

Research Article

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Optimizing Precursor pH for Enhanced WO₃/BiVO₄ Heterojunction Photoanode Performance

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Abstract

The pH of the precursor solution significantly influences the efficacy of WO₃/BiVO₄ heterojunction photoanodes; however, the exact impact on the photoelectrocatalytic (PEC) process remains unclear. This study objectively examines the influence of the pH of the WO₃ precursor on the structural, optical, and electrochemical characteristics of FTO/WO₃/BiVO₄ electrodes to enhance their performance in photoelectrochemical (PEC) applications. WO₃ and BiVO₄ are prepared via dip-coating, subsequently subjected to calcination at 500°C. The photoanode characteristic properties were examined using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), UV-Vis spectroscopy, and electrochemical impedance spectroscopy (EIS). The results indicated that the electrode efficiently segregated charge carriers due to its reduced bandgap energy (2.15 eV) and substantial light absorption ($\lambda = 576$ nm) at pH 11. In comparison to Ag/AgCl, we obtained a significant increase in current density (1.91 mA/cm²) with the utilization of visible light at 1.0 V. This addressed to a significant capacitance (CPE = 1.19×10^{-5} F) and a small charge transfer resistance (R_{ct} = 116 Ω). A uniform, detailed morphology was noted in the SEM images at a pH of 11, which enhanced interfacial bonding and charge transfer. The results emphasize the necessity of adjusting the precursor's pH to improve the efficacy of WO₃/BiVO₄ heterojunctions employed in solar-driven oxidation processes. These findings will facilitate the advancement of sophisticated photoelectrocatalytic applications for sustainable energy conversion.

Keywords: WO₃/BiVO₄ Heterojunction, Photoelectrocatalysis, Precursor pH, Charge Transfer Resistance, Bandgap Tuning

1. Introduction

The growing global need for renewable energy is increasing research into sustainable energy conversion technology. Photoelectrochemical (PEC) water splitting has attracted significant interest as an efficient technique for generating hydrogen fuel from solar energy (1). PEC systems employ semiconductor photoanodes to facilitate water oxidation under solar light, offering material selection an essential consideration in enhancing

efficiency. Tungsten oxide (WO₃) and bismuth vanadate (BiVO₄) were recognized as attractive photoanode materials owing to their advantageous bandgap energies, chemical stability, and ability to absorb visible light.

WO₃ is an extensively researched n-type semiconductor with bandgap energy between 2.6 and 2.8 eV, making it appropriate for visible-light-driven photoelectrochemical applications (2). Furthermore, WO₃ demonstrates exceptional charge transport characteristics,

facilitating effective charge extraction. However, a significant charge recombination rate impeded its overall PEC performance, affecting its photocatalytic efficiency. Conversely, BiVO_4 , possessing a bandgap energy of approximately 2.4 to 2.5 eV, is capable of absorbing a wider spectrum of visible light; nevertheless, its utilization is limited by low charge carrier mobility and inefficient charge transport efficiency (3).

To overcome these limitations, developing heterojunction photoanodes is recognized as a practical approach for enhancing charge separation and improving photocatalytic performance. The integration of WO_3 and BiVO_4 into a heterojunction structure has shown considerable promise in reducing charge recombination while utilizing the synergistic benefits of both materials (4-6). The establishment of a heterojunction between WO_3 and BiVO_4 engenders an internal electric field at the interface, enhancing charge transfer efficiency and improving the overall PEC performance (7). Achieving an optimal heterojunction necessitates meticulous regulation of material synthesis parameters, as the interfacial structure significantly affects charge transport kinetics.

The pH of the WO_3 precursor solution during synthesis is an essential factor influencing the quality and performance of $\text{WO}_3/\text{BiVO}_4$ heterojunctions. The pH of the precursor solution is crucial in influencing the structural, optical, and electrochemical characteristics of the deposited WO_3 layer, thereby impacting the heterojunction interface (8). Variations in pH might result in alterations in surface morphology, crystallinity, and charge transport properties, thereby affecting the overall effectiveness of the photoanode (9-11). Considering its importance, the optimization of precursor pH for improved heterojunction performance continues to be a subject of engaged research.

This study systematically investigates the influence of the pH adjustment in the WO_3 precursor solution on the enhancement of $\text{WO}_3/\text{BiVO}_4$ heterojunction photoanodes. We try to clarify the relationship between precursor pH, interfacial characteristics, and PEC performance by optimizing synthesis conditions. This research promises to provide significant insights into the function of solution chemistry in heterojunction engineering, accordingly

advancing high-efficiency photoanodes for solar-driven water oxidation.

2. Materials and Experiment

2.1 WO_3 , BiVO_4 precursor solution preparation

A 0.100 M WO_3 precursor solution preparation was carried out by dissolving 2.499 g of tungstic acid (H_2WO_4) in 100 mL of a 30% w/v ammonia solution. The pH of the WO_3 precursor solutions was adjusted to values of 3, 5, 7, 9, and 11 while avoiding the occurrence of precipitates or inappropriate phase transitions. The solution was refluxed at 60°C for 60 minutes prior to its use. A 50 mL solution of 0.100 M BiVO_4 precursor was prepared by combining 4.8517 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.5%) with 50 mL of acetylacetone and 2.65 g of $\text{VO}(\text{acac})_2$ (98%) in 99.5% acetone (CH_3COCH_3) solution. The combined solutions were shaken for an additional ten minutes to ensure uniformity. Subsequently, the homogeneity and stability of the combined solution were enhanced by sonication for 120 minutes.

2.2 Fabrication of $\text{WO}_3/\text{BiVO}_4$ film on anode electrode

Fluorine-doped tin oxide (FTO) conducting glass was used as the electrode substrate following cleaning with ethanol and deionized water. The first layer of the WO_3 coating was coated to the FTO substrate utilizing an automated dip-coating method. The FTO/ WO_3 electrode, after coating, was dried at 60°C for 5 minutes and subsequently calcined at 500°C for 30 minutes. The FTO/ WO_3 electrode was immersed in the BiVO_4 precursor solution, dried at 60°C for 5 minutes, and calcined at 500°C for 60 minutes to fabricate the FTO/ $\text{WO}_3/\text{BiVO}_4$ electrode. In this study, a single coating cycle was applied for both WO_3 and BiVO_4 layers, following optimized conditions reported in previous studies to ensure effective film formation and photoelectrochemical performance.

2.3 Characterization and photoelectrocatalytic properties study

The optical characteristics of the $\text{WO}_3/\text{BiVO}_4$ electrode were analyzed utilizing a UV-visible spectrophotometer. The films' surface morphology was investigated using a Scanning Electron Microscope (SEM), and their

elemental composition was assessed via Energy Dispersive X-ray Spectroscopy (EDX). The photocatalytic activities were examined using electrochemical investigation at an applied potential of 1.0 V under visible light irradiation. Electrochemical impedance was assessed via Electrochemical Impedance Spectroscopy (EIS) to validate enhancements in the charge transfer mechanism.

3. Results and Discussion

Initial investigation found that precursor solutions with a pH below 5 led to precipitate formation and reduced phase stability, hence affecting the uniformity and reproducibility of the films. Similarly, attempts to employ pH levels above 11 resulted in significant dissolution and unstable film formation, so limiting their appropriateness for systematic investigation. Therefore, we focused our efforts on the pH range of 5 to 11, wherein film stability, surface homogeneity, and adhesion were reliably attained. This pH range value provided the most effective and dependable conditions for evaluating the impact of pH on the morphology and photoelectrocatalytic efficacy of $\text{WO}_3/\text{BiVO}_4$ heterojunctions. Consequently, the subsequent experimental results will elucidate the impact of pH values ranging from 5 to 11 on the characteristics of the fabricated $\text{FTO}/\text{WO}_3/\text{BiVO}_4$ electrodes.

3.1 $\text{WO}_3/\text{BiVO}_4$ film characterization

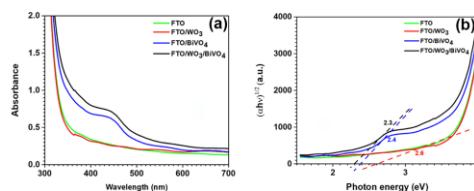


Figure 1 (a) Absorption spectra and (b) Relationship between the absorbance coefficient and the bandgap energy of FTO, FTO/WO₃, FTO/BiVO₄, and FTO/WO₃/BiVO₄ electrodes

The optical properties of the FTO/WO₃, FTO/BiVO₄, and FTO/WO₃/BiVO₄ electrodes were analyzed using UV-Vis spectroscopy, as shown in Figures 1(a) and 1(b). The absorption spectra of the FTO/WO₃/BiVO₄ electrodes can absorb a greater quantity of visible light spectrum, which is beneficial for improving photoelectrocatalytic efficacy. The enhanced photon absorption of the heterojunction electrode (FTO/WO₃/BiVO₄) suggests that the electric interactions between WO₃ and BiVO₄ are functioned effectively, leading to improved photon absorption. Tauc diagrams were employed to ascertain the bandgap energies of the conductors, as illustrated in Figure 1(b). The bandgap values for FTO/WO₃ are 2.6 eV, while those for FTO/BiVO₄ are 2.4 eV, and FTO/WO₃/BiVO₄ is 2.3 eV(5). The FTO/WO₃/BiVO₄ heterojunction's lower bandgap energy suggests that the bandgap is narrowed by the combination of WO₃ and BiVO₄, which facilitates the formation of charge carriers when visible light interacts with the junction. The reduced bandgap enhances the photocatalytic activity, enabling the utilization of a greater amount of solar energy and the expansion of the wavelength range that can be absorbed. We noticed that FTO/WO₃/BiVO₄ exhibited improved bandgap reduction and light absorbance. The heterojunction effect is responsible for this, as it enables the separation of charges and reduces recombination losses. Combining WO₃ (a material with a profound conduction band) and BiVO₄ (a material with strong visible-light absorption qualities) results in the most optimal electronic structure, which maximizes charge transfer efficiency. This characteristic is especially important for photoelectrocatalytic applications, particularly those involving water oxidation and similar substances. The results suggest that the WO₃/BiVO₄ heterojunction significantly increases optical absorption while concurrently decreasing the bandgap energy. This makes it a potential electrode material for photoelectrochemical applications. It is possible that the improved optical properties could be advantageous for solar-driven water splitting and other photocatalytic processes that necessitate improved light absorption and charge separation.

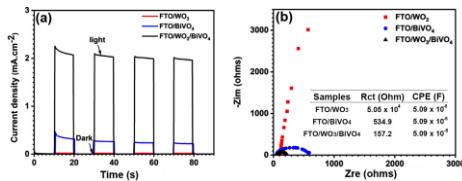


Figure 2 (a) Amperograms and (b) Nyquist plot of FTO/WO₃, FTO/BiVO₄, and FTO/WO₃/BiVO₄ electrodes in a 0.5 M NaCl solution at a potential of 1.0 V under visible light

The photocurrent density of FTO/WO₃, FTO/BiVO₄, and FTO/WO₃/BiVO₄ electrodes was investigated by under chopped illumination at 1.0 V vs. Ag/AgCl in a 0.5 M NaCl solution, as demonstrated in Figure 2(a). Compared to FTO/ BiVO₄ (blue line) and FTO/WO₃ (red line), the photocurrent reaction was greatest in the FTO/WO₃/BiVO₄ heterojunction electrode (black line). A heterojunction is created by WO₃ and BiVO₄, which facilitates the separation of charges and reduces the combination of electrons and holes. This is because either the charge carriers reassembled or the photoanode's surface deteriorated slightly due to improved exposure to light. However, the FTO/WO₃/BiVO₄ heterojunction exhibited significantly higher photocurrent levels than the other electrodes. The dimension of the half-circle in the Nyquist plot in Figure 2(b) is correlated with the charge transfer resistance (R_{ct}) at the electrode/electrolyte contact. The electrode composed of FTO/WO₃/BiVO₄ exhibited the smallest half-circle, with a resistance of 157.2 Ω implies that it possessed the lowest charge transfer resistance. This demonstrates that the heterojunction between WO₃ and BiVO₄ is highly effective in reducing the resistance at the contact and facilitating the movement of electrons. The capacitance of the FTO/WO₃/BiVO₄ electrode is the highest, as evidenced by the constant phase element (CPE) values. This confirms that it has a greater active surface area for accumulating and transporting charges. The findings are consistent with the trends in photocurrent density displayed in Figure 2(a). These trends demonstrate that decreased resistance facilitates the transport of charges, thereby improving the functionality of PEC. The WO₃/BiVO₄ heterojunction exhibits significantly greater photoelectrochemical

efficiency due to its ability to reduce charge transfer resistance and increase photocurrent density in the presence of visible light (6). Photoelectrocatalytic activities are well-suited to the heterojunction electrode, as it is capable of more effectively splitting charges and transferring electricity.

3.2 Effect of pH of precursor solution

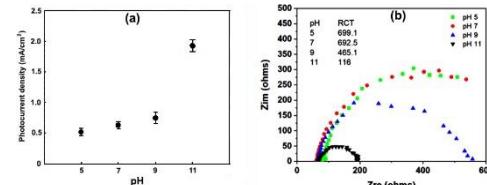


Figure 3 (a) Photocurrent density and (b) Nyquist plots of FTO/WO₃/BiVO₄ electrodes prepared with various WO₃ precursor solution pH conditions of 5, 7, 9, and 11 in 0.5 M NaCl solution at an applied potential of 1.0 V under visible light

Figure 3(a) presents the effect of WO₃ precursor solution pH on the photocurrent density of the FTO/WO₃/BiVO₄ electrodes under visible light illumination. The results demonstrate a clear trend of increasing photocurrent density with rising pH, reaching a maximum of 1.91 mA cm⁻² at pH 11. These results suggest that higher pH conditions enhance charge separation and photoactivity. The photocurrent density significantly increases at pH 11, indicating that charge carriers are more effectively separated and oxidation reactions are more efficient. This is likely because the WO₃/BiVO₄ heterojunction's structure and electrical properties are optimal at this pH level. The electrode that was produced at pH 11 was more stable in terms of photoelectrocatalysis than the electrode that was produced at a lower pH. The results also showed a relative standard deviation (RSD) of 6.08% for a pH electrode optimized at pH = 11, indicating that it can be trusted to ensure high efficiency and consistency in the fabricating process. This indicates that it has the potential to be employed in oxidation processes for an extended period of time. The electrochemical resistance of the electrode was investigated using electrochemical impedance spectroscopy (EIS). The Nyquist diagrams are illustrated in Figure 3(b). The pH 11 electrode condition exhibited a charge transfer resistance

that was significantly lower than that of the other electrode condition. In other words, the electrode produced with pH 11 is the most effective at conducting charges between interfacial electrode/electrolyte surfaces. It also demonstrates that it has a larger active surface area and can store charges more effectively, as evidenced by a constant phase element (CPE) value of 1.19×10^{-5} F at pH 11. This supports the notion that it functions more effectively as a photoelectrocatalyst. The PEC's overall functionality and the separation of charges are significantly affected by the pH of the WO_3 precursor, as evidenced by the correlation between a high photocurrent reaction and a low R_{ct} (12). The results indicate that the pH of the precursor solution significantly influences the electrochemical characteristics and PEC performance of the $\text{WO}_3/\text{BiVO}_4$ electrodes. The electrode produced at pH 11 was the most suitable for photoelectrocatalytic applications due to its superior photocurrent density and minimal resistance. The results demonstrate the crucial importance of increasing the pH of the precursor to facilitate improved light-induced oxidation and accelerate charge transfer.

The surface morphology of the FTO/ $\text{WO}_3/\text{BiVO}_4$ electrodes, which were produced using WO_3 precursor solutions with pH values of 5, 7, 9, and 11, was examined using scanning electron microscopy (SEM).

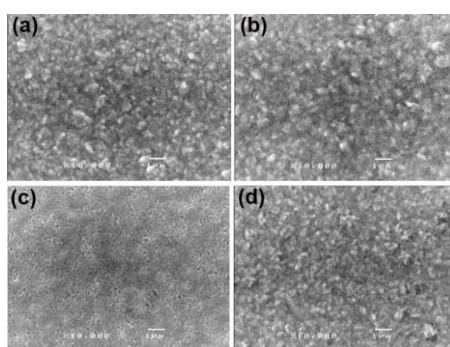


Figure 4 SEM image of the FTO/ $\text{WO}_3/\text{BiVO}_4$ electrode film prepared with WO_3 precursor solution pH conditions of (a) 5, (b) 7, (c) 9, and (d) 11

The microstructural variations between the films demonstrate the impact of the precursor solution's pH on the films' formation and the particles' dispersion. The electrode

surfaces exhibited rough, non-uniform structures with large and irregularly shaped particulates when the pH was between 5 and 7 (Figures 4a and 4b). These characteristics indicate that the film is formed erratically due to unregulated growth and incomplete nucleation. At these lower pH levels, the larger particle sizes may facilitate a greater amount of charge recombination, as evidenced by the lower photocurrent reactions observed in previously conducted electrochemical studies. The surface appeared smoother at pH 9 (Figure 4c), with a thicker structure and smaller granules packed closer together. This change suggests a transition to improved nucleation and controlled growth, which could result in improved charge movement and separation. When the pH level was 11, the FTO/ $\text{WO}_3/\text{BiVO}_4$ electrode exhibited the most uniform, smooth, and finely distributed particulates (Figure 4d). The film is more compact and free of defects due to the appropriate germination and growth conditions, as evidenced by the smaller particles and more even surface. The present study examines the impact of raising the pH of the WO_3 precursor solution on nucleation and particle growth, resulting in smoother, more uniform morphologies with a finer grain distribution at pH 11. This microstructural enhancement improves the interfacial contact between WO_3 and BiVO_4 , facilitating more effective charge separation and transport. This well-defined geometry is associated with improved photoelectrocatalytic performance and reduced charge transfer resistance, as observed in previous studies (13). The smaller particles should enhance the relationship between the electrode and the electrolyte at pH 11, reducing the recombination effect and enhancing the charge transfer efficiency. The structure of the $\text{WO}_3/\text{BiVO}_4$ coatings is significantly influenced by the pH of the precursor solution, as demonstrated by the SEM study. The optimal pH level is 11. This directly enhances the efficiency of charge separation and transfer by ensuring that the surface is uniform, smooth, and uniformly distributed. Conversely, when the pH is lower (between 5 and 7), the shapes are irregular and rugged, resulting in increased recombination and reduced photocurrent generation. The findings indicate that the structural features of FTO/ $\text{WO}_3/\text{BiVO}_4$ electrodes are significantly enhanced by altering the pH of the WO_3 precursor solution. The optimal

surface characteristics is observed at pH 11, which is associated with improved photoelectrocatalytic activity, lower charge transfer resistance, and a higher photocurrent density. These results demonstrate the critical role of the pH of the precursor solution in modifying the electrode's properties to enhance its photoelectrochemical characteristics. The elemental composition analysis of the FTO/WO₃ electrode using EDX indicated that the tungsten (W) content peaked at pH 11, demonstrating enhanced adhesion of WO₃ to the electrode surface. Furthermore, the high pH environment results in enhanced incorporation of WO₃, as corroborated by EDX, which facilitates improved electronic coupling and conduction pathways at the heterojunction interface. These modifications combined yield a diminished charge transfer resistance and an increased photocurrent density. This result supports previous studies, demonstrating that pH 11 is the optimal condition for the preparation of WO₃ precursors.

4. Conclusions

This study emphasizes the significant impact of the pH of the WO₃ precursor solution on the structural, optical, and electrochemical characteristics of WO₃/BiVO₄ heterojunction photoanodes for photoelectrochemical (PEC) water oxidation. By systematically altering the precursor pH from 5 to 11, we exhibited substantial enhancements in photocatalytic performance, with pH 11 producing the most advantageous characteristics. Optimized photoanodes demonstrated improved light absorption ($\lambda = 576$ nm), a reduced bandgap (2.15 eV), and the highest photocurrent density (1.91 mA/cm² at 1.0 V vs. Ag/AgCl), more significant than electrodes produced at other pH levels. The developed WO₃/BiVO₄ photoanode exhibited a significantly higher photocurrent density of 1.91 mA cm⁻² compared to the reported value of 0.39 mA cm⁻² for the TiO₂/Au/Cu₂O NRAs photoanode, indicating superior charge separation and photoelectrocatalytic performance (14). Electrochemical impedance spectroscopy (EIS) demonstrated that samples at pH 11 displayed the lowest charge transfer resistance (116 Ω), signifying enhanced charge transport, while morphological analysis validated a uniform and well-adhered film structure. These findings highlight precursor pH as a critical factor in

enhancing WO₃/BiVO₄ heterojunction surfaces, significantly impacting charge separation and PEC efficiency. The enhanced performance at pH 11 indicates that meticulous regulation of synthesis conditions can optimize photoanode efficacy, providing an approach for further progress in solar-driven hydrogen generation. Future studies should concentrate on enhancing long-term stability, exploring alternate fabrication methods, and using co-catalysts to enhance PEC performance and scalability for practical applications. Future studies should address scalability challenges, particularly film uniformity and consistency during large-area or continuous production.

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Declaration of Conflicting Interests

The authors declare they have no conflicts of interest for this article, and they alone are responsible for the content.

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