Supporting Information

Highly efficient photocatalysts constructed by rational assembly of dual-cocatalysts separately on different facets of BiVO₄

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**Samples preparation.** BiVO$_4$ was prepared by hydro-thermal method as previously reported.$^1$ Typically, the precursors NH$_4$VO$_3$ (36 mmol) and Bi(NO$_3$)$_3$·5H$_2$O (36 mmol) were dissolved in 300 mL of 2.0 M nitric acid solutions, and the pH value of the solution was then adjusted to 2.0 with ammonia solution under stirring. After aging for 2 hours, the orange precipitate at the bottom of the beaker was transferred to a 100 mL Teflon-lined stainless steel autoclave (70 % capacity) and hydrothermal treated at 200 °C for 24 h. After the autoclave was cooled to room temperature, a vivid yellow powder was separated by filtration, washed with de-ionized water for more than 3 times, and then dried at 60 °C for overnight.

The photo-deposition of the Co$_3$O$_4$ was achieved with Co (NO$_3$)$_2$ as the precursor, and NaIO$_3$ was employed as the electron acceptors. Typically, 0.5 g BiVO$_4$ powder was suspended in 100 ml NaIO$_3$ solutions (0.01 M), then 1.0 ml Co (NO$_3$)$_2$ solution (0.50 g/L) was added and the suspension was then irradiated by a 300 W Xe lamp ($\lambda \geq 420$ nm) under continuous stirring. After 3 h photo-deposition, the suspension was filtered, washed with de-ionized water for more than 3 times, and finally dried at 60 °C for overnight. The as-prepared samples are denoted as Co$_3$O$_4$/BiVO$_4$.

Pt(P.D.)/Co$_3$O$_4$(P.D.)/BiVO$_4$: 0.30 g as-prepared Co$_3$O$_4$/BiVO$_4$ was suspended in 100 ml H$_2$O solution, then 4.0 ml H$_2$PtCl$_6$ solution (0.373 g/L) was added and the suspension was irradiated by a 300 W Xe lamp ($\lambda \geq 420$ nm) under continuous stirring. After 3 h photo-deposition, the suspension was filtered, washed with de-ionized water for more than 3 times, and finally dried at 60 °C for overnight. The as-prepared
samples are denoted as Pt(P.D.)/CoO4(P.D.)/BiVO4. Pt /MnOx/BiVO4 was prepared with the similar method.

For comparison, Co3O4 (imp)/BiVO4 was prepared by typical impregnation method with Co (NO3)2 solution as precursor followed by post-calcination at 673 K for 2 h. Similarly, Pt (imp)/Co3O4 (P.D.)/BiVO4 sample was achieved by impregnation of Pt and photo-deposition of Co3O4, while Pt (P.D.)/Co3O4 (imp)/BiVO4 sample was prepared by photo-deposition of Pt and impregnation of Co3O4.

NiO (CuO, Fe2O3)/BiVO4 was prepared by impregnation method using Ni (NO3)2 , (Cu (NO3)2 and Fe (NO3)3) as the corresponding precursors followed by calcinations at 673 K for 2 h. The deposition amount and the detailed deposition process were the same with the Co3O4 (imp)/BiVO4 sample.

**Preparation of photoelectrodes.** BiVO4 film electrodes were prepared as previously reported. Co3O4 (P.D.)/BiVO4 electrode was prepared by in situ photochemical deposition method, which was carried out in a Pyrex reactor in 0.01 M Co (NO3)2 solutions containing 0.01 M NaIO3, and illuminated from the top using a 300 W Xe lamp. The loadings of different amounts of cocatalysts were carried out by controlling the deposition time. The Co3O4 (P.D.)/BiVO4 with optimized photo-deposition time was used for photoelectrochemical measurement. Co3O4 (imp)/BiVO4 electrodes were prepared by immersing BiVO4 electrode in Co (NO3)2 solutions (0.01 M) followed by calcination under 673 K for 2 h. The loading amount was also optimized and the best one was used for comparison.

**Tests of photocatalytic and photoelectrochemical performances.**
The photocatalytic O₂ evolution reactions were carried out in a closed gas circulation and evacuation system using a 300 W Xe lamp and optical cut-off filter (Kenko, L-42; λ≥420 nm). Normally, 0.15 g photocatalyst was dispersed in 150 mL 0.02 M NaIO₃ aqueous solution in a Pyrex reaction cell. Before irradiation, the reaction system was thoroughly degassed by evacuation in order to drive off the air inside. The amount of evolved O₂ was determined by an on-line gas chromatograph (Agilent, GC-7890, TCD, Ar carrier). The rate of O₂ evolution in the initial one hour was recorded for comparison. The amount of Pt cocatalyst was first optimized without oxidation cocatalyst and the optimal Pt amount was 0.1 wt%. Under the conditions of optimized Pt amount, different amounts of Co₃O₄ were deposited by photo-oxidation deposition. The optimal amount of Co₃O₄ was optimised to be 0.1 wt%.

The photocatalytic degradation of methyl orange and rhodamine B reaction were carried out using a 300 W Xe lamp and optical cut-off filter (Kenko, L-42; λ≥420 nm). Normally, 50 mg photocatalyst was dispersed in 100 mL 10 mg/L MO and RhB solutions with O₂ bubble. Prior to irradiation, the suspensions wet set to desorption-adsorption equilibrium with ultrasonic treatment for 10 min and then magnetically stirred in dark for 30 min. Top irradiation was used and the distance from light source to reaction solution is 10 cm. After different irradiation time, 2 ml suspensions were centrifuged and used for UV-vis characterization.

The photoelectrochemical performances of the photoanodes were measured in a three-electrodes setup, where Pt electrode and saturated mercury electrode (SCE) were employed as counter and reference electrode, respectively, and 0.5 M Na₂SO₄...
(pH=5.70) was used as the electrolyte solution. For linear sweep voltammetry, the potential was swept at a scanning rate of 10 mV/s. A shutter was used to record both the dark and photocurrent during a single scan. A 300 W Xe lamp (Ushio-CERMAXLX300) and optical cut-off filter (Kenko, L-42; λ≥420 nm) was used as the light source.

**Characterization of photocatalysts.** X-ray photoelectron spectroscopy (XPS) measurements, using a VG ESCALAB MK2 spectrometer with monochromatized Al-Kα excitation. The morphologies and particle sizes were examined by scanning electron microscopy (SEM) taken with a Quanta 200 FEG scanning electron microscope. HRTEM micrographs were taken on a FEI Tecnai G² F30 transmission electron microscope. UV-vis spectra was detected on V-650 UV/VIS spectrometer (JASCO), scanning range, 200-800 nm, scanning rate, 200 nm/min. The CO absorption for cocatalysts loaded samples were examined on AutoChem II 2920, before the absorption, all samples were treated with H₂ under the temperature of 673 K for 2 h to reduce the metal oxides to metal states.
Figure S1. The assignment about different facets of BiVO$_4$ crystal used in our experiment.
Figure S2. SEM image of Pt/MnOₓ/BiVO₄.

Figure S2 clearly shows that when Pt and MnOₓ are deposited on BiVO₄ simultaneously, the selectivity for both of them has not changed at all, namely, Pt particles can only be deposited on {010} facets and MnOₓ are on {110} facets selectively.
**Figure S3.** SEM image of Pt/Co$_3$O$_4$/BiVO$_4$.

Figure S3 shows that when Pt and Co$_3$O$_4$ are deposited on BiVO$_4$ simultaneously, the selectivity for both of them has not changed at all, namely, Pt particles can only be deposited on {010} facets and Co$_3$O$_4$ are on {110} facets selectively.
Figure S4. SEM images of cocatalysts deposited BiVO$_4$ by photo-deposition method. (a) MnO$_x$/BiVO$_4$, (b) PbO$_2$/BiVO$_4$, (c) Co$_3$O$_4$/BiVO$_4$, (d) Au/BiVO$_4$, (e) Pt/BiVO$_4$ and (f) Pt/MnO$_x$/BiVO$_4$. Scale bar, 500 nm.

Figure S4 shows the deposition of different cocatalysts deposited by photo-deposition method. Clearly we can observe that MnO$_x$, PbO$_2$ and Co$_3$O$_4$ are all photo-deposited on {110} facets and {010} facets shows almost the similar smoothness with the bare BiVO$_4$ crystal. The deposited particles are demonstrated to be MnO$_x$, PbO$_2$ and Co$_3$O$_4$ respectively by further XPS characterization. However, when the Au and Pt were deposited by photo-deposition method, the particles can only be found on {010} facets, while {110} facets are smooth enough without any particles deposited. The deposited particles are further demonstrated to be metal state by XPS. Combining both the photo-deposition of MnO$_x$ and Pt, we can clearly see the totally separation of different cocatalysts on different facets and the similar results can be achieved when Co$_3$O$_4$ and Pt were deposited simultaneously. From these results we can confirm that the deposited particles on {110} facets are MnO$_x$ and Co$_3$O$_4$, meanwhile, the deposited particles on {010} facets are Pt.
Figure S5. SEM images of cocatalysts deposited BiVO₄ by impregnation method. (a) Pt/BiVO₄, (b) MnOₓ/BiVO₄, (c) Pt/MnOₓ/BiVO₄, (d) Co₃O₄/BiVO₄ and (e) Pt/Co₃O₄/BiVO₄. Scale bar, 500 nm.

Figure S5 shows the deposition of different cocatalysts deposited by impregnation method. The deposited particles of Pt, MnOₓ or Co₃O₄ are all distributed on every facets of BiVO₄ without any selectivity. When both of Pt and MnOₓ (Co₃O₄) are deposited by impregnation method, the similar results can be achieved. So when compared with single deposition of Pt (MnOₓ or Co₃O₄) and dual-deposition of Pt and MnOₓ (Co₃O₄), we can make sure the distribution sites of different cocatalysts. Combined with the results of Figure S4 and Figure S5, we can get a clear description about selectively distribution and randomly distribution of cocatalysts to confirm the assignment of different cocatalysts on different facets.
Figure S6. EDX analysis of different ranges on BiVO₄ crystal. The selected range located on \{110\} facets (a,b), and on \{010\} facets (c,d). The selected range can be seen in rectangular box denoted.

Figure S6 shows that the selected range was located on the particles deposited on \{110\} facets, only Mn peak can be observed. However, when the selected range was located on the particles deposited on \{010\} facets, only Pt peak was observed. This phenomenon can also be found when Co₃O₄ and Pt were deposited.
**Figure S7.** The Co 2p XPS spectra of Co₃O₄ (a) and Mn 2p XPS spectra of MnOₓ (b) deposited by photo-deposition and impregnation method (P.D., photo-deposition method; imp, impregnation method).
Scheme S1: The thermaldynamic analysis of water oxidation reaction using IO₃⁻ as sacrificial reagent.

The reaction can be divided into two half reactions, one is water oxidation, the other is the reduction of IO₃⁻ to I⁻. Both of them can be summarized as the following equations.

\[2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \]  \hspace{1cm} (1)
\[4H^+ + \frac{2}{3} IO_3^- + 4e^- \rightarrow \frac{2}{3} I^- + 2H_2O \]  \hspace{1cm} (2)

when combine with (1) and (2), we can get a net reaction as equation (3).

\[\frac{2}{3} IO_3^- \rightarrow \frac{2}{3} I^- + O_2 \]  \hspace{1cm} (3)

The Enthalpies and Gibbs Energies of IO₃⁻ (aq), I⁻ (aq) and O₂(g) are obtained from Lange’s handbook of chemistry (The 16th edition, inorganic chemistry section, page 1253).

\[\Delta_fH^\theta (IO_3^-) = -221.3 \text{ kJ/mol}, \Delta_fG^\theta (IO_3^-) = -128.0 \text{ kJ/mol}, S^\theta (IO_3^-) = 118.4 \text{ J/mol.K} \]
\[\Delta_fH^\theta (I^-) = -56.8 \text{ kJ/mol}, \Delta_fG^\theta (I^-) = -51.6 \text{ kJ/mol}, S^\theta (I^-) = 118.4 \text{ J/mol.K} \]
\[\Delta_fH^\theta (O_2) = 0 \text{ kJ/mol}, \Delta_fG^\theta (O_2) = 0 \text{ kJ/mol}, S^\theta (O_2) = 205.1 \text{ J/mol.K} \]

The Gibbs energy of equation (3) can be calculated as follows:

\[\Delta G = \frac{2}{3}\Delta_fG^\theta (I^-) + 0 - \frac{2}{3}\Delta_fG^\theta (IO_3^-) = 50.9 \text{ kJ/mol} \]

It means that the reaction of equation (3) a thermodynamically unfavorable process, namely, the reaction of equation (1) and (2) is not thermodynamically feasible and it need extra energy to make it happen. Therefore, the exited photons from photocatalysts should supply energy to overcome this uphill reaction. Namely, energy conversion in this reaction is from solar energy to chemical energy.
Figure S8. The photoelectrochemical performances of Co$_3$O$_4$/BiVO$_4$ deposited by impregnation and photo-deposition method, respectively.

Reaction conditions: 0.5 M Na$_2$SO$_4$ (pH=5.70) was used as the electrolyte solution, scanning rate, 10 mV/s, 300 W Xe lamp (Ushio-CERMAXLX300) and optical cut-off filter (Kenko, L-42; $\lambda \geq$420 nm) was used as the light source.
Figure S9. Photocatalytic degradation performances of BiVO₄ with cocatalysts deposited by different methods. (a) Pt/MnOₓ/BiVO₄ for degradation of methyl orange (MO); (b) Pt/Co₃O₄/BiVO₄ for degradation of MO; (c) Pt/MnOₓ/BiVO₄ for degradation of rhodamine B (RhB); (d) Pt/Co₃O₄/BiVO₄ for degradation of RhB; (e) The UV-vis spectra of MO after reaction using Pt(P.D.)/MnOₓ(P.D.)/BiVO₄ as photocatalyst; (d) The UV-vis spectra of RhB after reaction using Pt(P.D.)/MnOₓ(P.D.)/BiVO₄ as photocatalyst.

Reaction conditions: 50 mg Cat., 100 mL dye solution with concentration of 10 mg/L, O₂ bubble, 300 W Xe lamp (λ≥420 nm), top irradiation.
**Scheme S2.** The reaction processes of photocatalytic degradation (oxidation) of environmental pollutants.

\[
\text{semiconductor} + \text{hv} \rightarrow e^- + h^+
\]

\[
\text{Dye}_{ads} + h^+ \rightarrow \text{Dye}_{ads}^{*+}
\]

\[
O_2 + e^- \rightarrow O_2^-
\]

\[
O_2^- + H^+ \rightarrow \text{HO}_2^- \rightarrow \cdot OH
\]

\[
\text{Dye}_{ads}^{*+} + \text{O}_2^- (\text{or} \cdot \text{OH}) \rightarrow \text{peroxylated or hydroxylated intermediates} \rightarrow \text{degraded or mineralized products}
\]
Table S1. The amount of CO absorption for Pt/BiVO$_4$ and Co$_3$O$_4$/BiVO$_4$ with different deposition methods of cocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Active metal surface area ($\text{m}^2/\text{g}$)</th>
<th>Monlayer uptake ($\mu\text{mol}/\text{g}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiVO$_4$</td>
<td>$4.5 \times 10^{-5}$</td>
<td>$9.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>Pt(P.D.)/BiVO$_4$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>$4.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Pt(imp)/BiVO$_4$</td>
<td>$2.5 \times 10^{-3}$</td>
<td>$5.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>Co$_3$O$_4$(P.D.)/BiVO$_4$</td>
<td>$6.5 \times 10^{-4}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>Co$_3$O$_4$(imp)/BiVO$_4$</td>
<td>$7.6 \times 10^{-4}$</td>
<td>$2.1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Conditions: Before the absorption, the samples were treated with H$_2$ under the temperature of 673 K for 2 h to reduce the metal oxides to metal states. The amount of deposition for Pt and Co$_3$O$_4$ was 0.5 wt% with different deposition method. As the absorption amount for all these samples is very low, the deposition amount of cocatalysts (0.5 wt%) is larger than samples used for photocatalytic reactions (0.1 wt%).
References.