Supplementary Information

Promoting Effect of Y doped and FeOOH Loaded for Efficient Photoelectrochemical Activity on the BiVO₄ Electrodes

Yuwei Guo⁵, Wei Han⁵, Kaichen Zhao⁵, Shaojun Hao⁵, Shenggang Shi⁵, and Yongping Ding⁵,⁎

⁵ Department of Chemistry, Baotou Teachers' College, Baotou 014030, P. R. China
⁶ Institute of Rare Earth Applications, Department of Chemistry, Baotou Teachers' College, Baotou 014030, P. R. China

⁎ Corresponding author. E-mail address: guoding821227@126.com (Yongping Ding)
Experimental Section

Synthesis of BiVO$_4$ and Y-doped BiVO$_4$ electrodes

The BiVO$_4$ film was prepared using a previously reported method $^{[1-2]}$. In a typical synthesis, 0.04 M Bi(NO$_3$)$_3$·5H$_2$O was dissolved into 50 mL HNO$_3$ aqueous solution (pH = 1.7). Then, 0.4 M KI was added to this solution with stirring until completely dissolution. 20 mL of ethanol containing 0.23 M p-benzoquinone was mixed to the above solution with another 15 min stirring. The electrodeposition of BiOI precursor was carried out potentiostatically at $-0.1$ V vs. Ag/AgCl for 180 s at room temperature, using a typical three-electrode system, where a FTO as the working electrode (WE), a saturated Ag/AgCl as the reference electrode (RE), and a Pt net as the counter electrode (CE). After electrodeposition, the BiOI electrodes were washed thoroughly with DI water and dried at room temperature. In order to transform BiOI to BiVO$_4$, ~200 μL of DMSO solution containing 0.2 M VO(acac)$_2$ was dropped onto the BiOI electrode (1 cm × 1 cm) surface and then annealed at 450°C for 2 h (heating rate = 2°C min$^{-1}$). The redundant V$_2$O$_5$ on the BiVO$_4$ surface was removed by immersing in 1 M NaOH solution for 30 min. Finally, the BiVO$_4$ electrodes were washed with DI water and dried at room temperature. The Y-doped was prepared by adding a certain amount Yttrium Acetylacetonate into DMSO solution containing 0.2 M VO(acac)$_2$.

Preparation of FeOOH/Y-BiVO$_4$ electrodes

FeOOH/Y-BiVO$_4$ electrodes were synthesized by a facile chemical bath deposition method. The reaction precursor was obtained by dissolving FeCl$_3$ in 50 mL of distilled water. Before impregnation, the pH values of solution were adjusted to 3.42 by adding 1 M NaOH or HCl. Then, the obtained Y-doped BiVO$_4$ electrodes were put in FeCl$_3$ solution for 24 h at room temperature. Then the FeOOH/Y-doped BiVO$_4$ was washed with DI water and dried at room temperature.
Characterizations

The X-ray photoelectron spectroscopy (XPS) analyses were performed on a Thermo VG ESCALAB 250 X-ray photoelectron spectrometer using Al Kα radiation at a pressure of about 2×10⁻⁹ Pa. UV-visible absorptance spectra were measured by a Hitachi U-3010 UV-Vis spectrometer equipped with an integrating sphere assembly and 100% commercial BaSO₄ as the reflectance sample. SEM images were obtained by field emission scanning electron microscopy (Hitachi S-4800) combined with energy dispersive X-ray (EDX) spectroscopy. PL spectra were measured at room temperature by using a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150W Xe lamp as an excitation source at room temperature.

Photoelectrochemical measurements

Photoelectrochemical measurements were performed at room temperature using an electrochemical workstation (CHI660E, CH Instruments, Inc.) in a three-electrode configuration cell. The light source was under AM 1.5 illumination (PLS-SXE300, Beijing Perfectlight), and a 0.2 M Sodium sulphate solution (Na₂SO₄, pH=7) was used as the electrolyte. The as-prepared BiVO₄ electrode on the Fluoride–tin oxide (FTO) glass slice with an area of 1 cm², a saturated Ag/AgCl, and a Pt were configured as working, reference and counter electrodes, respectively. The photocurrents were measured by linear scanning voltammetry (LSV) with a scanning rate of 25 mV s⁻¹ from −0.6 to 0.8 V Ag/AgCl both in dark and under illumination. The conversion between potentials vs. Ag/AgCl and vs. RHE is performed using the equation below.

\[
E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl vs. NHE}} + 0.0591 \times pH
\]  

Where \(E_{\text{RHE}}\) refers to the converted potential vs. RHE. The value of \(E_{\text{Ag/AgCl}}\) is 0.197 V vs. RHE at room temperature (25 °C) and \(E_{\text{Ag/AgCl vs. NHE}}\) is the obtained potential vs. Ag/AgCl.

The applied bias photon-tocurrent efficiency (ABPE) of BiVO₄ electrode were calculated according to \(J-V\) curve:

\[
\text{ABPE (\%)} = \frac{{J (mA \ cm^{-2}) \times (1.23 - V_{\text{bias}})}}{{P_{\text{light}}(mW \ cm^{-2})}}
\]

Where \(J\) is the photocurrent density, \(V_{\text{bias}}\) is the applied external potential vs. RHE and
$P_{\text{light}}$ is the power density of the illumination (100 mW cm$^{-2}$).

PEC measurements with NaSO$_3$ as a hole scavenger were recorded in 0.2 M NaSO$_4$ with the addition of 0.5 mol L$^{-1}$ NaSO$_3$.

The charge separation efficiency ($\eta_{\text{separation}}$) was calculated according to eq 3:

$$\eta_{\text{separation}} = \frac{J_{\text{NaSO3}}}{J_{\text{abs}}}$$

Where $J_{\text{abs}}$ is the theoretical maximum water oxidation photocurrent, which is up to 7.5 mA/cm$^2$[3].

Electrochemical impedance spectroscopy (EIS) was performed on the electrochemical workstation mentioned above at an open circuit voltage of 1.23 V vs. RHE under illumination with 0.1 V amplitude of perturbation and a frequency between 100 kHz and 0.1 Hz. Mott–Schottky plots were evaluated at a DC potential range from −0.6 to −0.1 V vs. Ag/AgCl at a frequency of 1 kHz at room temperature in the dark.

**Photoelectrochemical degradation experiments**

Degradation experiments were performed using tetracycline hydrochloride (TCH) as a model pharmaceutical contaminant. The electrode was immersed into an aqueous solution of 0.5 mol/L Na$_2$SO$_4$ which contained TCH (100 mL, 0.2 mg/L). The system was protected from light for 30 min to reach adsorption equilibrium and uniform dispersion.

The Electrochemical degradation and photoelectrocatalytic degradation experiments were performed on an electrochemical workstation and amperometric i-t curve measurement was used during the degradation process. The thin film electrode was used as the working electrode and a fixed bias potential of 0.7 V was applied on the working electrode, while a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference electrode. At a certain intervals (30 min), the concentration of TCH was determined by measuring the absorbance in step time using the UV–vis. Antibiotic degradation efficiency ($D_{\text{TCH}}$) was determined according to eq 4:

$$D_{\text{TCH}} = \frac{C_0 - C}{C_0}$$

where $C_0$ and $C$ are the initial and final concentrations of the contaminant,
respectively.

**Supplementary Figures and Tables**

Figure S1. (a) XRD patterns of BiVO₄ with different amounts of Y³⁺ and (b) details of XRD patterns in the range of 2θ from 28.5° to 31°.

Figure S2. XPS spectrum of are Y 3d region of 2% Y³⁺ doped BiVO₄ thin film.

Figure S3. TEM images of BiVO₄ and FeOOH/1% Y-BiVO₄
Figure S4. Elemental compositional spectrum of FeOOH/Y-BiVO₄

Figure S5. LSV curves with different amounts of the Y³⁺ ion.

Figure S6. LSV curves measured in 0.5 M Na₂SO₄ under dark condition.
Figure S7. Charge separation efficiency of BiVO₄, 1%Y-BiVO₄ and FeOOH/1%Y-BiVO₄ photoelectrode.

Figure S8. Photostability of FeOOH/Y-BiVO₄ photoanode for degradation of TCH

Figure S9. LSV curves measured of BiVO₄, FeOOH/BiVO₄ and FeOOH/Y-BiVO₄ electrode.
Table S1. Photocurrent density (at 1.23 V vs. RHE) of BiVO$_4$, Y-BiVO$_4$, FeOOH/BiVO$_4$ and FeOOH/Y-BiVO$_4$ photoanodes (data from Figure 4a and Figure S8).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Parameters</th>
<th>Photocurrent density (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO$_4$</td>
<td></td>
<td>0.93</td>
</tr>
<tr>
<td>1%Y-BiVO$_4$</td>
<td></td>
<td>2.80</td>
</tr>
<tr>
<td>FeOOH/BiVO$_4$</td>
<td></td>
<td>2.51</td>
</tr>
<tr>
<td>FeOOH/1%Y-BiVO$_4$</td>
<td></td>
<td>3.84</td>
</tr>
</tbody>
</table>

Table S2. Comparison table of different modified BiVO$_4$ applied to PEC activities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocurrent density at 1.23 $V_{RHE}$ (mA/cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb-BiVO$_4$</td>
<td>2.01</td>
<td>[4]</td>
</tr>
<tr>
<td>3AMo:BV</td>
<td>1.91</td>
<td>[5]</td>
</tr>
<tr>
<td>VMo-BiVO$_4$</td>
<td>3.18</td>
<td>[6]</td>
</tr>
<tr>
<td>5-Ni-BiVO$_4$</td>
<td>2.39</td>
<td>[7]</td>
</tr>
<tr>
<td>α-FeOOH(P-II)/BiVO$_4$</td>
<td>2.64</td>
<td>[8]</td>
</tr>
<tr>
<td>F-BiVO$_4$@NiFe-LDH</td>
<td>2.67</td>
<td>[9]</td>
</tr>
<tr>
<td>MIL-101(Fe)/Mo:BiVO$_4$</td>
<td>4.01</td>
<td>[3]</td>
</tr>
<tr>
<td>1%Y-BiVO$_4$</td>
<td>2.80</td>
<td>This work</td>
</tr>
<tr>
<td>FeOOH/1%Y-BiVO$_4$</td>
<td>3.84</td>
<td>This work</td>
</tr>
</tbody>
</table>


9. Liu, J.; Li, J.; Li, Y.; Guo, J.; Xu, S.-M.; Zhang, R.; Shao, M.,