



Review

Photoelectrochemical Production of Peroxydisulfate (PDS), a Clean Oxidant: Recent Development and Challenges

Zeeshan Haider ^{1,2,*}, Muhammad Imran ³  and Tahir Muhmood ^{4,*} 

¹ Department of Physics and Semiconductor Science, Gachon University, Seongnam-si 13120, Republic of Korea

² Gachon Bionano Research Institute, Gachon University, Seongnam-si 13120, Republic of Korea

³ Department of Chemistry, Faculty of Science, Research Center for Advanced Materials Science (RCAMS), King Khalid University, P.O. Box 960, Abha 61421, Saudi Arabia

⁴ International Iberian Nanotechnology Laboratory, 4715-310 Braga, Portugal

* Correspondence: zeeshanhaider@gachon.ac.kr (Z.H.); tahir.muhmood@inl.int or muhmoodtahir@yahoo.com (T.M.)

Abstract

Peroxydisulfate (PDS, $S_2O_8^{2-}$) is an important oxidant for a wide range of industrial applications, including organic synthesis, polymer preparation, wastewater treatment and environmental remediation. Currently, PDS is commercially produced by electrolysis of sulfate solution. Photoelectrochemistry (PEC) provides an alternative approach to PDS generation by reducing the energy required to drive this process. Because PEC uses solar light as an abundant, free resource, it is an attractive technique for PDS generation compared to electrolysis. WO_3 , owing to its excellent stability in acidic environments, is an excellent metal oxide candidate for producing PDS. Withstanding stronger acidic pH as well as absorption of visible light as a major fraction of solar light renders WO_3 a promising material for PEC-based PDS production when compared with other semiconductors. This mini review examines light-assisted, sustainable production of PDS on WO_3 photoanodes. It mainly involves the oxidation of the anion bisulfate, HSO_4^- , in a highly acidic pH. The efficiency of photoelectrochemical generation of PDS is greatly influenced by important factors, including suppressing recombination of photoinduced charge carriers, cocatalyst loading, minimizing competing side reactions, and establishing coupled reactions. In this review, we briefly discussed the key highlights to date in the application of WO_3 as a stable photoanode material for producing PDS. It provides insight into the potential of photocatalysis as an emerging route for the sustainable synthesis of PDS as a valuable chemical oxidant. Besides the significant progress made so far, the PDS production rate remains low, and minimizing the recombination tendency to achieve a higher photocurrent density could further boost PEC-based PDS production.

Keywords: peroxydisulfate (PDS); photoelectrochemistry; anion oxidation; sustainable oxidant synthesis; WO_3



Academic Editor: Luyi Zou

Received: 21 February 2026

Revised: 16 March 2026

Accepted: 21 March 2026

Published: 27 March 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

1.1. Importance of Peroxydisulfate (PDS) and Its Applications

Peroxydisulfate (PDS), a dimeric peroxide of sulfate and a strong oxidant, is commonly used as the sodium [1], potassium [2], or ammonium salt [3]. Peroxydisulfate is sometimes also referred to simply as persulfate [4]. The standard reduction potential of the $S_2O_8^{2-}$ anion (2.1 V) is higher compared to that of H_2O_2 (1.8 V) [5]. It enables PDS to be used as a potential oxidant for diverse applications. The $\cdot OH$ radical-mediated oxidative

degradation of organics is an important route for decontamination [6]. PDS is commonly applied in sulfate radical-mediated degradation of organics [7]. Sulfate radicals have a high oxidation potential compared to hydroxyl radicals [8]. It can be activated through electron or energy transfer processes to produce sulfate radicals, which can effectively degrade organic contaminants [9]. PDS is frequently applied for the degradation of dyes and organic pollutants [10]. Besides AOP, PDS is also commonly applied as an oxidative reagent in sulfate radical-mediated organic synthesis [11–13], heterocycle formation [14] and as an initiator in polymerization [15] and hydrogel formation [16].

1.2. Limitations of Conventional Approaches for PDS Production

Traditionally, PDS is produced through electrochemical methods [17–20]. It involves anodic oxidation of sulfate (SO_4^{2-}) and hydrogen sulfate or bisulfate (HSO_4^-) anions, as shown in the following equations [21]. A typical electrochemical cell applied for the electrochemical production of PDS is shown in Figure 1.

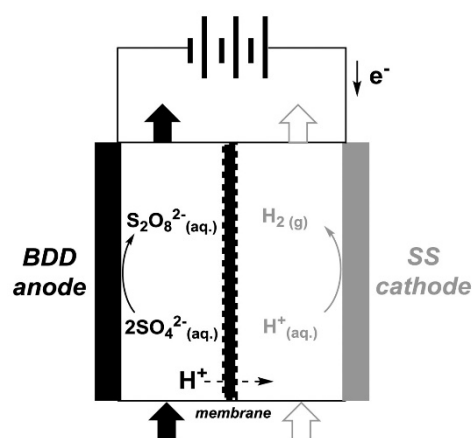
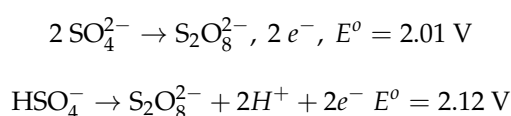


Figure 1. A representative electrochemical cell for the production of peroxydisulfate, adopted from reference [17].

Various electrode materials have been used to produce PDS to date. This includes Pt [22], Ti/IrO₂ [23], Ti/RuO₂ [24], boron-doped diamond (BDD) [25] and TiO₂ [26].

There are certain limitations in the electrochemical synthesis of PDS, including [27] (i) high amount of overpotential needed to drive this reaction, (ii) high cost of conventionally adopted electrodes, (iii) competition with oxygen evolution reaction (OER) at anode (iv) decreasing current efficiency over the elongated electrolysis for PDS production and (v) requiring higher in-put of electrical energy.

1.3. PEC Anion Oxidation vs. Water Oxidation

The use of light to catalyze chemical conversions is a very sustainable approach for chemical synthesis [28]. Photoelectrochemistry (PEC) is a very useful strategy to produce PDS based on exploiting earth-abundant metal oxides [29]. PEC strategy can be considered as a hybrid approach that utilizes both electrical energy and a light source [30,31]. It reduces the amount of input electrical energy, making it economically feasible [32]. Metal oxides have been extensively applied as photoanodes for PEC water oxidation to produce oxygen via the oxygen evolution reaction (OER) [31,33,34]. However, at the photoanode, by replacing OER, value-added chemicals can be produced, as shown in Figure 2. Among

these products, PDS is especially important given its wide range of applications. Producing PDS instead of oxygen at the photoanode is more economically valuable. PEC-based PDS production at oxide photoanodes may face the OER as a competing side reaction. PDS production and OER both are derived from photogenerated holes. The oxidation potential of $\text{S}_2\text{O}_8^{2-}/\text{HSO}_4^-$ and $\text{O}_2/\text{H}_2\text{O}$ are +2.12 and +1.23 V respectively vs. RHE. It indicates that PDS production occurs at a higher potential than OER, and the former reaction is thermodynamically less favored [35,36]. Therefore, careful attention to tuning reaction conditions and modifying the anode material is needed to maintain higher selectivity for PDS production and to reduce the oxygen evolution from water splitting as a competing side reaction. Although photoelectrochemistry at oxide photoanodes has been extensively investigated for oxidation of water to produce oxygen gas as a product, the application of these electrodes for alternate oxidation reactions, such as PDS generation, has been relatively less explored [37–39]. However, producing PDS rather than oxygen at the photoanode is of more economical value [40,41]. Therefore, emphasis in this direction could open new opportunities to apply photoelectrochemistry for sustainable catalysis.

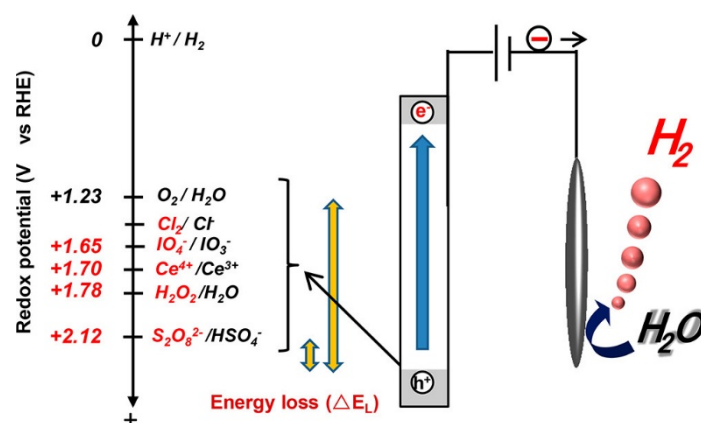


Figure 2. Principles of producing high-value-added chemicals on photoanodes adopted from reference [36].

1.4. Acidic Stability and Band Alignment of WO_3 for PEC-Based PDS Production

Although several oxide photoanodes have the potential to be exploited for PEC-based PDS generation, there are certain conditions that should be met for the consideration of an ideal candidate to drive this reaction. Many of the commonly applied photoanodes, such as ZnO [42,43], Fe_2O_3 [44] and BiVO_4 [45,46] for PEC water splitting, cannot withstand the stronger acidic pH needed for PDS production. For instance, ZnO is considered a stable oxide for solar cells [47]. It is also commonly used for solution-phase photochemical reactions such as photodegradation of dyes [48]. However, it can be corroded under stronger acidic electrolytes [49], limiting its use in wide pH ranges. Therefore, such oxide semiconductors may not be suitable for driving PEC-based PDS production, unless their stability is enhanced through realistic modifications under acidic electrolyte conditions [46]. Furthermore, the photoanode material should have sufficient thermodynamic potential to drive the formation of PDS. Titanium dioxide (TiO_2) also has relatively higher stability in acidic electrolytes [50]. However, the drawback associated with TiO_2 is its wide band gap (3.2 eV) and absorption of ultraviolet radiation, which is a smaller fraction of solar radiation (<3%) [51]. Tungsten trioxide (WO_3), due to its narrow band gap (2.5–2.8 eV), can absorb visible light [52], which accounts for about 43% proportion of the solar spectrum [53]. WO_3 as an important oxide is commonly applied in optoelectronics and electrochromic devices [54,55]. Considering solution phase chemistry, WO_3 exhibits relatively higher stability under acidic conditions [56]. Moreover, its thermodynamic potential is also

sufficient to drive PEC-based PDS production [57]. It makes WO_3 an attractive condition to produce PDS through a photoelectrochemical approach.

In this review, we have briefly discussed the advancements made so far in driving photocatalytic PDS production over WO_3 -based materials. It includes the photochemical and photoelectrochemical approaches for producing PDS over the WO_3 photocatalyst. We have discussed the mechanism involving PDS production over WO_3 photocatalysts. Various strategies and approaches, such as co-catalyst loading, work functional tuning, blocking layer to prevent charge recombination, coupled photo redox reactions and fabricating three-dimensional hierarchical structure, have been discussed. We have also discussed existing limitations and proposed new strategies to make significant advancements in this research direction.

2. Fundamental Mechanism of PDS Formation on WO_3

WO_3 photocatalyst upon excitation generates holes in the valence band and electrons in the conduction band. As shown in Equation (1), the amount of potential required for converting HSO_4^- anion to $\text{S}_2\text{O}_8^{2-}$ is 2.12 V, whereas the valence band potential of WO_3 is much more positive (ca 2.97 V vs. NHE at PH = 0), which is required to drive this reaction [35]. Hence, photogenerated holes in VB of conduction band drive the oxidation of HSO_4^- anion to $\text{S}_2\text{O}_8^{2-}$. Since photogenerated holes and electrons have a tendency to recombine with each other, if the conduction band electrons are utilized for coupled reactions such as oxygen reduction reaction (ORR) facilitated by a co-catalyst such as Pt, it can discourage the recombination of electron and hole pair, which can promote the formation of PDS. However, for the case of photoanode-driven PDS production, application of external bias facilitates the separation of charge carriers.

3. Advancements in Dispersed Powder Photocatalytic Systems

Loading metal-based co-catalysts is a promising approach to suppress the recombination of electron-hole pairs, thereby promoting the oxidative capability of WO_3 photocatalysts [58]. An overview of WO_3 -based photocatalysts for producing PDS under illumination is summarized in Table 1.

Huang et al. have demonstrated the effectiveness of loading bimetallic Au and Pt nanoparticles over WO_3 (Au@Pt WO_3) for PDS generation in a powdered photocatalytic system [59]. In this bimetallic design, Au served as the core and Pt as the shell. It has been helpful to modulate the electronic states of Pt and expose the active catalytic sites by efficient collection of photogenerated electrons. The scheme for the fabrication of Au@Pt/WO_3 and Pt-Au/WO_3 is shown in Figure 3. TEM image, line scanning and elemental mapping of Au@Pt/WO_3 are shown in Figure 4a–f. It was observed that Au existed mainly in the core, and Pt was uniformly distributed. Loading of such core-shell nanoparticles over WO_3 has resulted in a significant improvement in photocatalytic PDS production, which was found to be 1.7 times higher as compared to Pt-loaded WO_3 (Pt/WO_3). It has produced a quantum efficiency of 5.2% at 420 nm. It is notable that the performance of Au@Pt WO_3 for PDS generation was superior to that of introducing Pt-Au bimetallic alloy over WO_3 . In this setup, electrons were involved in the oxygen reduction reaction over Au@Pt , and photogenerated holes actively participated in the oxidation of HSO_4^- anion to $\text{S}_2\text{O}_8^{2-}$ species. Effective electron trapping is essential for avoiding the recombination with holes, which can support higher oxidation of HSO_4^- anions. The mechanism involving the photoredox reaction over Au@Pt WO_3 for PDS generation is shown in Figure 4g. Time-dependent production of PDS over various samples given in Figure 4h shows that the highest activity was observed for the Au@Pt WO_3 , which was found to be much higher than all other samples, including WO_3 , Pt/WO_3 , Au/WO_3 , as well as Pt-Au/WO_3 . Even

though Pt-Au/WO₃ contains both Pt and Au, a negligible amount of PDS generation over it reflects that rational structure design of bimetallic Au and Pt structure is important for optimizing the photocatalytic activity of WO₃ towards PDS generation. Although Pt is an important co-catalyst for trapping the electron, it is important to control the form of Pt existing on the catalyst to precisely control the selectivity of photo redox reactions. The higher activity of Au@Pt/WO₃ was due to the formation and exposure of higher Pt⁰ at the surface.

Table 1. Summary of PDS production over WO₃-based photocatalysts.

Catalyst	Approach	Electrolyte	PDS Production Rate	Photocurrent	FE	ABPE	QE	Reference
Au@Pt/WO ₃	Photochemical	1.0 M H ₂ SO ₄	36 µmol (3 h)	-	-	-	5.2% 420 nm	[59]
WO ₃ /Pt	Photochemical	1.0 M H ₂ SO ₄	33.9 µmol (3 h)	-	-	-	3.8% 420 nm	[60]
m-H-WO ₃ /TiO ₂	PEC	0.5 M H ₂ SO ₄ 0.5 M Na ₂ SO ₄ (pH 6.0)	4 mM (2 h) 1.2 V vs. RHE	0.8 mA cm ⁻² at 1.23 V vs. RHE,	99% (20 min)	-	-	[61]
WO ₃	PEC	1.0 M H ₂ SO ₄	Approx. ^a 7 µmol (2 h)	3.04 mA cm ⁻² at 1.50V _{RHE}	Approx. ^a 100%	2.45% at 1.26V _{CE}	-	[62]
WO ₃	PEC	1.0 M H ₂ SO ₄	Approx. ^a 38 µmol (2 h)	Approx. ^a 2.7 at 1.5 V RHE	Approx. ^a 100%	2.2% at 1.13 V vs. CE	-	[63]
WO ₃	PEC	0.5 H ₂ SO ₄	-	-	84% at CV 1.8 V	-	-	[64]
WO ₃	PEC	1.0 m H ₂ SO ₄	Approx. ^a 36 µmol (2 h)	2.6 mAcm ⁻² at 1.23 V vs. RHE	95% at 1 mAcm ⁻²	-	-	[65]

Approx. ^a: Values are approximated from the Figures from corresponding references.

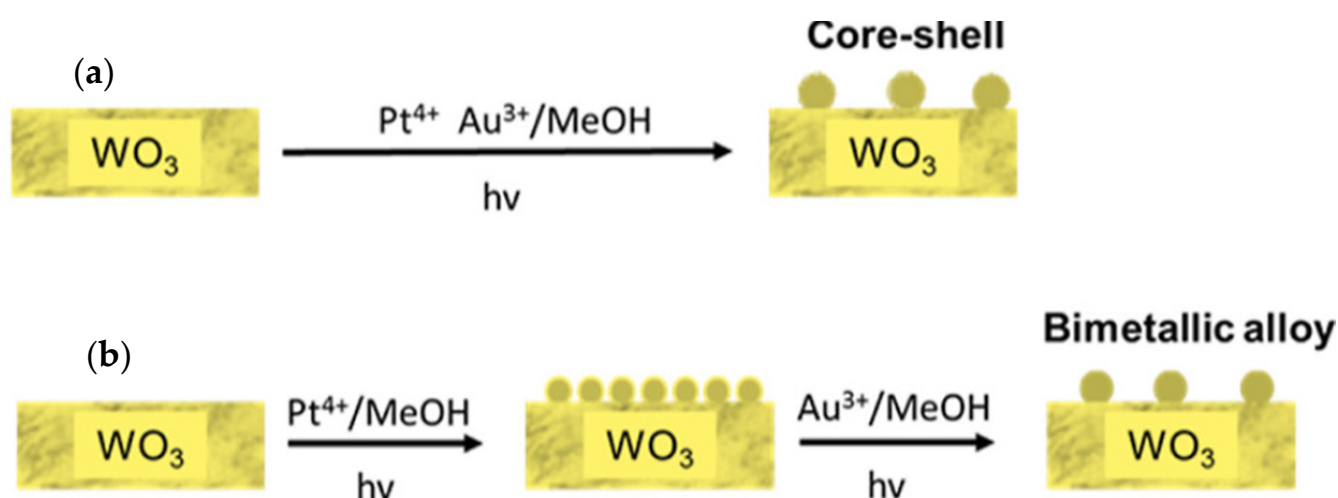


Figure 3. Fabrication Process of (a) Au@Pt/WO₃ and (b) Pt-Au/WO₃ adopted from reference [59].

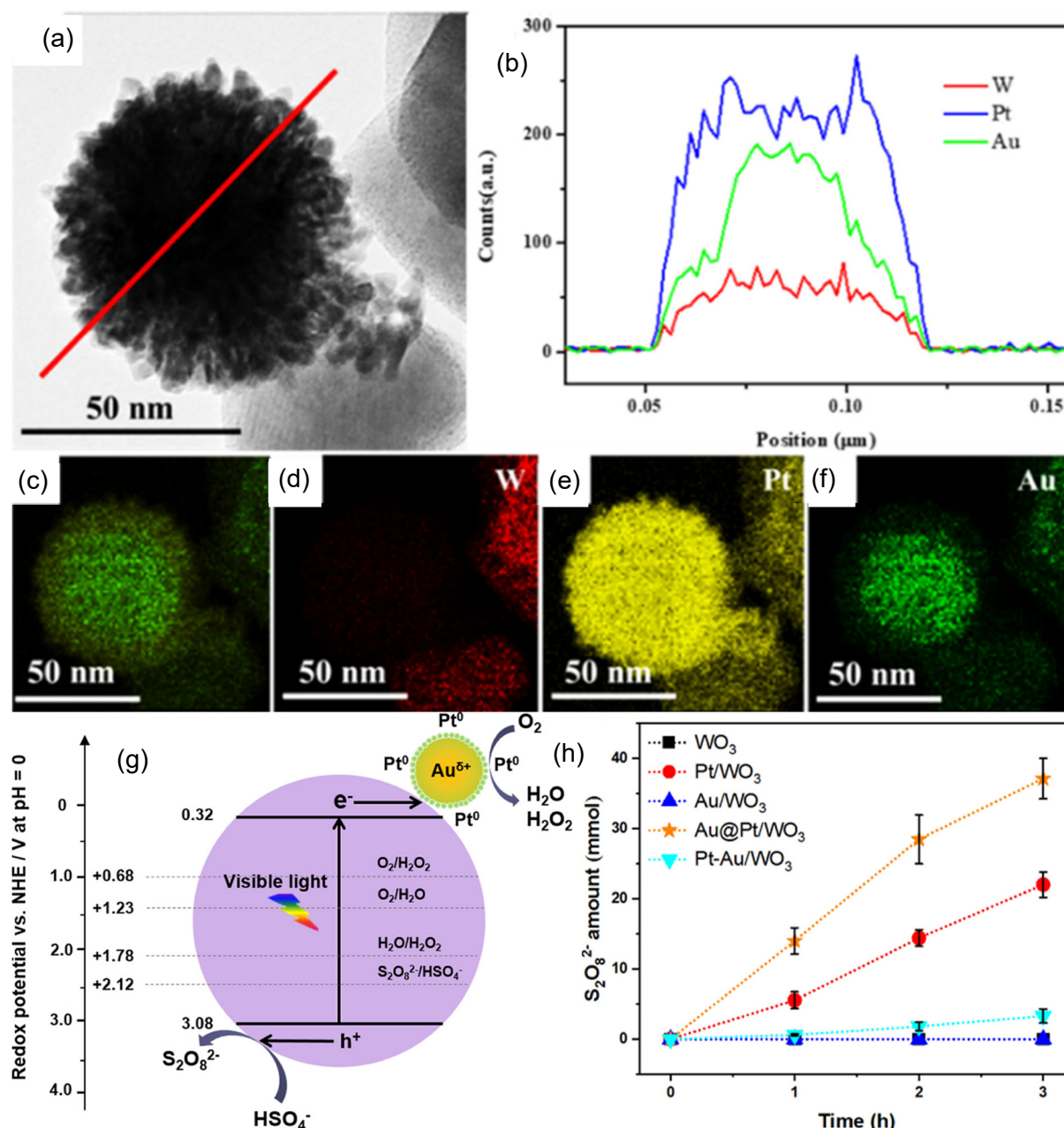


Figure 4. (a) selected TEM image for mapping; (b) line scan; (c) EDS combination of Pt and Au elements; (d) W element; (e) Pt element; and (f) Au element distribution of Au@Pt/WO₃. (g) proposed photocatalytic generation of S₂O₈²⁻ and H₂O₂ over Au@Pt/WO₃ and (h) time course of S₂O₈²⁻ amount under 3 h of irradiation adopted from reference [59].

Huang et al. have further demonstrated powder-based photocatalyst systems for PDS generation over WO₃ modified with noble metals [60]. For that purpose, a photo deposition strategy was adopted to introduce Pt, Au, Ru, and Rh over WO₃. For the sake of comparison, H₂WO₄, BiVO₄, g-C₃N₄, and P-25 were also tested for their activity toward PDS generation. A photocatalytic test was performed by dispensing catalysts in H₂SO₄ or NaHSO₄ aqueous solutions, and O₂ was purged during reaction to drive the ORR to utilize photogenerated electrons and avoid their recombination with photogenerated holes. The catalyst efficiency was analyzed by measuring S₂O₈²⁻ concentration and determining the quantum efficiency at 420 nm. The stability of the photocatalyst was examined by repeating the 6 cycles and analyzing the XPS spectrum before and after photocatalysis to determine

the surface state of the photocatalyst. Photo deposition has resulted in the deposition of Pt nanoparticles tens of nanometers in size on WO_3 particles. Under O_2 purging conditions, bare WO_3 has produced a negligible amount of $\text{S}_2\text{O}_8^{2-}$, whereas Pt-loaded WO_3 has shown significant improvement in performance, resulting in a yield of $33.9 \mu\text{mol}$ of $\text{S}_2\text{O}_8^{2-}$ during 3 h of photocatalytic reaction in the presence of H_2SO_4 . The corresponding quantum efficiency was observed to be 3.8%. It is notable that a quite similar yield ($33.0 \mu\text{mol}$) of $\text{S}_2\text{O}_8^{2-}$ was observed when NaHSO_4 was used instead of H_2SO_4 , reflecting that $\text{S}_2\text{O}_8^{2-}$ production is mainly dependent upon HSO_4^- anions. Compared to Pt, other noble metals have shown very low performance. Similarly, other photocatalysts such as TiO_2 , BiVO_4 , and $\text{g-C}_3\text{N}_4$ have shown much lower performance than WO_3 .

It confirms WO_3 and Pt are appropriate catalyst and co-catalyst, respectively, for producing $\text{S}_2\text{O}_8^{2-}$. Another important aspect authors have demonstrated is the capability of noble metal-loaded WO_3 to drive oxygen reduction reaction (ORR), to consume the photogenerated electrons so that they are not combined with photogenerated holes and thus minimizing energy loss in wasteful recombination. When no O_2 purging was done, it produced only a trace amount of $\text{S}_2\text{O}_8^{2-}$. It was further confirmed by analyzing the ORR in H_2SO_4 by making a thin film of catalysts over an FTO substrate, and Pt has shown the highest current density of oxygen reduction compared to various noble metals (Pd, Rh, Au, Ru) and bare FTO. The authors have proposed that photogenerated holes in the valence band of WO_3 play an important role in the oxidation of HSO_4^- to $\text{S}_2\text{O}_8^{2-}$, whereas the role of Pd as co-catalyst has been suggested to participate in the reverse reaction of reducing back $\text{S}_2\text{O}_8^{2-}$ to HSO_4^- . The effect of the electrolyte was examined by choosing H_2SO_4 and NaHSO_4 at varying concentrations. The amount of $\text{S}_2\text{O}_8^{2-}$ was gradually increased by increasing the electrolyte concentration, reaching a maximum at 1 M of H_2SO_4 . On the basis of these findings, the mechanism of formation and decomposition of PDS over metal-loaded WO_3 has been proposed. Authors have suggested that Pt-loaded WO_3 has promoted O_2 reduction to H_2O_2 , which is further reduced to H_2O_2 . This has been found helpful for producing a higher concentration of PDS via an oxidation reaction catalyzed by valence band holes, whereas Pd-loaded WO_3 has been suggested to participate in the decomposition of $\text{S}_2\text{O}_8^{2-}$ to HSO_4^- . Overall, this study provides insight into the co-catalytic effect of noble metals on WO_3 and reveals an important connection between ORR and $\text{S}_2\text{O}_8^{2-}$ producing reactions.

4. Advancements in Photoelectrochemical WO_3 Photoanodes

Gu et al. have demonstrated an interface modulation approach in a microfluidic platform to boost the performance of WO_3 -based electrodes for PEC production of PDS [61]. Their designed system was composed of hierarchically structured WO_3/TiO_2 fabricated on porous carbon fiber as a substrate. The three-dimensional configuration of designed microfluidic channels has accelerated the PEC oxidation of HSO_4^{4-} anions and greatly enhanced the production yield and efficiency of PDS generation. The design of this work highlights the significance and potential of tailoring heterostructures for sustainable oxidant generation coupled with solar energy conversion. Providing a strong basis for engineering advanced nanostructures for solar to chemical conversions, maintaining high selectivity and efficiency.

The designed architecture has been favorable for boosting charge carrier separation and efficient mass transfer, which ultimately supported higher PEC performance for PDS generation. In this architecture, carbon fiber served as an affordable substrate for growing porous, three-dimensional WO_3 nanostructures, whereas the TiO_2 overlayer helped to suppress the recombination of photogenerated charge carriers. Adopting a photoelectrode instead of a dispersed catalyst could improve performance and make the catalyst easier to

reuse. Therefore, instead of a dispersed slurry-based catalyst, photoelectrode fabrication can be considered as a preferred strategy for solar-assisted production of PDS. Mass transfer limitations in conventional photoelectrodes could hamper the higher yield of production formation. Microfluidics device design based on a 3D porous configuration, as adopted in this work, could promote efficient mass transfer phenomena leading to a higher rate of production formation. PL imaging techniques used to investigate the separation of charge carriers indicate that coupling TiO_2 with WO_3 has promoted interfacial charge transfer. A thin layer of TiO_2 was coated on WO_3 , and the size of the TiO_2 structure was observed to be around 50 nm. ESR analysis has confirmed the presence of oxygen vacancies in m-H- WO_3 and m-H- WO_3/TiO_2 structures by the appearance of a signal corresponding to $g = 2.003$.

The electrode fabrication process was composed of seed-layer-mediated growth of the WO_3 layer on carbon cloth. For that purpose, the substrate was dipped in a tungsten precursor solution and annealed at 400 °C. The process was repeated three times and then followed by hydrothermal growth of the WO_3 layer on the seed-coated carbon fiber substrate. The hydrothermal process was repeated twice to grow a thick WO_3 layer, followed by annealing at 500 °C for 2 h. Oxygen vacancies were introduced to the WO_3 structure through reduction annealing at moderately higher temperature (350 °C) in the presence of a mixture 10% H_2 in Ar. The prepared electrode was referred to as m-H- WO_3 . For the comparison, pl-H- WO_3 was also prepared in a similar way by replacing the carbon cloth substrate with FTO. A TiO_2 coating over m-H- WO_3 was achieved using a wet chemical method by adopting ammonium hexafluorotitanate solution, followed by reductive annealing 10% H_2 in Ar for creating oxygen vacancies. It was observed that the average diameter of carbon fiber was around 8 μm , whereas 2 μm thick WO_3 nanoplates were grown on it. The TiO_2 coating over WO_3 plates was confirmed by elemental mapping.

The presence of oxygen vacancies was further confirmed by the appearance of two peaks at 34.8 eV and 36.6 eV in XPS analysis, assigned to $4f_{7/2}$ and $4f_{5/2}$ of W^{5+} . JV characterization in the presence of Na_2SO_4 electrolyte has confirmed that m-H- WO_3/TiO_2 exhibits a higher current density than m- WO_3/TiO_2 and bare m- WO_3 . It shows that oxygen vacancies have played an important role in producing higher current density. The m-H- WO_3/TiO_2 has shown significant improvement in photocurrent density at 1.23 V vs. RHE compared to pl-H- WO_3 electrodes. These improvements in charge carrier separation and higher photocurrent generation have been reflected in a corresponding increase in the efficiency of PDS generation. After 120 min of PEC reaction, m-H- WO_3/TiO_2 has produced nearly 4 mM of $\text{S}_2\text{O}_8^{2-}$ which is significantly higher than that observed for pl-H- WO_3 , being only 2.4 mM. It confirms the unique advantages of microfluidic design having a defective heterostructure for effective PDS production.

Nakajima et al. have designed a WO_3 nano sponge-based photoanode for PEC PDS production coupled with H_2 production at the cathode over a Pt counter electrode [62]. The aim of this study was to improve the photocurrent density of the WO_3 photoanode by tailoring inter-particle connections to enhance PDS production. The WO_3 photoanode was fabricated using a nanoparticle/solution hybrid dispersion-deposition strategy as shown in Figure 5a. For that purpose, an ink was prepared in which WO_3 was mixed with tungsten phenoxide in the presence of PEG. Spin coating and heating cycles were repeated to fabricate a thick WO_3 film, having a thickness of several micrometers, as shown in Figure 5b. Nanopores in the photoanode contributed to achieving an absorbed photon-to-current efficiency of nearly 95.4% at 410 nm. The $\text{S}_2\text{O}_8^{2-}$ was produced with Faradaic efficiencies for PDS at the anode and H_2 at the cathode near to 100%, reflecting highly selective catalysis as shown in Figure 5c,d. Moreover, the applied bias photon-to-current efficiency was observed as 2.45% at 1.26 VCE. This is higher than the previously reported

2.2% efficiency for WO_3 electrodes. The highest photocurrent observed for the optimized photoanode was about $3.04 \text{ mA}/\text{cm}^2$ at 1.05 V RHE .

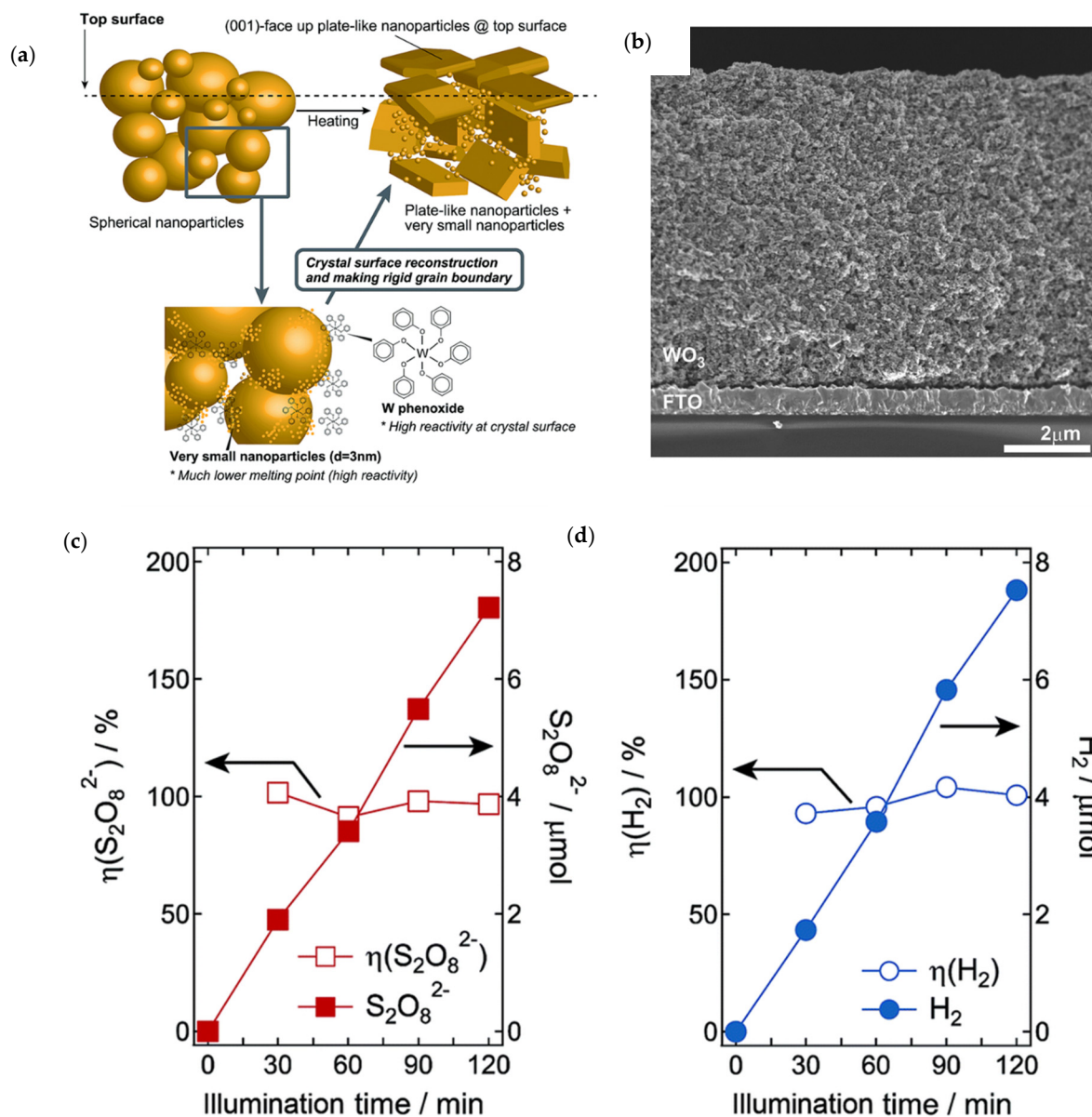


Figure 5. (a) Schematic illustration of crystal growth of WO_3 by NPS hybrid dispersion ink, (b) cross-sectional view of FESEM for photoanode WO_3 , (c) time dependence of Faraday efficiency and generated amounts of (a) $\text{S}_2\text{O}_8^{2-}$ (anode) and (d) H_2 (cathode). The reaction was carried out under 1 Sun simulated sunlight illumination from the back of the W3 photoanode with a steady photocurrent at 0.2 mA adopted from reference [62].

Kusama et al. have performed DFT calculations to unfold the mechanism involving electrochemical oxidation of H_2SO_4 to PDS over WO_3 and SnO_2 anodes [66]. In all cases, proton-coupled electron transfer (PCET) was identified as the rate-determining step. Free energy changes have suggested SnO_2 -deposited WO_3 is a more favorable anode for PDS production than SnO_2 alone. Their experimental findings have further confirmed the higher Faradaic efficiency of WO_3/FTO compared to FTO electrodes, reaching a maximum of 89% for $8 \text{ M H}_2\text{SO}_4$ at 10 mA for 100 s . Although this contribution does not use light irradiation, it provides useful insight about the preferred activity of PDS generation over WO_3/FTO as compared to the bare FTO anode. Fuku et al. have fabricated porous WO_3 electrodes for

PEC-based PDS production coupled with H₂ evolution [63]. The WO₃ electrode applied in this work has been fabricated through spin coating of H₂WO₄ solution in the presence of polyethylene glycol. The optimized thickness of the WO₃ electrode was around 2.7 μm. Photocurrent generated from WO₃ in H₂SO₄ electrolyte reflects superior response for back-side illumination as compared to front-side illumination. It is associated with better charge collection from back-side illumination.

The authors observed a correlation between H₂SO₄ concentration and the amount of PDS generation. A gradual increase in PDS generation was observed as the concentration of H₂SO₄ was increased to 1 M. Their fabricated electrode produced PDS with a Faradaic efficiency of nearly 100%, and ABPE of 2.2% was achieved at 1.13 V vs. CE. Although the developed WO₃ electrode has also demonstrated oxidation of Ce⁴⁺ and IO₄[−], its efficiency remains lower compared to the PDS production process. Furthermore, it was integrated with dye-sensitized solar cells (DSSCs) to establish a bias-less PDS production process. Tandem design was achieved by connecting 2 DSSCs in series with WO₃ as the photoanode and Pt as the cathode to produce PDS and H₂, respectively. This tandem design has shown a highly stable photocurrent response over 1 h in the presence of H₂SO₄ electrolyte. Using this approach, 5.2% solar conversion efficiency was achieved by exploiting the absorption of longer wavelengths of radiation in the IR range. This work demonstrates an interesting concept of approaching tandem design for solar-assisted synthesis of PDS without applying external bias. It can be potentially extended to the synthesis of value-added chemical oxidants.

Petruleviciene et al. achieved PEC-based generation of PDS over WO₃ prepared by the solution deposition technique using different alcohols [64]. The thin films were annealed at different temperatures to monitor the effect of synthesis conditions on morphology and PEC performance. PEC performance was evaluated by measuring PDS production using H₂SO₄ solution. Alcohols (methanol, ethanol, isopropanol, and butanol) adopted in this synthesis acted as reductants for the synthesis of WO₃. Two different heating conditions (400 °C and 500 °C) were used to anneal WO₃ films. For the purpose of PEC characterization, a 0.5 M H₂SO₄ solution was used. PEC experiments were adopted using WO₃ as the photoanode and Pt as the dark cathode to produce PDS and H₂, respectively. WO₃ prepared by annealing at a higher temperature of 500 °C has shown more enhanced crystallinity, whereas the sample annealed at 400 °C has shown inferior crystallinity as observed in the form of broad peaks in XRD patterns. The PEC response of WO₃ electrodes annealed at 400 °C and 500 °C has revealed that those annealed at 400 °C exhibit better performance with earlier saturation of photocurrent density. The authors attribute this behavior to the efficient generation and separation of photogenerated charge carriers. Among various alcohols used as reductants, isopropanol has revealed the best photocurrent response. It was observed that the WO₃ photoanode prepared in the presence of different alcohol reductants showed a decline in the efficiency for PDS generation upon prolonged irradiation, except for the photoanode prepared with IsoPrOH. Such samples have shown a rather improvement in Faradaic efficiency from 53% to 61%, while other samples have shown a significant decline. This work highlights the significant influence of electrode preparation parameters on the morphology, crystallinity, and stability of the photoanode, which ultimately influences the Faradaic efficiency of WO₃ toward PEC-based PDS generation.

It is notable that the Faradaic efficiency of WO₃-based electrodes toward PEC-based PDS production has been reported nearly to 100% in a few studies. It means that the bottleneck to improve the PDS production over WO₃-based electrodes is to overcome the challenges in terms of photocurrent generation. If a higher amount of photocurrent generation is achieved, this could lead to an enhanced rate of PDS production. Although in the literature, several studies have been reported highlighting the effective modification of

WO₃-based photoanode to improve the photocurrent generation, there are still challenges to overcome the limitations of charge carrier recombination. Due to such factors, the photocurrent generation over WO₃ remains low as compared to theoretically predicted values for WO₃. In order to overcome such issues, several strategies have been explored to prevent the recombination of charge carriers to boost the PEC activity. Ahn et al., in an interesting work, have explored the role of the interfacial layer between substrate and WO₃ photoanodes to prevent the unwanted recombination for improving the rate of PDS production [65]. Their study has concluded that a mesoporous blocking layer is more effective in preventing recombination when compared to a random particle-based layer. They have achieved an optimized photocurrent density of 2.6 mA cm² at 1.23 V vs. RHE, resulting in PEC-based PDS production with a Faradaic efficiency reaching near to 95%. The interface between conducting substrates such as fluorine-doped tin oxide (FTO) and WO₃ could play an important role in charge collection efficiency. Preventing the recombination at this interface can improve the availability of charges to effectively perform photo-driven redox reactions. The authors have investigated the effect of the morphology of WO₃-based blocking layers on improving the PEC activity. For that purpose, a WO₃-based blocking layer was introduced over the FTO substrate in two different forms: a randomly structured vs. a mesoporous WO₃-based blocking layer. The random WO₃ blocking layer was introduced by adopting the sol-gel method and introducing the precursor solution via spin coating. The mesoporous blocking layer has been introduced by the same approach, except adding poly(vinyl chloride)-g-poly(oxyethylene methacrylate), as a grafting polymer in the solution. After spin coating, both blocking layers were heated at 500 °C for 30 min, followed by the growth of WO₃ nanoflakes over them. PEC performance of fabricated electrodes has been investigated in the presence of 1 M H₂SO₄ while adding 0.5 M of H₂O₂ as a scavenger in it. There were clear morphological differences in the blocking layers prepared by both approaches. The random layer, owing to a bigger particle size and agglomeration, has exhibited voids in the film, whereas the mesoporous blocking layer has shown the continuity of the blocking layer. This has resulted in a clear difference in corresponding PEC activities. The variation in photocurrent density based on the thickness of the blocking layers highlighted that a moderately thin mesoporous layer has shown optimum performance during the PEC test. Corresponding IPCE results have further confirmed that mesoporous interlayers have superior performance as compared to random blocking layers. EIS analysis has confirmed that the random blocking layer has shown higher charge transfer resistance as compared to the mesoporous blocking layer. The WO₃-based photoanode fabricated by introducing the mesoporous blocking layer has reflected the Faradaic efficiency of about 95%. This work highlights the significance of interface tuning to promote the PEC oxidation of H₂SO₄ for the efficient production of PDS as a valuable oxidant.

Mi et al., in a pioneering work, investigated the suitability of WO₃ photoanodes for oxidizing HSO₄[−] in the presence of aqueous and non-aqueous electrolytes, examining their influence on PEC oxidation of anions [67]. Various electrolytes investigated in this study include water, acetonitrile, and propylene carbonate. Besides oxidation of HSO₄[−], oxidation of other anions including CH₃SO₃[−], HSO₄[−] and ClO₄[−]. Efforts dedicated by authors to investigate the oxidation of anions in water and non-aqueous electrolytes provide useful insight into the PEC oxidation of the WO₃ photoanode. WO₃ photoanode was developed by electrodeposition on either FTO or “W” as a substrate. On account of exploring the photoelectrochemistry of the WO₃ photoanode, various characterizations, including voltammogram, internal quantum yield, and electrochemical impedance analysis, have been performed. PEC oxidation of various anions, including HSO₄[−], in various solvents was examined. For the case of aqueous phase, 1.0 M of H₂SO₄ was used, whereas

in the case of a protic solvent, 0.5 M of tetra(n-butyl) ammonium salt, such as TBAHSO₄, has been adopted. The order of increasing internal quantum yield for HSO₄[−] oxidation over WO₃/FTO in the presence of various electrolytes has been observed as follows: PC, 0.87 > ACN, 0.63 > water, 0.55. Mott–Schottky analysis has confirmed that electrolytes affect the flat-band potential of WO₃/FTO anode, which has an influence on photocurrent onset. This study highlights the influence of various electrolytes of aqueous and non-aqueous compositions on the PEC oxidation of bisulfate anions.

Hill et al. have also investigated the oxidation of sulfate anions (SO₄^{2−}) instead of HSO₄[−] to oxidize it into PDS over WO₃ photoanode under different pH (1, 3 and 5) [35] on account of exploring long term stability, they have found that photocurrent was gradually decreased upon prolong illumination under all pH conditions such as 1, 3 and 5 as shown in Figure 6a. They further investigated the competing reaction of water oxidation to sulfate anion oxidation over the photoanode. Figure 6b shows the photocurrent density and O₂ evolution rate vs. the theoretically expected, assuming 100% FE. The effect of various pH levels was reflected in the photocurrent to oxygen conversion efficiency, which was observed as 35%, 63%, and 88% for pH 1, 3, and 5, respectively. It indicates that when pH was higher, such as 5, it was more favorable for O₂ evolution from water oxidation, while a more acidic pH, such as 1, was favorable for the formation of peroxo formation and sulfate oxidation to persulfate. This study confirms that sulfate oxidation to persulfate can be greatly affected by electrolyte pH; a more acidic pH could be more favorable for the sulfate oxidation reaction, suppressing water oxidation as a competing reaction.

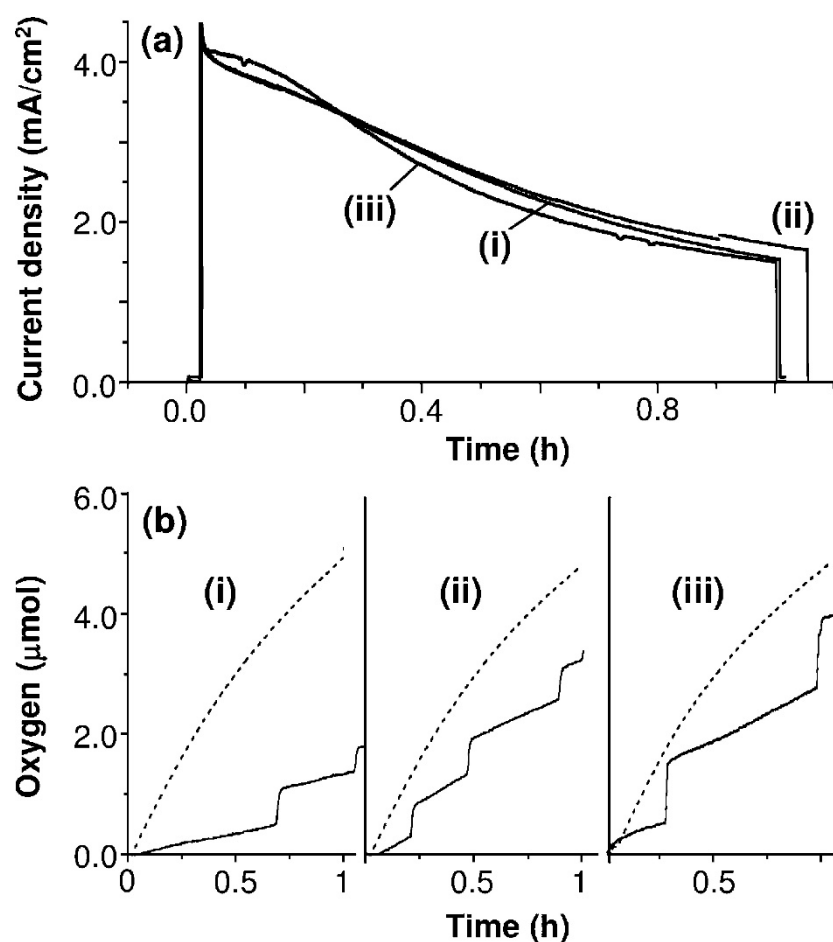


Figure 6. (a) Photocurrent and (b) oxygen measurements of a WO₃ photoanode obtained at 0.9 V vs. Ag/AgCl in 0.1 M Na₂SO₄ solution with pH adjusted to (i) 1, (ii) 3, and (iii) 5 under 400 mW/cm²

illumination with an AM 1.5 G filter. In (b), actual amounts of O₂ produced (—) are compared to expected amounts of O₂ (---) calculated from photocurrent assuming 100% photocurrent to O₂ conversion efficiency adopted from reference [35].

5. Challenges and Outlook

Although various strategies have been developed to enhance the capability of WO₃ for light-induced PDS generation, there is ample room for further advances in this research direction. The critical challenges that remain unsolved are as follows: (i) production of a much lower amount and diluted concentration of PDS during the PEC oxidation process. (ii) The photocurrent generation is low, which limits the extent to which the application of PEC for large-scale production of PDS. (iii) Applying a dispersed or slurry type of photocatalyst to produce PDS under illumination has challenges in recovering the catalyst for reuse. (iv) Most of the work dedicated to PEC-based PDS production is limited to WO₃, whereas the application of earth-abundant photoanodes remains less explored. (v) Exploiting suitable co-catalysts for selectively promoting PDS generation is lacking. (vi) There is a critical challenge of maintaining the stability of photoanodes during long-term applications, considering the corrosive nature of the electrolyte. To address the existing challenges, the following future research directions are suggested as follows: (i) In order to avoid the challenge of the lower production rate of PDS, the achievement of higher photocurrent generation over photoanodes should be focused on. This can be achieved by minimizing the recombination of photoinduced charge carriers. At present, photocurrent generation over WO₃ photoanodes is lower than theoretically predicted values. Rationalized modifications of electrodes, such as heterostructure engineering and dopant introduction, can facilitate extended charge carrier separation. (ii) Use of metal-based co-catalysts should be extended to bimetallic configuration for tuning the work function and regulating charge transfer dynamics. It can effectively enhance charge carrier separation. (iii) Attention should be paid to passivating the surface of oxide photoanodes by coating the protective layers to avoid the problem of corrosion. (iv) Development of novel electrode materials that can sustain corrosive acidic electrolytes should be explored for diversifying PEC anodes for PDS generation. (v) Modification of photoanodes should be achieved to minimize the amount of overpotential needed to drive PDS production. (vi) The selectivity of PDS production should be tailored by reducing the occurrence of competing side reactions of OER at the photoanodes. (vii) Diverse strategies should be adopted to tailor the PEC response of photoanodes, including crystal facet engineering, preferred crystallographic orientation, defect engineering, tailoring oxygen vacancies and fabrication of bilayer and hierarchical three-dimensional nanostructures. (viii) Future research should focus on developing a paired PEC reaction with an appropriate reaction at the cathode and approaching an external bias-free PEC design that can solely rely on solar energy. It reduces the energy input needed to drive PDS production. (ix) To get maximum advantage of solar radiation as an abundant and free resource, such a photoanode should be designed that can absorb panchromatic radiation. It can extend the light absorption and harvesting capabilities. (x) DFT calculations should be performed for a deeper understanding of the reaction mechanism and unfolding the role of catalytic composition on boosting the selectivity and activity. We believe that investigating the above-suggested research direction can bring significant developments in developing advanced nanoscale architecture for light-assisted PDS production in an efficient manner.

Author Contributions: Conceptualization, Z.H. and T.M.; methodology, writing—original draft preparation, T.M., M.I. and Z.H., writing—review and editing, T.M. and M.I., supervision, T.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend their appreciation to the Deanship of Research and Graduate Studies at King Khalid University, Saudi Arabia, through the Large Research Project under grant number RGP-2/691/46.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

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

References

1. Ma, X.; Wang, Z. Removal of ciprofloxacin from wastewater by ultrasound/electric field/sodium persulfate (US/E/PS). *Processes* **2022**, *10*, 124.
2. Mir, B.A.; Rajamanickam, S. Potassium persulfate as an eco-friendly oxidant for oxidative transformations. In *Green Chem-New Perspectives*; IntechOpen: London, UK, 2022.
3. Pratiwi, H.; Kusmono; Wildan, M.W. Oxidized cellulose nanocrystals from durian peel waste by ammonium persulfate oxidation. *ACS Omega* **2023**, *8*, 30262–30272. [\[CrossRef\]](#)
4. Venkatesh, R.; Chaudhary, P. Green chemistry spotlight: Metal-free organic transformations mediated by potassium persulfate. *RSC Adv.* **2025**, *15*, 43198–43237. [\[CrossRef\]](#)
5. Thirumurugan, M.; Mariappan, S.; Rajendran, M.; Subramanyan, V. Parametric Investigation of Electrochemical Synthesis of Ammonium Persulfate in Flow Reactor. *ChemElectroChem* **2025**, *12*, e202500307. [\[CrossRef\]](#)
6. Jitae, K.; Taeyoung, K.; Thi-Huong, P. Degradation of nonpoint source pollutants derived from plastic waste using WO₃/g-C₃N₄ heterojunction photocatalyst. *Process Safety Environ. Protect.* **2025**, *195*, 106704.
7. Gim, G.; Haider, Z.; Suh, S.-I.; Ahn, Y.-Y.; Kim, K.; Kim, E.-J.; Lee, H.; Kim, H.-i.; Lee, J. Low-temperature hydrogenation of nanodiamond as a strategy to fabricate sp³-hybridized nanocarbon as a high-performance persulfate activator. *Appl. Catal. B Environ.* **2022**, *316*, 121589.
8. Yin, R.; Zhang, Y.; Wang, Y.; Zhao, J.; Shang, C. Far-UVC photolysis of peroxydisulfate for micropollutant degradation in water. *Environ. Sci. Technol.* **2024**, *58*, 6030–6038. [\[CrossRef\]](#) [\[PubMed\]](#)
9. Lee, J.; Von Gunten, U.; Kim, J.-H. Persulfate-based advanced oxidation: Critical assessment of opportunities and roadblocks. *Environ. Sci. Technol.* **2020**, *54*, 3064–3081. [\[CrossRef\]](#)
10. Le, H.S.; Tran, V.A.; Doan, V.-D.; Joo, S.-W.; Vasseghian, Y. Enhanced photocatalytic degradation of reactive blue 19 using zeolitic imidazolate framework-8 composited with Fe₃O₄/MnO₂ heterojunction. *J. Ind. Eng. Chem.* **2022**, *115*, 345–354.
11. Ghosh, K.; Mal, D. Bhatt–Hauser Oxidation: A Site-Selective Late-Stage Benzylic C–H Oxidation. *Synlett* **2025**, *36*, 1679–1691.
12. Kushwaha, P.; Rashi. K₂S₂O₈/DMSO-Mediated Organic Transformations: A Comprehensive Report. *Chem.–Asian J.* **2025**, *21*, e70351.
13. Minisci, F.; Citterio, A.; Giordano, C. Electron-transfer processes: Peroxydisulfate, a useful and versatile reagent in organic chemistry. *Acc. Chem. Res.* **1983**, *16*, 27–32.
14. Varala, R.; Seema, V.; Kamsali, M.M.A.; Hussein, M.; Alam, M.M. K₂S₂O₈ (Potassium Persulfate)-Mediated Heterocyclic Ring Formations. *ChemistrySelect* **2025**, *10*, e03555. [\[CrossRef\]](#)
15. Yilmaz, G.; Calis-Ismetoglu, G.; Unal, H.I. Dielectric, Electrorheological Efficiency and Creep-Recovery Characteristics of Vibration Damping Industrial Hemp Fiber/Polyaniline Composite. *Polym. Compos.* **2026**, *47*, 4041–4055.
16. Meng, J.; Tan, Z.; Chen, Y.; Fan, W.; Zhang, C.; Li, L.; Liu, T. Host-Guest All-in-One Supercapacitors Enabled by 3D-Printed Zwitterionic Gel Microlattices for Advanced Energy Storage. *Adv. Func. Mater.* **2025**, *36*, e20575. [\[CrossRef\]](#)
17. Zhu, J.; Hii, K.K.; Hellgardt, K. Toward a green generation of oxidant on demand: Practical electrosynthesis of ammonium persulfate. *ACS Sustain. Chem. Eng.* **2016**, *4*, 2027–2036. [\[CrossRef\]](#)
18. Lavrenko, V.; Shchur, D.; Zolotareno, A.D.; Zolotareno, A.D. Electrochemical synthesis of ammonium persulfate (NH₄)₂S₂O₈ using oxygen-depolarized porous silver cathodes produced by powder metallurgy methods. *Powder Metall. Metal Ceram.* **2019**, *57*, 596–604. [\[CrossRef\]](#)
19. Serrano, K.G. A critical review on the electrochemical production and use of peroxo-compounds. *Curr. Opin. Electrochem.* **2021**, *27*, 100679. [\[CrossRef\]](#)
20. Evseev, A.; Khubutiya, M.S.; Gol'din, M.; Volkov, A.; Koldaev, A. Electrochemical synthesis of peroxodisulfates from dilute sulfate solutions for detoxification of biological media. *Russ. J. Electrochem.* **2008**, *44*, 901–909. [\[CrossRef\]](#)
21. Zhang, F.; Sun, Z.; Cui, J. Research on the mechanism and reaction conditions of electrochemical preparation of persulfate in a split-cell reactor using BDD anode. *RSC Adv.* **2020**, *10*, 33928–33936. [\[CrossRef\]](#)

22. Tazhibayeva, A.; Tanash, A.; Zhigalenok, Y.; Abdimomyn, S.; Malik, S.; Zhumadil, K.; Nechipurenko, S.; Malchik, F. Peroxodisulphuric acid synthesis in a flow electrolyser and its potential utilisation for black mass leaching. *RSC Adv.* **2025**, *15*, 42450–42459. [CrossRef]
23. Fukuda, K.-I.; Iwakura, C.; Tamura, H. The mechanism of the anodic formation of $S_2O_2^{--8}$ ions on a Ti-supported IrO_2 electrode in mixed aqueous solutions of H_2SO_4 , $(NH_4)_4SO_4$ and NH_4F . *Electrochim. Acta* **1979**, *24*, 363–365. [CrossRef]
24. Fukuda, K.-I.; Iwakura, C.; Tamura, H. Anodic processes on a titanium-supported Ruthenium dioxide electrode at high potentials in a mixture of sulfuric acid and ammonium sulfate. *Electrochim. Acta* **1978**, *23*, 613–618. [CrossRef]
25. Davis, J.R.; Baygents, J.C.; Farrell, J. Effect of current density and sulfuric acid concentration on persulfuric acid generation by boron-doped diamond film anodes. *J. Appl. Electrochem.* **2014**, *44*, 841–848. [CrossRef]
26. Bui, V.K.H.; Park, D.; Pham, T.N.; An, Y.; Choi, J.S.; Lee, H.U.; Kwon, O.-H.; Moon, J.-Y.; Kim, K.-T.; Lee, Y.-C. Synthesis of $MgAC-Fe_3O_4/TiO_2$ hybrid nanocomposites via sol-gel chemistry for water treatment by photo-Fenton and photocatalytic reactions. *Sci. Rep.* **2019**, *9*, 11855, Correction in *Sci. Rep.* **2019**, *9*, 17000. [CrossRef]
27. Rossberger, E. Process for the Electrolytic Production of Sodium Peroxodisulfate. 1973. Available online: <https://patents.google.com/patent/US3915816A/en> (accessed on 20 February 2026).
28. Haider, Z.; Archana, R.; Ju, H. Recent Advancements in Photocatalytic Synthesis of Five Membered Nitrogen Heterocycles and Their Derivatives. *Molecules* **2025**, *30*, 3490. [CrossRef]
29. Raub, A.A.M.; Bahru, R.; Nashruddin, S.N.A.M.; Yunas, J. Advances of nanostructured metal oxide as photoanode in photoelectrochemical (PEC) water splitting application. *Heliyon* **2024**, *10*, e39079. [CrossRef] [PubMed]
30. Li, B.; Oldham, L.I.; Tian, L.; Zhou, G.; Selim, S.; Steier, L.; Durrant, J.R. Electrochemical versus photoelectrochemical water oxidation kinetics on bismuth vanadate (photo) anodes. *J. Am. Chem. Soc.* **2024**, *146*, 12324–12328. [CrossRef] [PubMed]
31. Xi, Z.; Liu, M. Advancing photoelectrochemical systems for sustainable energy and chemical production: Challenges and opportunities. *npj Mater. Sustain.* **2025**, *3*, 18. [CrossRef]
32. Chen, H.; Ding, C.; Li, Y.; Wang, L.; Li, C.; He, J. Bias-free photoelectrochemical system mediates hydrogen production and biomass conversion at high current density. *J. Environ. Chem. Eng.* **2024**, *12*, 112614. [CrossRef]
33. Selvaraj, A.R.; Kasirajan, K.; Hur, J. Fabrication and Photoelectrochemical Activity of In_2S_3 Infused TiO_2 Nanorod Heterostructure Photoelectrodes for Solar Water Splitting. *Nanomaterials* **2025**, *16*, 44. [CrossRef]
34. Kwon, J.; Choi, H.; Choi, S.; Sun, J.; Han, H.; Paik, U.; Choi, J.; Song, T. Improved Charge Carrier Dynamics by Unconventional Doping Strategy for $BiVO_4$ Photoanode. *Small Sci.* **2025**, *5*, 2500051. [CrossRef]
35. Hill, J.C.; Choi, K.-S. Effect of electrolytes on the selectivity and stability of n-type WO_3 photoelectrodes for use in solar water oxidation. *J. Phys. Chem. C* **2012**, *116*, 7612–7620. [CrossRef]
36. Sayama, K. Production of high-value-added chemicals on oxide semiconductor photoanodes under visible light for solar chemical-conversion processes. *ACS Energy Lett.* **2018**, *3*, 1093–1101. [CrossRef]
37. Kim, W.; Tachikawa, T.; Monllor-Satoca, D.; Kim, H.-i.; Majima, T.; Choi, W. Promoting water photooxidation on transparent WO_3 thin films using an alumina overlayer. *Energy Environ. Sci.* **2013**, *6*, 3732–3739. [CrossRef]
38. Wu, H.; Zhang, L.; Qu, S.; Du, A.; Tang, J.; Ng, Y.H. Polaron-mediated transport in $BiVO_4$ photoanodes for solar water oxidation. *ACS Energy Lett.* **2023**, *8*, 2177–2184.
39. Liu, H.; Cong, H.; Yang, G.; Gong, C.; Ding, J.; Fu, Y.Y.; Cui, J.; Song, K.; Chen, B.; He, C.; et al. Surface hole polaron site tuning governs charge carrier separation in $BiVO_4$ photoanodes. *Nature Commun.* **2026**, *17*, 2562. [CrossRef]
40. Suryawanshi, M.P.; Ghorpade, U.V.; Toe, C.Y.; Suryawanshi, U.P.; He, M.; Zhang, D.; Jang, J.S.; Shin, S.W.; Kim, J.H.; Hao, X. Earth-abundant photoelectrodes for water splitting and alternate oxidation reactions: Recent advances and future perspectives. *Prog. Mater. Sci.* **2023**, *134*, 101073. [CrossRef]
41. Jin, S. What else can photoelectrochemical solar energy conversion do besides water splitting and CO_2 reduction? *ACS Energy Lett.* **2018**, *3*, 2610–2612. [CrossRef]
42. Liu, C.-F.; Lu, Y.-J.; Hu, C.-C. Effects of anions and pH on the stability of ZnO nanorods for photoelectrochemical water splitting. *ACS Omega* **2018**, *3*, 3429–3439. [CrossRef]
43. Pawar, A.U.; Kim, C.W.; Kang, M.J.; Kang, Y.S. Crystal facet engineering of ZnO photoanode for the higher water splitting efficiency with proton transferable nafion film. *Nano Energy* **2016**, *20*, 156–167. [CrossRef]
44. Benavente Llorente, V.; Jenewein, K.J.; Bierling, M.; Körner, A.; Hutzler, A.; Kormányos, A.; Cherevko, S. Photocorrosion of hematite photoanodes in neutral and alkaline electrolytes. *J. Phys. Chem. C* **2023**, *127*, 19687–19697. [CrossRef]
45. Zhang, S.; Ahmet, I.; Kim, S.-H.; Kasian, O.; Mingers, A.M.; Schnell, P.; Kölbach, M.; Lim, J.; Fischer, A.; Mayrhofer, K.J. Different photostability of $BiVO_4$ in near-pH-neutral electrolytes. *ACS Appl. Energy Mater.* **2020**, *3*, 9523–9527. [CrossRef]
46. An, Z.; Li, C.-G.; Zhang, Y.-S.; Zhang, L.; Duan, H.-M.; Mo, L.-M.; Wang, H.-Y. N-doped carbon dots as electrolytes to boost photoelectrochemical water oxidation for a photo-assisted zinc–air battery. *Chem. Commun.* **2025**, *61*, 8276–8279. [CrossRef]
47. Suchikova, Y.; Nazarovets, S.; Konuhova, M.; Popov, A.I. Binary Oxide Ceramics (TiO_2 , ZnO , Al_2O_3 , SiO_2 , CeO_2 , Fe_2O_3 , and WO_3) for Solar Cell Applications: A Comparative and Bibliometric Analysis. *Ceramics* **2025**, *8*, 119. [CrossRef]

48. Sreedhar, A.; Pabba, D.P.; Koyyada, G.; Alodhayb, A.N.; Pandiaraj, S.; Reddy, N.R.; Joo, S.W. Green-synthesized metal oxide nanostructures for solar-driven photocatalysis: Advances, challenges, and environmental applications. *J. Alloys Compd.* **2025**, *1036*, 182080. [\[CrossRef\]](#)
49. Dworschak, D.; Brunnhofer, C.; Valtiner, M. Photocorrosion of ZnO single crystals during electrochemical water splitting. *ACS Appl. Mater. Interfaces* **2020**, *12*, 51530–51536. [\[CrossRef\]](#)
50. O'Rourke, C.; Mills, A. Water oxidation by P25 TiO₂ photoanodes in acidic solution. *Chemosphere* **2021**, *271*, 129847. [\[CrossRef\]](#) [\[PubMed\]](#)
51. Haider, Z.; Yim, H.W.; Lee, H.W.; Kim, H.-i. Surface and bulk modification for advanced electrode design in photoelectrochemical water splitting. *Int. J. Hydrogen Energy* **2020**, *45*, 5793–5815. [\[CrossRef\]](#)
52. Li, L.; Li, J.; Kim, B.-H.; Huang, J. The effect of morphology and crystal structure on the photocatalytic and photoelectrochemical performances of WO₃. *RSC Adv.* **2024**, *14*, 2080–2087. [\[CrossRef\]](#)
53. Kawawaki, T.; Akinaga, Y.; Yazaki, D.; Kameko, H.; Hirayama, D.; Negishi, Y. Promoting photocatalytic carbon dioxide reduction by tuning the properties of cocatalysts. *Chem.—A Eur. J.* **2023**, *29*, e202203387. [\[CrossRef\]](#)
54. Usha, K.; Lee, S.Y.; Sivakumar, R.; Sanjeeviraja, C. Effect of thermal treatment on thin films of NiO: WO₃ for optoelectronic applications. *Optical Mater.* **2025**, *158*, 116419. [\[CrossRef\]](#)
55. Usha, K.; Lee, S.Y. Fast-switching electrochromic smart windows based on WO₃ doped NiO thin films. *J. Alloys Compd.* **2024**, *1009*, 176774. [\[CrossRef\]](#)
56. Mayer, L.M.; Marschall, R. Tailoring the Film Thickness of Template-Assisted Sol–Gel-Derived Porous WO₃ Photoanodes for Highly Efficient Photoelectrochemical Water Oxidation. *ChemPhotoChem* **2025**, *9*, e202500191. [\[CrossRef\]](#)
57. Dutta, V.; Sharma, S.; Raizada, P.; Thakur, V.K.; Khan, A.A.P.; Saini, V.; Asiri, A.M.; Singh, P. An overview on WO₃ based photocatalyst for environmental remediation. *J. Environ. Chem. Eng.* **2021**, *9*, 105018. [\[CrossRef\]](#)
58. Wang, Z.; Einaga, H. WO₃-based Materials for Photocatalytic and Photoelectrocatalytic Selective Oxidation Reactions. *Chem-CatChem* **2023**, *15*, e202300723. [\[CrossRef\]](#)
59. Huang, Z.; Chen, Y.; Wu, J.; Xie, W.; He, X.; Ma, M.; Sayama, K.; Zhou, Y. Modulating Pt Interaction in Au@ Pt Nanoparticle/WO₃ Photocatalysts for Enhanced Production of Peroxodisulphate. *ACS Appl. Nano Mater.* **2022**, *5*, 12797–12805. [\[CrossRef\]](#)
60. Huang, Z.; Miseki, Y.; Sayama, K. Solar-light-driven photocatalytic production of peroxydisulfate over noble-metal loaded WO₃. *Chem. Commun.* **2019**, *55*, 3813–3816. [\[CrossRef\]](#)
61. Gu, Z.; An, X.; Liu, R.; Xiong, L.; Tang, J.; Hu, C.; Liu, H.; Qu, J. Interface-modulated nanojunction and microfluidic platform for photoelectrocatalytic chemicals upgrading. *Appl. Catal. B Environ.* **2021**, *282*, 119541. [\[CrossRef\]](#)
62. Nakajima, T.; Hagino, A.; Nakamura, T.; Tsuchiya, T.; Sayama, K. WO₃ nanosponge photoanodes with high applied bias photon-to-current efficiency for solar hydrogen and peroxydisulfate production. *J. Mater. Chem. A* **2016**, *4*, 17809–17818. [\[CrossRef\]](#)
63. Fuku, K.; Wang, N.; Miseki, Y.; Funaki, T.; Sayama, K. Photoelectrochemical Reaction for the Efficient Production of Hydrogen and High-Value-Added Oxidation Reagents. *ChemSusChem* **2015**, *8*, 1593–1600. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Petrulėviciene, M.; Parvin, M.; Savickaja, I.; Gece, G.; Naujokaitis, A.; Pakstas, V.; Pilipavicius, J.; Gegeckas, A.; Gaigalas, G.; Juodkazyte, J. WO₃ coatings for photoelectrochemical synthesis of persulfate: Efficiency, stability and applicability. *J. Solid. State Electrochem.* **2022**, *26*, 1021–1035. [\[CrossRef\]](#)
65. Ahn, S.H.; Zhao, J.; Kim, J.H.; Zheng, X. Effect of interfacial blocking layer morphology on the solar peroxydisulfate production of WO₃ nanoflakes. *Electrochim. Acta* **2017**, *244*, 184–191. [\[CrossRef\]](#)
66. Kusama, H.; Koder, M.; Sayama, K. Selective Oxidation of Sulfuric Acid to Peroxydisulfuric Acid on a Tungsten Trioxide Anode. *ChemistrySelect* **2023**, *8*, e202300114. [\[CrossRef\]](#)
67. Mi, Q.; Coridan, R.H.; Brunschwig, B.S.; Gray, H.B.; Lewis, N.S. Photoelectrochemical oxidation of anions by WO₃ in aqueous and nonaqueous electrolytes. *Energy Environ. Sci.* **2013**, *6*, 2646–2653. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.