efficient charge separation and hydroxyl radical generation for pollutant degradation. The highest photocurrent was observed for nanostructures synthesized in water without solvents. In contrast, the addition of isopropanol altered the response of the nanostructures, those synthesized with 25% isopropanol retained a moderate response. At 50% isopropanol, the response declined further, and at 75% the photocurrent increase was barely distinguishable. This is consistent with FE-SEM images, that suggest that isopropanol affects morphology and particle size, reducing charge transport efficiency and, consequently, the photocurrent response. The use of formamide resulted in a drastic reduction in photocurrent, with almost no visible light/dark cycles. This suggests that formamide does not enhance charge separation or improve the photocatalytic efficiency of the material.

Overall, the results indicate that the choice of solvent influences key parameters such as charge carrier separation and recombination rates, being water the optimal solvent for synthesizing WO3 nanostructures with superior photoelectrochemical properties, while increasing concentrations of isopropanol or formamide negatively impact performance due to unfavorable morphological and structural changes.



*Figure 3: Water splitting results of the WO3 nanostructures synthesized using different solvents in the electrolyte: Water; 25 % isopropanol, 50 % isopropanol, 75 % isopropanol, 25 % formamide and 50 % formamide.*

* 1. Hydrogen production

The theoretical hydrogen production was estimated from the photocurrent density values obtained during the water-splitting experiments via photoelectrocatalysis, using WO3 nanostructures as photoanodes. Additionally, considering an annual solar irradiation of 2600 hours in Valencia, the yearly hydrogen production per square meter was estimated. The hydrogen production results are summarized in Table 1.

Table 1: Theoretical hydrogen production for the nanostructures synthesized with different solvents and proportions.

|  |  |  |  |
| --- | --- | --- | --- |
| Nanostructure | i (mA/cm2) | Hydrogen production  (L·H2 /h·m2) | Daily hydrogen production  (L H2 /m2·d) |
| Water | 0.629 | 2.87 | 20.41 |
| 25 % Isopropanol | 0.388 | 1.77 | 12.60 |
| 50 % Isopropanol | 0.122 | 0.56 | 3.97 |
| 75 % Isopropanol | 0.014 | 0.06 | 0.45 |
| 25 % Formamide | 0.038 | 0.17 | 1.22 |
| 50 % Formamide | 0.026 | 0.12 | 0.85 |

As commented in the photoelectrochemical results, the highest values of photocurrent density, and consequently, of hydrogen production are obtained for the nanostructures synthesized in water. Water-synthesized nanostructures exhibited the highest photocurrent density (0.629 mA/cm²), leading to a theoretical hydrogen production of 2.87 L H₂/h·m² and a daily yield of 20.41 L H2 /m2·d.

Furthermore, as the concentration of isopropanol or formamide in the electrolyte increased, both photocurrent density and hydrogen production decreased significantly. The presence of isopropanol in the electrolyte reduced the photoelectrochemical performance, with nanostructures synthesized in 25% isopropanol showing a lower hydrogen production (1.77 L H₂/h·m²). Higher concentrations (50%, 75%) further diminished the efficiency, with the 75% isopropanol sample producing only 0.06 L H₂/h·m². Similarly, the addition of formamide resulted in a substantial drop in hydrogen production. The best-performing sample in this group (25% formamide) achieved just 0.17 L H₂/h·m², significantly lower than the water-based nanostructures.

These findings confirm that water is the most effective solvent for synthesizing WO3 nanostructures with optimal photoelectrochemical performance. Increasing the proportion of isopropanol or formamide negatively impacts the morphology and charge transport properties, leading to lower hydrogen production.

* 1. Conclusions

This study demonstrates that the choice of solvent plays a critical role in the synthesis of WO₃ nanostructures and their subsequent photoelectrochemical performance for hydrogen production.

* From the current density transients, it is observed that the solvent significantly influences the formation process of WO₃ nanostructures. The optimal conditions for nanostructure growth were found with water, while increasing concentrations of isopropanol and formamide led to lower current densities, indicating poorer formation and performance.
* FE-SEM images show that the choice of solvent affects the morphology of the WO₃ nanostructures. Water-based synthesis resulted in homogeneous nanorod structures, while higher concentrations of isopropanol and formamide led to morphological degradation, reducing the uniformity and density of the nanostructures.
* Water-splitting tests indicate that the photoelectrochemical performance of the WO₃ nanostructures is best when synthesized in water. This is reflected in the clear light/dark cycles and efficient charge separation observed in the water-based samples.
* T he theoretical hydrogen production obtained from the best-performing water-synthesized nanostructures was 2.87 L H₂/h·m². In contrast, increasing isopropanol and formamide concentrations led to a significant decrease in hydrogen production, highlighting the importance of solvent choice in optimizing performance.

Acknowledgments

Authors would like to express their gratitude to AEI (PID2019-105844RB-I00/ AEI/10.13039/501100011033) for the financial support. M. Cifre-Herrando thank Ministerio de Universidades for the concession of the pre-doctoral grant (FPU19/02466). G. Roselló-Márquez also thanks the UPV for the concession of a post-doctoral grant (PAID-10-21) and the grant for the promotion of postdoctoral research at UPV (PAID-PD-22). Finally, project co-funded by FEDER operational programme 2014-2020 of Comunitat Valenciana (IDIFEDER/18/044) is acknowledged.

References

Acar, C., Dincer, I., & Naterer, G. F., 2016, Review of photocatalytic water-splitting methods for sustainable hydrogen production. In International Journal of Energy Research,40,1449–1473.

Boateng, E., Thind, S. S., Chen, S., & Chen, A.,2022, Synthesis and electrochemical studies of WO3-based nanomaterials for environmental, energy and gas sensing applications. In Electrochemical Science Advances, 2.

Cifre-Herrando, M., Roselló-Márquez, G., García-García, D. M., & García-Antón, J., 2022, Degradation of Methylparaben Using Optimal WO3 Nanostructures: Influence of the Annealing Conditions and Complexing Agent. Nanomaterials, 12.

Fernández-Domene, R. M., Roselló-Márquez, G., Sánchez-Tovar, R., Cifre-Herrando, M., & García-Antón, J.,2021, Synthesis of WO3 nanorods through anodization in the presence of citric acid: Formation mechanism, properties and photoelectrocatalytic performance. Surface and Coatings Technology, 422.

Kumar, M., Meena, B., Subramanyam, P., Suryakala, D., & Subrahmanyam, C., 2022, Recent trends in photoelectrochemical water splitting: the role of cocatalysts. Nature Research,14.

Lassner, Erik., & Schubert, W.-Dieter., 1999, Tungsten : properties, chemistry, technology of the element, alloys, and chemical compounds. Kluwer Academic/Plenum Publishers.

Reichardt, C., & Welton, T., 2011, Solvents and solvent effects in organic chemistry. John Wiley & Sons.

Wilke, T., Schricker, D., Rolf, J., & Kleinermanns, K., 2012, Solar Water Splitting by Semiconductor Nanocomposites and Hydrogen Storage with Quinoid Systems. Open Journal of Physical Chemistry, 2, 195–203.

Zhou, J., Lin, S., Chen, Y., & Gaskov, A. M., 2017, Facile morphology control of WO3 nanostructure arrays with enhanced photoelectrochemical performance. Applied Surface Science, 403, 274–281.