ESI:

Facile one-pot solvothermal preparation of Mo-doped Bi$_2$WO$_6$ biscuit-like microstructures for visible-light-driven photocatalytic water oxidation

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The quantum efficiency (QE) for O\textsubscript{2} production under visible-light illumination was determined using the following equation:

\[
\text{QE}[\%] = \frac{\text{the number of evolved } O_2 \text{ molecules} \times 4}{\text{the number of incident photons}} \times 100\%
\]

The quantum efficiency QE could also be evaluated by the equation:

\[
\text{QE} = 4n_{O_2}/n_p \times 100\%
\]

The mole of photons absorbed by the photosensitizer \((n_p)\) was determined by the following equation:

\[
n_p = \frac{Pt\lambda}{N_Ahc}
\]

Where \(n_p\) represents moles of photons absorbed by the photosensitizer, \(P(W)\) is the absorbed power of the light, \(t\) is the irradiation time (21600 s), \(\lambda\) is the irradiation wavelength number (420, 450 and 500), \(N_A\) is the Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\), \(h\) is the Planck constant \((6.63 \times 10^{-34} \text{ J} \cdot \text{s})\) and \(c\) is the speed of the light \((3 \times 10^8 \text{ m} \cdot \text{s}^{-1})\).

The measured light power is 151.9, 174.7 and 212.5mW at 420, 450 and 500nm, respectively. The evolved O\textsubscript{2} \((n_{O_2})\) were determined to be \(8.83 \times 10^{-5} \text{ mol}\) and \(3.66 \times 10^{-5} \text{ mol}\) for Bi\textsubscript{2}Mo\textsubscript{0.21}W\textsubscript{0.79}O\textsubscript{6} and Bi\textsubscript{2}WO\textsubscript{6} by GC after 6h light irradiation, respectively. For Bi\textsubscript{2}Mo\textsubscript{0.21}W\textsubscript{0.79}O\textsubscript{6} sample, the apparent QE values were 3.1 %, 2.5%, and 1.8% at 420, 450 and 500 nm, respectively, representing that the value decreased gradually as the incident light wavelength increased. However, the apparent QE at 420 nm of pristine Bi\textsubscript{2}WO\textsubscript{6} was measured to be 1.2%, indicating almost 3 fold enhancement after Mo doping.
Fig. S1 XRD patterns of as-prepared Bi$_2$WO$_6$, Bi$_2$MoO$_6$ and Mo-doped Bi$_2$WO$_6$ samples.
Table S1 Lattice parameters as a function of Mo$^{6+}$ dopant concentration.

<table>
<thead>
<tr>
<th>photocatalysts</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B$_2$WO$_6$</td>
<td>5.610</td>
<td>5.571</td>
<td>16.819</td>
</tr>
<tr>
<td>Bi$<em>2$Mo$</em>{0.25}$W$_{0.75}$O$_6$</td>
<td>5.630</td>
<td>5.588</td>
<td>16.765</td>
</tr>
<tr>
<td>Bi$<em>2$Mo$</em>{0.5}$W$_{0.5}$O$_6$</td>
<td>5.654</td>
<td>5.608</td>
<td>16.754</td>
</tr>
<tr>
<td>Bi$<em>2$Mo$</em>{0.75}$W$_{0.25}$O$_6$</td>
<td>5.650</td>
<td>5.628</td>
<td>16.615</td>
</tr>
</tbody>
</table>

Fig S2 α, β and γ angles as a function of Mo$^{6+}$ dopant concentration.
Fig. S3 XPS spectra of Bi\textsubscript{2}Mo\textsubscript{0.21}W\textsubscript{0.79}O\textsubscript{6} PBMs: (a) Survey spectrum, (b) O 1s, (c) Bi 4f, (d) W 4f and (e) Mo 3d.
**Fig. S4** SEM images of the as-prepared (a) \( \text{Bi}_2\text{WO}_6 \), (b) \( \text{Bi}_2\text{MoO}_6 \) nanostructures, (c, d) \( \text{Bi}_2\text{Mo}_{0.35}\text{W}_{0.65}\text{O}_6 \), (e, f) \( \text{Bi}_2\text{Mo}_{0.65}\text{W}_{0.35}\text{O}_6 \).
Fig. S5 SEM images of the products obtained (a) room temperature under continuous stirring after 20 min, (b) 180 °C for 1.5 h, (c) 180 °C for 5 h and (d) 180 °C for 10 h.
Fig. S6 SEM images of the products obtained at 180°C (a) using water as solvent, (b) using ethylene glycol as solvent.
Fig. S7 \( \text{N}_2 \) adsorption–desorption isotherm and pore-size distribution curve of the as-obtained \( \text{Bi}_{2}\text{Mo}_{0.21}\text{W}_{0.79}\text{O}_6 \) PBMs.
Fig. S8 Partial density of states (PDOS) of (a) Bi$_2$WO$_4$, (b) Bi$_2$Mo$_{0.25}$W$_{0.75}$O$_6$, (c) Bi$_2$Mo$_{0.5}$W$_{0.5}$O$_6$, and (d) Bi$_2$Mo$_{0.75}$W$_{0.25}$O$_6$ samples.
To rule out the heat driven O\textsubscript{2} evolution, a series of experiments were carried out at 40°C and 60°C by a precision bath circulator (Tianheng, THD-05) without visible-light irradiation, respectively. In a typical reaction, 100mg of Bi\textsubscript{2}Mo\textsubscript{0.21}W\textsubscript{0.79}O\textsubscript{6} PBM\textsubscript{s} in 100 mL aqueous solution containing 0.1 M NaOH, 0.02 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} were added to the reactor under magnetic vigorous stirring to ensure the mixture suspense. The suspension was purged with argon for at least 90 min to drive off the air inside. Analysis of the evolved O\textsubscript{2} was performed using an online gas chromatograph (Agilent Technologies GC-7890B, TCD, Ar carrier gas). As it can be seen in Fig. S10 (see ESI†), no O\textsubscript{2} was produced after 6 h at 40°C or 60°C. This result demonstrates that the O\textsubscript{2} can only be generated under visible-light irradiation. In our experiment, the photocatalytic water oxidation was carried out at 20°C±2 C by a continuous water circulator. The relevant modifications were mentioned in the manuscript.

![Fig. S9](image)

**Fig. S9.** O\textsubscript{2} evolution reference tests with Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/Co\textsubscript{3}O\textsubscript{4}-Bi\textsubscript{2}Mo\textsubscript{0.21}W\textsubscript{0.79}O\textsubscript{6} PBM\textsubscript{s} at 40°C after (a) 1h, (b) 3h, (c) 6h and at 60°C after (d) 1h, (e) 3h and (f) 6h.
Fig. S10 Repeat photocatalytic oxygen evolution and standard deviations from water splitting over Bi$_2$WO$_6$, Bi$_2$Mo$_{0.21}$W$_{0.79}$O$_6$, Bi$_2$Mo$_{0.35}$W$_{0.65}$O$_6$, Bi$_2$Mo$_{0.65}$W$_{0.35}$O$_6$ and Bi$_2$MoO$_6$ samples (and samples with 5%wt deposited Co$_3$O$_4$) under visible-light irradiation. Reaction conditions: 0.1 g photocatalyst, 100 mL 0.1 M NaOH and 0.02 M Na$_2$S$_2$O$_8$ aqueous solution.
<table>
<thead>
<tr>
<th>Photocatalysts</th>
<th>$O_2$ evolution, rate(μmol.g$^{-1}$)</th>
<th>Evolved $O_2$, 6h (μmol.h$^{-1}$,g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Bi}_2\text{WO}_6$</td>
<td>225.6</td>
<td>37.6</td>
</tr>
<tr>
<td>$\text{Co}_3\text{O}_2$-$\text{Bi}_2\text{WO}_6$</td>
<td>366.47</td>
<td>61.07</td>
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<tr>
<td>$\text{Bi}<em>2\text{Mo}</em>{0.32}$-$\text{W}_{0.68}$O$_6$</td>
<td>439.88</td>
<td>73.31</td>
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<tr>
<td>$\text{Co}_3\text{O}<em>2$-$\text{Bi}<em>2\text{Mo}</em>{0.32}$-$\text{W}</em>{0.68}$O$_6$</td>
<td>863.16</td>
<td>147.2</td>
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<tr>
<td>$\text{Co}_3\text{O}<em>2$-$\text{Bi}<em>2\text{Mo}</em>{0.36}$-$\text{W}</em>{0.64}$O$_6$</td>
<td>719.9</td>
<td>119.98</td>
</tr>
<tr>
<td>$\text{Co}_3\text{O}<em>2$-$\text{Bi}<em>2\text{Mo}</em>{0.66}$-$\text{W}</em>{0.34}$O$_6$</td>
<td>527.46</td>
<td>87.91</td>
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<tr>
<td>$\text{Bi}_2\text{MoO}_6$</td>
<td>223.05</td>
<td>37.17</td>
</tr>
<tr>
<td>$\text{Co}_3\text{O}_2$-$\text{Bi}_2\text{MoO}_6$</td>
<td>376.67</td>
<td>62.77</td>
</tr>
</tbody>
</table>

Table S2: Photocatalytic oxygen evolution rates for all the samples
**Fig. S11** Schematic diagram showing possible water oxidation reaction catalyzed by the Co$_3$O$_y$/Bi$_2$Mo$_{0.21}$W$_{0.79}$O$_6$ PBM samples under UV-visible light irradiation ($\lambda > 420$ nm).
Fig. S12  electrochemical impedance spectra of the as-prepared Bi$_2$WO$_6$, Bi$_2$MoO$_6$ and Bi$_2$Mo$_{0.21}$W$_{0.79}$O$_6$ PBMs.
Fig. S13 Photocurrent response of the different samples under visible-light illumination.