Electronic Supplementary Information

Ultrafast fabrication of highly active BiVO₄ photoanodes by hybrid microwave annealing for unbiased solar water splitting

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Supplementary Calculation

Surface/bulk charge separation efficiencies ($\eta_{surf}$)

For quantitative assessment of charge separation efficiency, photocurrent comparison between water oxidation/hole scavenger (SO$_3^{2-}$) was used.

Water oxidation: $2\text{H}_2\text{O} + 4h^+ \rightarrow 4\text{H}^+ + \text{O}_2$, $E^\circ = 1.23$ V RHE

Sulfite oxidation: $\text{SO}_3^{2-} + h^+ \rightarrow \text{SO}_3^-$, $E^\circ = 0.73$ V RHE

Light absorption by a photocatalyst generates absorbed photocurrent ($J_{abs}$) that undergoes two major losses of bulk and surface recombination. Hence the measured photocurrent during water oxidation ($J_{H2O}$) is expressed by:

$$J_{H2O} = J_{abs} \times \eta_{bulk} \times \eta_{surf}$$

where $\eta$ denotes the charge separation yield in the bulk of semiconductor ($\eta_{bulk}$) or on the surface ($\eta_{surf}$). Since the surface charge separation yield of SO$_3^{2-}$ is almost 100% ($\eta_{surf} = 1$), as discussed above, the photocurrent from its oxidation can be expressed as follows:

$$J_{SO3} = J_{abs} \times \eta_{bulk}$$

The $J_{abs}$ value of BiVO$_4$/WO$_3$ was estimated to be $\sim 5$ mA/cm$^2$ from calculation from AM 1.5G radiation region and UV-vis absorbance spectrum shown below. $\eta_{bulk}$, $\eta_{surf}$ can be derived in photocurrent comparison form.

For calculation, correlation between absorbance and radiation proposed by Choi’s group$^1$ was used as below.

$$P_d = P_0 \times 10^{-A}$$

$P_0$ (unit : mWcm$^{-2}$nm$^{-1}$) is provided power by solar simulator (in this case, AM 1.5G), $P_{abs}$ is power of light actually absorbed by photoanode and $P_d$ is power of light not absorbed to photoanode but dissipated (reflection and penetration). $A$ is absorbance of photoanode and LHE (light harvesting efficiency) is defined as $1 - 10^{-A}$. So light which is not absorbed at photoanode will be $10^{-A}$. Integrated $P_{abs}(\lambda)$ (mWcm$^{-2}$nm$^{-1}$) along with wavelength $\lambda$ gives total power (unit of mWcm$^{-2}$) which is power of light absorbed by photoanode (maximum power of photoanode). Below formula shows such relationship photon absorption ($J_{abs}$).

$$J_{abs}(\frac{mA}{cm^2}) = \int \frac{\lambda}{1240} P_{abs}(\lambda) d\lambda \left( \frac{mW}{cm^2} \right)$$
Supplementary Table

Table S1: Surface elemental composition analyzed by XPS spectra.

<table>
<thead>
<tr>
<th>Photoanode/annealing system (time)</th>
<th>C (%)</th>
<th>O (%)</th>
<th>Bi (%)</th>
<th>V (%)</th>
<th>Mo (%)</th>
<th>W (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BiVO₄</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA (300 min)</td>
<td>42.1</td>
<td>37.8</td>
<td>13.6</td>
<td>6.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMA (6 min)</td>
<td>45.8</td>
<td>33.6</td>
<td>15.1</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1% Mo:BiVO₄</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA (300 min)</td>
<td>34.0</td>
<td>46.4</td>
<td>12.9</td>
<td>6.3</td>
<td>0.4</td>
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<tr>
<td>HMA (6 min)</td>
<td>45.9</td>
<td>35.0</td>
<td>13.9</td>
<td>4.9</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td><strong>BiVO₄/WO₃</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA (300 min)</td>
<td>43.0</td>
<td>35.0</td>
<td>11.9</td>
<td>5.8</td>
<td>0.3</td>
<td></td>
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<tr>
<td>HMA (6 min)</td>
<td>42.1</td>
<td>37.0</td>
<td>13.4</td>
<td>5.6</td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. (a) XRD spectra of BiVO$_4$/WO$_3$ fabricated by FA with different lengths of annealing time. (b) Comparison of BiVO$_4$/WO$_3$ films made by FA (300 min) and HMA (6 min).
Figure S2. (a) Photographs of BiVO$_4$ films prepared with two annealing methods (FA and HMA). Optical properties (LHE=1-10$^{-4}$absorbance, transmittance) of BiVO$_4$ (b), 1% Mo:BiVO$_4$ (c) and BiVO$_4$/WO$_3$ (d). Light harvesting efficiency (LHE) of samples corresponded to $J_{abs} = \sim 3.6$ mA/cm$^2$ (BiVO$_4$, 1% Mo:BiVO$_4$) and $\sim 4.5$ mA/cm$^2$ (BiVO$_4$/WO$_3$).
Figure S3. (a) Photographs of BiVO₄ films prepared by HMA with different susceptors (graphite, no susceptor and n-type Si wafer). (b) XRD patterns of the films. The letter ‘T’ stands for pattern of FTO (SnO₂). Reference pattern for scheelite monoclinic BiVO₄, ICSD 01-075-1866 is also shown.
Figures S4. Scanning electron micrographs of (a, b) BiVO$_4$, (c, d) 1% Mo: BiVO$_4$ and (e, f) BiVO$_4$/WO$_3$ with different annealing methods. (a,c,e) FA, (b,d,f) HMA. Annealing times are set for 300 min (FA) and 6 min (HMA). Scale bar: 5.0 μm.
**Figure S5.** Particle size count from SEM image (count area: 500 nm X 1000 nm) for (a) BiVO₄, (b) 1% Mo:BiVO₄ and (c) BiVO₄/WO₃ annealed with FA and HMA. Overall count number of HMA samples (~35) is lower than furnace (~45) owing to larger portion of pores on HMA samples on same count area size. Average feature size was decided via using top 2nd, 3rd highest count. Calculated result was marked at Table 1.
Figure S6. Cross section SEM image of (a, b) BiVO₄, (c, d) 1% Mo:BiVO₄ and (e, f) BiVO₄/WO₃ film with different annealing system (furnace and HMA).
Figure S7. X-ray photoelectron spectra (XPS) of (a) C 1s (284.5 eV for C-C, 288.0 eV for carbonate or hydrocarbon), (b) O 1s (529.8 eV for metal oxide, 531.3 eV for –OH), (c) Bi 4f (159.1 eV for Bi$^{3+}$ as metal oxide), (d) V 2p (515.9 eV for V$^{5+}$ as metal oxide), (e) Mo 3d and (f) W 4f (35.5 eV for W$^{6+}$ for WO$_3$). Samples used for analysis are BiVO$_x$, 1% Mo:BiVO$_4$ and BiVO$_4$/WO$_3$ made with FA (300 min) and HMA (6 min). Information of binding energy was referred from $^2$-$^5$.
**Figure S8.** Nyquist plots in 0.5 M KPi buffer under illumination of 1 sun (100 mW/cm²) with applied bias of 0.63 V vs. Ag/AgCl.

**Figure S9.** IV curves of (a) MAPbI₃ perovskite solar cell and (b) 2p (parallel alignment) c-Si solar cell with/without BiVO₄/WO₃ (HMA, 6min) filter.
**Figure S10.** IV curves of NiOOH/FeOOH/BiVO$_4$/WO$_3$ (HMA, 6min) photoanode – 2p c-Si tandem cell measured in (a) two and (b) three electrode configurations. Measurements were conducted under AM 1.5G (100 mW/cm$^2$) illumination in 0.5 M KPi (pH 7.0), the scan rate of 20 mV/cm$^2$ (backward) and front side illumination. Active area was 0.42 cm$^2$. Electrolyte was purged with Ar gas.

**SUPPLEMENTARY REFERENCES**