Photoelectrocatalytic properties of $CuWO_4$|$MnWO_4$|$BiVO_4$ double-heterojunction photoanode

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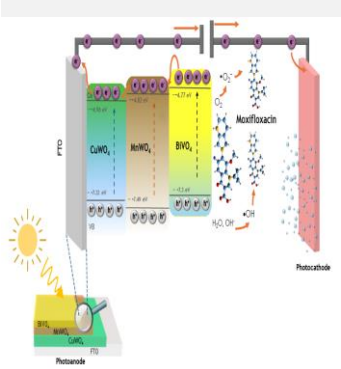

Photoelectrocatalysis (PEC) has been known as a promising environmental remediation strategy because it combines the advantages of photocatalysis and electrocatalysis. In this study, to achieve efficient PEC degradation of Moxifloxacin, an FTO|$CuWO_4$|$MnWO_4$|$BiVO_4$ double-heterojunction photoanode was prepared using spin coating and electrodeposition methods. The gradient energy band alignment and applied bias potential inhibit the recombination of electron-hole pairs and contribute to the production of active species for antibiotic degradation under visible light. The FTO|$CuWO_4$|$MnWO_4$|$BiVO_4$ photoanode displayed lower charge carrier transfer resistance than pure $CuWO_4$, and the photocatalytic activity reached 45 % after 165 min PEC treatment.

Introduction

Emerging contaminants (ECs) represent a broad range of chemical compounds, including pharmaceuticals, personal care products, pesticides, surfactants, and dyes. These ECs disrupt the natural resource quality and interfere with environmental biochemical processes, affecting the health of living species. Consequently, the elimination of ECs, such as antibiotics, from wastewater is a crucial concern [1].

Heterogeneous photocatalysis (HP) based on semiconductors can potentially be employed to photodegradation pollutants. This method utilizes solar energy to activate the photocatalyst and generate charge carriers. The photogenerated electron-hole pairs can initiate redox reactions or recombine during the photocatalytic reaction. The main limitation of HP is the high charge carrier recombination rates [2].

Several strategies, including heterojunction formation, have been proposed to efficiently separate the electron-hole pairs in semiconductor photocatalysts. Proper band structure alignment in heterojunctions promotes a broader absorption spectrum and reduces the electron-hole recombination rate, resulting in enhanced photocatalytic activity [3].

Among photocatalysts, copper tungstate ($CuWO_4$) has been regarded as a promising semiconductor for photoanode. This can be attributed to the small band gap energy (2.2 − 2.4 eV) and chemical stability in a wide pH range. On the other hand, the photocatalytic performance of pure $CuWO_4$ is severely limited due to the low carrier mobility and the rapid recombination of photogenerated carriers. The construction of quality interfaces in double-heterojunction can improve carrier separation efficiency [4].

This study evaluated the photoelectrocatalytic efficiency of FTO|$CuWO_4$|$MnWO_4$|$BiVO_4$ double-heterojunction photoanode in removing Moxifloxacin (MOX) from aqueous media. $BiVO_4$ and $MnWO_4$ have a favorable band alignment to CuWO4, enabling the formation of a cascade double-heterojunction, which improves the separation of the e-/h+ pairs and increases photocatalytic performance.

Material and Methods

The copper tungstate ($CuWO_4$) and manganese tungstate ($MnWO_4$) oxides were synthesized via the microwave-assisted hydrothermal method, while the photoanodes were prepared using the spin-coating technique. Bismuth vanadate ($BiVO_4$) was electrodeposited utilizing fluorine-doped tin oxide (FTO) conductive glass.

Results and Discussion

Fig. 1 shows the XRD patterns of $CuWO_4$, $MnWO_4$, $BiVO_4$, and double-heterojunction. The diffraction peaks of $CuWO_4$ and $MnWO_4$ indicate triclinic (ICSD No. 16009) and monoclinic (ICSD nº. 230638) structures, respectively [5]. On the other hand, $BiVO_4$ also exhibits a monoclinic structure in accordance with the JCPDS Card No. 75–1867. All films indicated characteristic planes of FTO glass, which are highlighted with a red rhombus. The double-heterojunction is evidenced by the XRD patterns of $CuWO_4$, $MnWO_4$, and $BiVO_4$ phases in the 2θ position range from 20 to 35° (Fig. 1b) [6].

Fig. 2 illustrates the photoelectrochemical behavior of the films through linear sweep

voltammetry and Nyquist curves in borate buffer (pH = 9.0) as the supporting electrolyte.

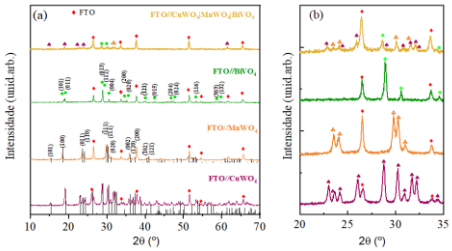

Figure 1. (a) XRD pattern of $CuWO_4$, $MnWO_4$, $BiVO_4$ and $CuWO_4|MnWO_4|BiVO_4$. (b) area zoom between 20° and 35°.

The photocurrent response of $FTO|CuWO_4|MnWO_4|BiVO_4$ heterojunction films shows intermediate values of photocurrent (55 μA/cm2 at 1.23 V vs. RHE) and resistance compared to pure oxides, as observed in Fig. 2b. The double heterojunction presented lower photocurrent response than pure $BiVO_4$. However, the synergy of the $CuWO_4|MnWO_4|BiVO_4$ may result in slower recombination kinetics and increased photoelectrocatalytic activity.

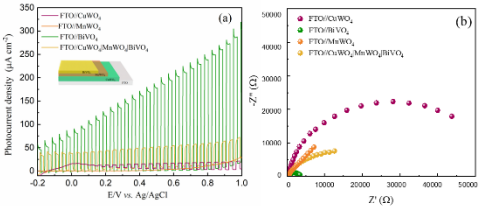

Figure 2. (a)Linear sweep voltammetry curves under chopped light illumination ($5mVs^{-1}$) and (b) Nyquist plots.

Fig. 3 shows MOX degradation rates (C_n/C_0) without and with the photocatalyst. Under photolysis conditions, only 2% of the antibiotic was removed. In the presence of the photocatalyst and bias in the electrochemically assisted system (EHP), the photoanodes achieved degradation rates of 22%, 24%, 28%, and 45% for the $MnWO_4$, $CuWO_4$, $BiVO_4$, and $FTO|CuWO_4|MnWO_4|BiVO_4$, respectively.

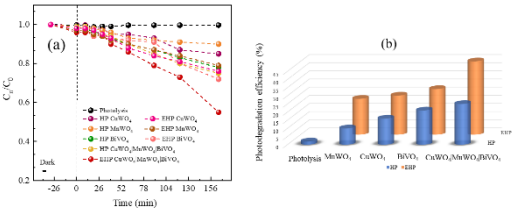

Figure 3. The degradation rate of materials (b) photodegradation efficiency.

Fig.3b compares the photodegradation efficiency of the materials in the photocatalytic and photoelectrocatalytic systems. The results show that the double-heterojunction promoted a better photoelectrocatalytic response. The synergy of the double-heterojunction due to energy band alignment induced slower recombination kinetics, leading to excellent photocatalytic performance in the degradation of antibiotics [7,8].

Conclusions

In this study, we evaluated the photoelectrocatalytic performance of the $FTO|CuWO_4|MnWO_4|BiVO_4$ double-heterojunction photoanode in the degradation of Moxifloxacin. The formation of the heterojunction was confirmed by X-ray diffraction. The photocurrent density and charge transfer resistance demonstrate a good response for the heterojunction compared to pure $CuWO_4$. The photoelectrocatalysis of the double-heterojunction was enhanced by the synergy of band alignment, achieving better results with 45% PEC efficiency. Kinetic studies of charge recombination time will be conducted to confirm the inhibition of the recombination process for the heterojunction.

Acknowledgments

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