Supporting Information

Enhanced Photoelectrochemical Oxidation of Glycerol to Dihydroxyacetone Coupled with Hydrogen Generation via Acceerative Middle Hydroxyl Dehydrogenation over a Bi⁰/Bi³⁺ Interface of Cascade Heterostructure

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Experimental Section

Chemicals and materials

Ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$•xH$_2$O, AR, ≥99.5%), bismuth nitrate pentahydrate (Bi(NO$_3$)$_3$•5H$_2$O, AR, ≥99.0%), ammonium metavanadate (NH$_4$VO$_3$, AR, ≥99.5%) were purchased from Macklin Reagent Co., ltd. Sulfuric acid (H$_2$SO$_4$, AR, 98%), hydrogen nitrate (HNO$_3$, AR, 65-68%), hydrochloric acid (HCl, AR, 37%) sodium sulfate (Na$_2$SO$_4$, AR, ≥99.5%), oxalic acid (C$_2$H$_2$O$_4$, AR, ≥99.5%) citric acid (C$_6$H$_8$O$_7$, AR, ≥99.5%), and hydrazine hydrate were obtained from Sinopharm Chemical Reagent Co., Ltd. All the reagents were used without further purification.

PEC performance for photoanodes

The PEC performance was performed on an electrochemical workstation (CHI760E), the electrolyte was 0.5 M Na$_2$SO$_4$ mixed with 0.1 M glycerol electrolyte with pH adjusted to 2 by H$_2$SO$_4$, the light source was a 300 W Xe lamp (CEL-PF300-T8) with an AM 1.5G filter, and the standard three-electrode configuration consisted of a working electrode (as-prepared photoanodes), a counter electrode (platinum foil) and a reference electrode (Ag/AgCl electrode).

Electrochemical impedance spectroscopy (EIS) was employed to determine the charge carrier mobility. EIS spectra were monitored with 5 mV AC voltage amplitude, where the frequency range was set to be 0.1-10$^6$Hz. The transient photocurrent response was performed without bias voltage under irradiation of a xenon lamp with an interval of 30 s for light on and off. Mott-Schottky (MS) curves were collected at the amplitude of 5 mV scanning from -0.5 V to 0.5 V (vs. Ag/AgCl) with a 1000 Hz frequency under dark condition.

The reversible hydrogen electrode (RHE) potentials were converted from the measured potentials according to the followed equation:

\[ E_{RHE} = E_{Ag/AgCl} + E_{Ag/AgCl vs. NHE} + 0.059 \times pH \]  

where \( E_{Ag/AgCl vs. NHE} \) is 0.197 V at 25 °C.

Selectivity of DHA was calculated by:

\[ \text{Selectivity (DHA)} = \frac{c_{DHA}}{(c_{DHA} + c_{GLD} + c_{GA} + c_{FA})} \times 100\% \]
Faradaic efficiency was calculated by:

\[
\text{Faradaic efficiency} = \frac{e_{\text{products}} \times n_{\text{products}} \times N}{Q/n} \times 100\%
\]  

(3)

where \(e_{\text{products}}\) is the number of holes required to oxidize glycerol molecule to products, including DHA \(e = 2\), GLD \(e = 2\), GA \(e = 2\), FA \(e = 8\), \(n_{\text{products}}\) is the productivity of products, \(N\) is Avogadro’s constant \((N = 6.02 \times 10^{23})\), \(Q\) is the quantity of electric charge, and \(n\) is the elementary charge \((e = 1.602 \times 10^{-19}\text{C})\).

Fig. S1. (a) SEM image of BiVO\(_4\) (top-view). (b) SEM image of BiVO\(_4\) (cross-view). (c) SEM image of WO\(_3\)/BiVO\(_4\) (top-view). (d) SEM image of WO\(_3\)/BiVO\(_4\) (cross-view).
Fig. S2. (a) Top-view SEM image of WO$_3$/BiVO$_4$-30. (b) Top-view SEM image of WO$_3$/BiVO$_4$-40. (c) Top-view SEM image of WO$_3$/BiVO$_4$/Bi-0.15%. (d) Top-view SEM image of WO$_3$/BiVO$_4$/Bi-0.20%.

Fig. S3. XRD patterns of WO$_3$/BiVO$_4$/Bi and WO$_3$/BiVO$_4$/Bi-0.20%.
Fig. S4. LSV curves of WO$_3$/BiVO$_4$-10, WO$_3$/BiVO$_4$-20 (WO$_3$/BiVO$_4$), WO$_3$/BiVO$_4$-30 and WO$_3$/BiVO$_4$-40 photoanodes.

Fig. S5. LSV curves of WO$_3$/BiVO$_4$/Bi-0.05%, WO$_3$/BiVO$_4$/Bi-0.10%, WO$_3$/BiVO$_4$/Bi-0.15% and WO$_3$/BiVO$_4$/Bi-0.20% photoanodes.
Fig. S6. High performance liquid chromatography (HPLC, UV detector = 210 nm) spectra of the PEC glycerol oxidation products over WO$_3$/BiVO$_4$/Bi photoanode for 1 h.

Fig. S7. DHA selectivity and faradaic efficiency in 0.5 M Na$_2$SO$_4$ (pH = 2) with 0.1 M glycerol over WO$_3$, BiVO$_4$, WO$_3$/BiVO$_4$ and WO$_3$/BiVO$_4$/Bi photoanodes at 1.2 V vs. RHE under AM 1.5G illumination (100 mW cm$^{-2}$).
Fig. S8. J-t stability tests of WO₃ and WO₃/BiVO₄/Bi photoanodes measured at 1.2 V vs. RHE for 10 h.

Fig. S9. H₂ productivity in the WO₃/BiVO₄/Bi-Pt tandem cell measured at 1.2 V vs. RHE with and without glycerol.

**Table S1.** Bi element contents of electrolyte after reaction for 1 h, 5 h and 10 h by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrolyte (1 h)</td>
<td>&lt;0.0001%</td>
</tr>
<tr>
<td>electrolyte (5 h)</td>
<td>&lt;0.0001%</td>
</tr>
<tr>
<td>electrolyte (10 h)</td>
<td>&lt;0.0001%</td>
</tr>
</tbody>
</table>
Fig. S10. Productivity of products in the WO$_3$/BiVO$_4$/Bi-Pt tandem cell measured at 1.2 V vs. RHE for 10 h.

Fig. S11. Photographs of the the large size (5 × 4 cm$^2$) photoanodes. (a, b) WO$_3$ photoanode (c, d) WO$_3$/BiVO$_4$ photoanode (e, f) WO$_3$/BiVO$_4$/Bi photoanode.
Fig. S12. (a) Photograph of the large size WO$_3$/BiVO$_4$/Bi photoanodes (divided into 6 areas). (b) SEM and corresponding element mapping images in the above six areas.
Fig. S13. Photoelectrocatalytic production rate of oxidation products on large-sized as-prepared photoanodes.

Fig. S14. Schematic energy band diagrams of WO$_3$, BiVO$_4$ and BiVO$_4$/Bi before contact. $E_g$, band gap; $E_F$, Fermi level; $E_C$, conduction band position; $E_V$, valence band position.