Supporting Information

Facile Synthesis of a Micro–Nano-Structured $FeOOH/BiVO_4/WO_3$ Photoanode with Enhanced Photoelectrochemical Performance

Ruixin Li [a], Faqi Zhan [a,*], Guochang Wen [a], Bing Wang [a], Jiahao Qi [a], Yisi Liu [b], Chenchen Feng [a,*], Peiqing La [a]

[a] State Key Laboratory of Advanced Processing and Recycling of Non-Ferrous Metals, School of Materials Science and Engineering, Lanzhou University of Technology, Lanzhou 730050, China.

[b] Institute of Advanced Materials, Hubei Normal University, Huangshi, 415000, China.

[*]Corresponding author. Tel.: 0931-2976688; fax: 0931-2976688.

E-mail addresses: zhanfaqi@lut.edu.cn (F. Zhan), fengcc@lut.edu.cn (C. Feng)

1. Experimental section

1.1 Preparation of photoanodes films

WO_3 films: The WO_3 plate-like arrays film was prepared according to previous literature method of our group [27].

$BiVO_4/WO_3$ film: To prepare the precursor solution for electrodeposition, a BiOI film is initially deposited on hydrothermally grown WO_3, which is subsequently converted to a $BiVO_4$ film. Dissolve 3.32 g of KI in 50 mL of deionized water, stir well, and adjust the pH of the solution to 1.6-1.8 using HNO_3. Add 0.97 g of $Bi(NO_3)_3 \cdot 5H_2O$, stir for 20 min, and then add 20 mL of 0.23 M benzoquinone ethanol solution, stirring vigorously for 30 min to obtain the electrodeposition solution [28]. Electrodeposition is performed using a three-electrode system at a deposition temperature of 25 ℃, a deposition potential of -0.1 V vs. Ag/AgCl, and a deposition time of 5 min. After electrodeposition, rinse the photoanode with deionized water to remove any residual solution, and then air dry it for later use. Drop 100 μL of 0.2 M $VO(acac)_2$ DMSO solution onto the WO_3/BiOI film, and heat treat it at 450 °C for 2 h with a heating rate of 2 °C/min. After the reaction, allow it to cool naturally to room temperature, and then soak the sample in 1 M NaOH solution with gentle stirring for 30 min to remove excess V_2O_5. Air dry the sample naturally to obtain the $BiVO_4/WO_3$ photoanode.

FeOOH/$BiVO_4/WO_3$ film: FeOOH is loaded onto the surface of the $BiVO_4/WO_3$ composite photoanode, prepared by the aforementioned method, using the impregnation technique. The $BiVO_4/WO_3$ composite photoanode is soaked in 10 mL of 0.01 M $FeCl_3 \cdot 6H_2O$ aqueous solution for 15 min, then removed. Subsequently, 0.05

mL of 1 M NaOH aqueous solution and 10 mL of deionized water are added to the impregnation solution and stirred well. Continue soaking for an additional 45 min, then remove the photoanode, rinse it thoroughly with deionized water, and dry it overnight in an oven at 80 ℃ to obtain the $FeOOH/BiVO_4/WO_3$ composite photoanode. (Unless otherwise specified, $FeOOH/BiVO_4/WO_3$ is electrodeposited for 5 min with an impregnation concentration of 10 mM). The entire experimental synthesis process is shown in Fig. S1.

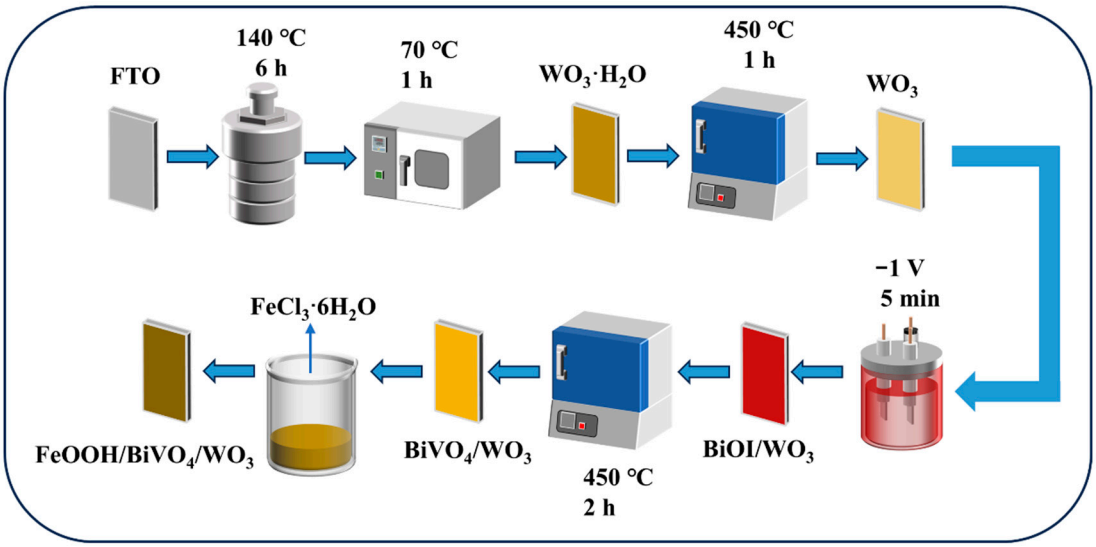


Figure S1. Experimental roadmap.

1.2 Characterization

The microscopic morphologies were examined by field-emission scanning electron microscope (FESEM, Nova Nano SEM 230) and high resolution transmission electron microscope (HRTEM, G2 F20). The surface chemical compositions and states of the films were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 XPS system). The crystal structures of all films were analysed by X-ray diffraction (XRD, D/Max2250, Rigaku Corporation, Japan) with Cu K_α (λ=0.15406 nm) radiation,

and the UV-vis spectra were recorded by a diffused reflectance spectrophotometer with an integrating sphere (DR-UVS, Shimadzu 2450 spectrophotometer).

1.3 Photoelectrochemical measurements

Photoelectrochemical (PEC) performances of the as-prepared films were investigated using an electrochemical analyzer (Zennium, Zahner) in a standard three-electrode system with the samples as the working electrode, Pt plate as the counter electrode and an Ag/AgCl electrode as the reference electrode. A solution of 0.5 M Na_2SO_4 (pH=7) was used as the electrolyte. Simulated 1 sun light irradiation condition (100 mW/cm^2) was provided by a 500 W Xenon lamp with AM 1.5 G filters. All photoelectrodes were illuminated from the backside. The scan rate of the photocurrent-potential curve (J-V) was 20 mV/s.

The Applied Bias Photon-to-Current Efficiency (ABPE) can be calculated from the experimentally measured photocurrent density curve, using the following formula (1):

$$ABPE(\%) = \frac{(J_{light} - J_{dark}) \times (1.23 - V_{RHE})}{P_{total}} \times 100\% \quad (1)$$

Where J_{light} is the photocurrent density, J_{dark} is the dark current density, VRHE is the applied bias versus the reversible hydrogen electrode, and Ptotal is the light intensity during testing (100 mW cm^{-2}).

When calculating charge injection efficiency and separation efficiency, the electrolyte used is 0.5 M Na_2SO_3. The charge injection efficiency (η_{bulk}) and charge separation efficiency ($\eta_{surface}$) can be calculated using the following formulas (2-3):

$$\eta_{bulk} = \frac{J_{sulfite}}{J_{abs}} \quad (2)$$

$$\eta_{surface} = \frac{J_{water}}{J_{sulfite}} \quad (3)$$

J_{abs}: Theoretical photocurrent density under complete photon absorption, $J_{sulfite}$: Sulfite ion oxidation current, J_{water}: Photocurrent density of the photoanode in aqueous solution.

The measured potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation (4) [39]:

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + E^{\Theta}_{Ag/AgCl} \quad (4)$$

Where E_{RHE} is the converted potential vs. RHE, $E^{\Theta}_{Ag/AgCl}$=0.1976 V at 25 ℃, and $E_{Ag/AgCl}$ is the experimentally measured potential against an Ag/AgCl reference. The photoelectrochemical measurements were carried out in 0.2 M Na_2SO_4 (pH=7) at room temperature; therefore,

$$E_{RHE} = E_{Ag/AgCl} + 0.6\text{V} \quad (5)$$