Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Highly efficient photocatalysts constructed by rational assembly of dual-cocatalysts separately on different facets of $BiVO_4$

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Samples preparation. $BiVO_4$ was prepared by hydro-thermal method as previously reported.[1] Typically, the precursors NH_4VO_3 (36 mmol) and $Bi(NO_3)_3 \cdot 5H_2O$ (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 ^{o}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 ^{o}C for overnight.

The photo-deposition of the Co_3O_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 □ for overnight. The as-prepared samples are denoted as $Co_3O_4/BiVO_4$.

$Pt(P.D.)/Co_3O_4(P.D.)/BiVO_4$: 0.30 g as-prepared $Co_3O_4/BiVO_4$ was suspended in 100 ml H_2O solution, then 4.0 ml H_2PtCl_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 ^{o}C for overnight. The as-prepared samples are denoted as Pt(P.D.)/Co_3O_4(P.D.)/$BiVO_4$. Pt /MnO_x/$BiVO_4$ was prepared with the similar method.

For comparison, Co_3O_4 (imp)/$BiVO_4$ was prepared by typical impregnation method with Co $(NO_3)_2$ solution as precursor followed by post-calcination at 673 K for 2 h. Similarly, Pt (imp)/Co_3O_4 (P.D.)/$BiVO_4$ sample was achieved by impregnation of Pt and photo-deposition of Co_3O_4, while Pt (P.D.)/Co_3O_4 (imp)/$BiVO_4$ sample was prepared by photo-deposition of Pt and impregnation of Co_3O_4.

NiO (CuO, Fe_2O_3)/$BiVO_4$ was prepared by impregnation method using Ni $(NO_3)_2$, (Cu $(NO_3)_2$ and Fe $(NO_3)_3$) 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 Co_3O_4 (imp)/$BiVO_4$ sample.

Preparation of photoelectrodes. $BiVO_4$ film electrodes were prepared as previously reported. Co_3O_4 (P.D.)/$BiVO_4$ electrode was prepared by in situ photochemical deposition method, which was carried out in a Pyrex reactor in 0.01 M Co $(NO_3)_2$ solutions containing 0.01 M $NaIO_3$, 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 Co_3O_4 (P.D.)/$BiVO_4$ with optimized photo-deposition time was used for photoelectrochemical measurement. Co_3O_4 (imp)/$BiVO_4$ electrodes were prepared by immersing $BiVO_4$ electrode in Co $(NO_3)_2$ 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 photocactalytic and photoelectrochemical performances.

The photocatalytic O_2 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; $\lambda \geq 420$ nm). Normally, 0.15 g photocatalyst was dispersed in 150 mL 0.02 M $NaIO_3$ 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 O_2 was determined by an on-line gas chromatograph (Agilent, GC-7890, TCD, Ar carrier).The rate of O_2 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 Co_3O_4 were deposited by photo-oxidation deposition. The optimal amount of Co_3O_4 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; $\lambda \geq 420$ nm).Normally, 50 mg photocatalyst was dispersed in 100 mL 10 mg/L MO and RhB solutions with O_2 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 irridation 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 Na_2SO_4

(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; $\lambda \geq 420$ 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 G^2 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 H_2 under the temperature of 673 K for 2 h to reduce the metal oxides to metal states.

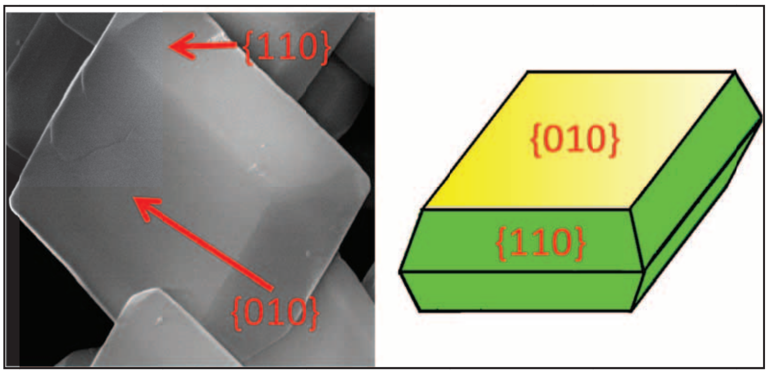

Figure S1. The assignment about different facets of $BiVO_4$ crystal used in our experiment..

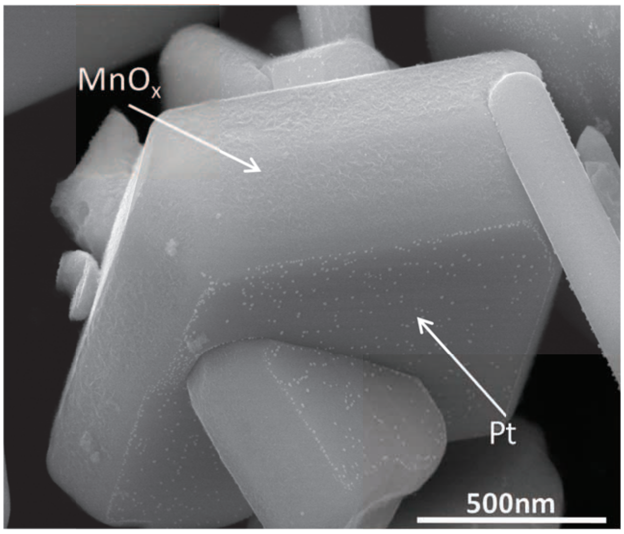

Figure S2.SEM image of Pt/MnO$_x$/BiVO$_4$.

Figure S2 clearly shows that when Pt and MnO$_x$ are deposited on BiVO$_4$ simutaniously, the selectivity for both of them has not changed at all, namely, Pt particles can only be deposited on {010} facets and MnO$_x$ are on {110} facets selectively.

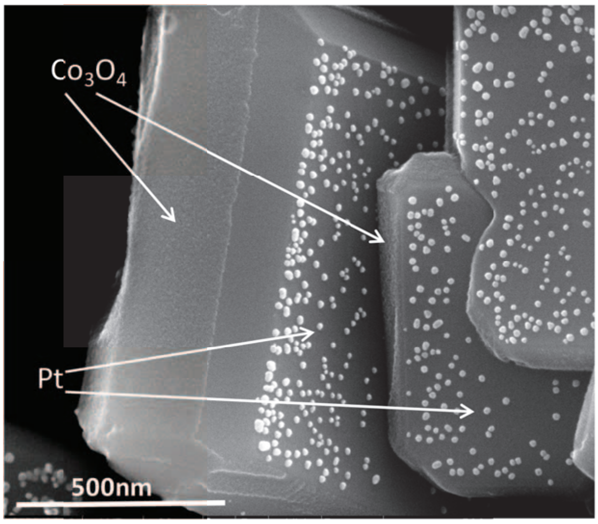

Figure S3.SEM image of Pt/Co_3O_4/$BiVO_4$.

Figure S3 shows that when Pt and Co_3O_4 are deposited on $BiVO_4$ simutaniously, the selectivity for both of them has not changed at all, namely, Pt particles can only be deposited on {010} facets and Co_3O_4 are on {110} facets selectively.

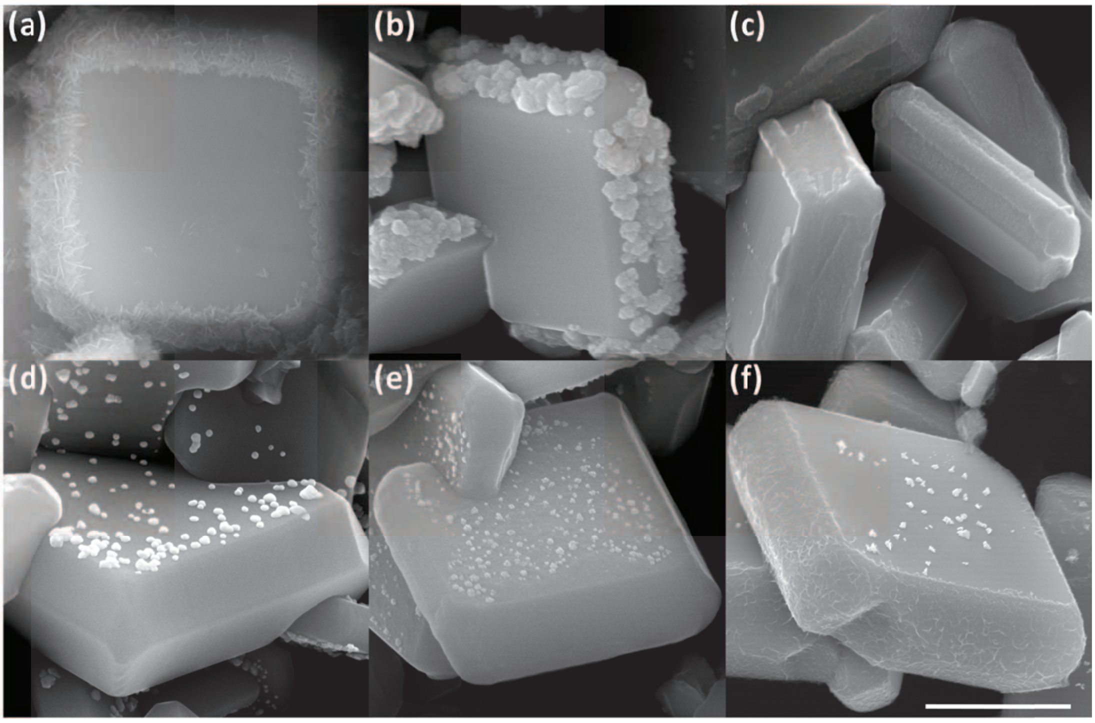

Figure S4. SEM images of cocatalysts deposited $BiVO_4$ by photo-deposition method. (a) $MnO_x/BiVO_4$, (b) $PbO_2/BiVO_4$, (c) $Co_3O_4/BiVO_4$, (d) $Au/BiVO_4$, (e) $Pt/BiVO_4$ and (f) $Pt/MnO_x/BiVO_4$. Scale bar, 500 nm.

Figure S4 shows the deposition of different cocatalysts deposited by photo-deposition method. Clearly we can observe that MnO_x, PbO_2 and Co_3O_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_3O_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_3O_4 and Pt were deposited simultaneously. From these results we can confirm that the deposited particles on {110} facets are MnO_x and Co_3O_4, meanwhile, the deposited particles on {010} facets are Pt.

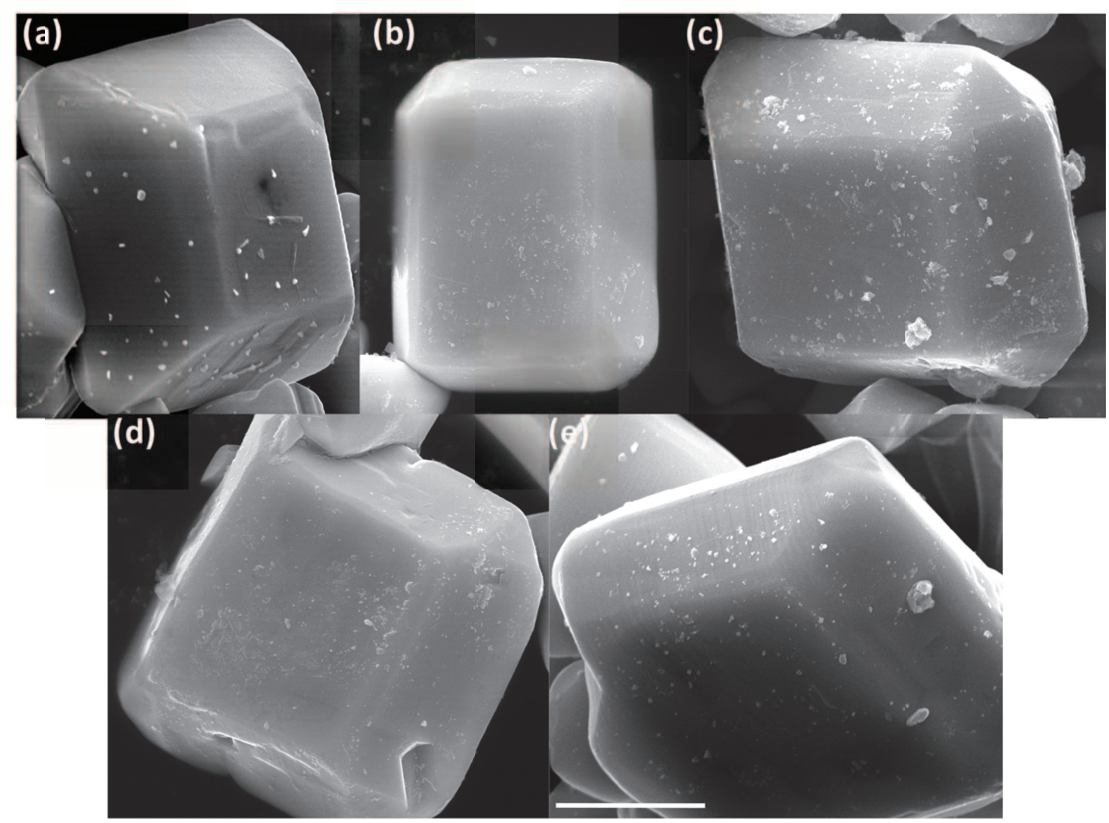

Figure S5. SEM images of cocatalysts deposited $BiVO_4$ by impregnation method. (a) $Pt/BiVO_4$, (b) $MnO_x/BiVO_4$, (c) $Pt/MnO_x/BiVO_4$, (d) $Co_3O_4/BiVO_4$ and (e) $Pt/Co_3O_4/BiVO_4$. Scale bar, 500 nm.

Figure S5 shows the deposition of different cocatalysts deposited by impregnation method. The deposited particles of Pt, MnO_x or Co_3O_4 are all distributed on every facets of $BiVO_4$ without any selectivity. When both of Pt and MnO_x (Co_3O_4) are deposited by impregnation method, the similar results can be achieved. So when compared with single deposition of Pt (MnO_x or Co_3O_4) and dual-deposition of Pt and MnO_x (Co_3O_4), 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.

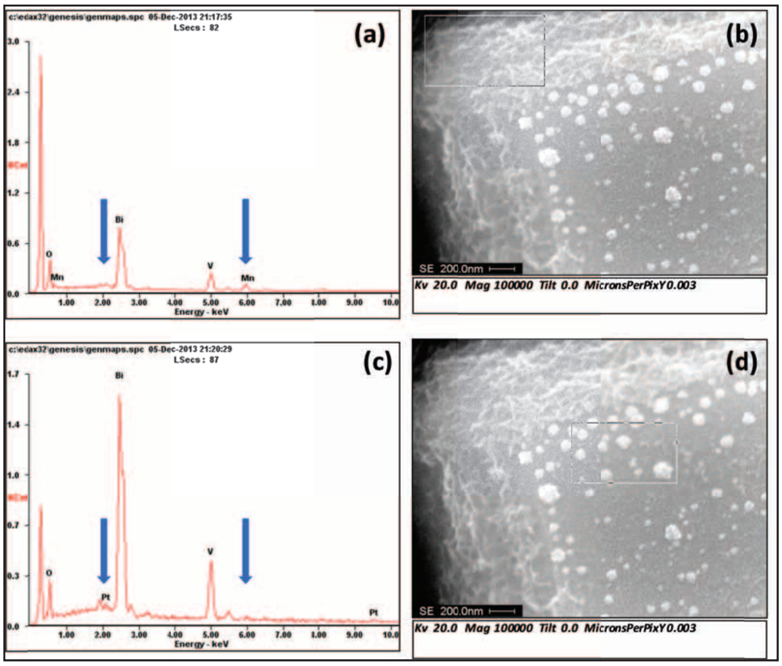

Figure S6. EDX analysis of different ranges on $BiVO_4$ crystal. the selected range located on {110} facets (a,b), and on {010}facets (c,d). The selected range can be seen in rectangular box denoted.

Figure S6 shows that we 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 Co_3O_4 and Pt were deposited.

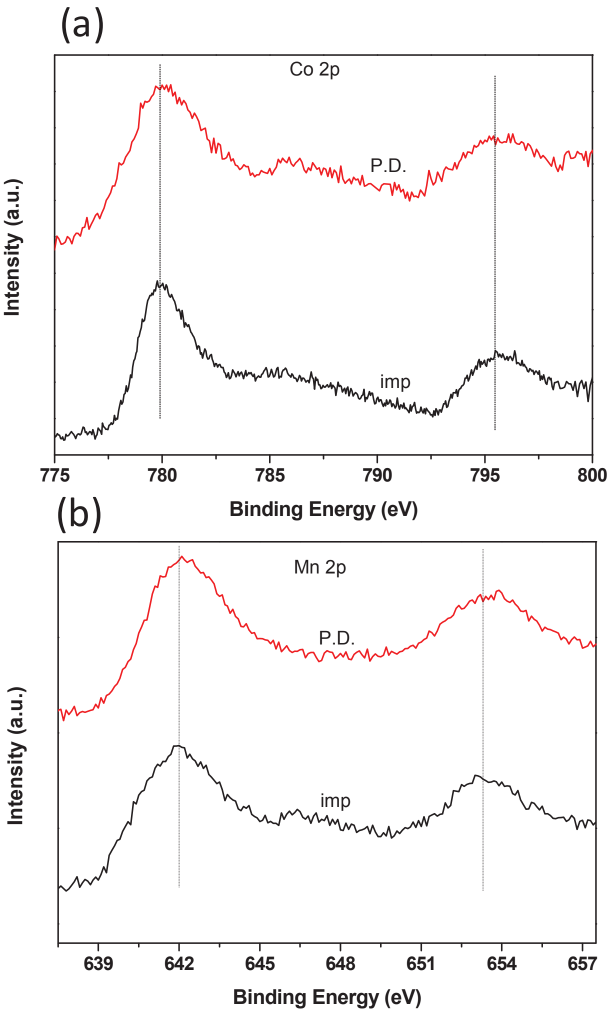

Figure S7. The Co 2p XPS spectra of Co_3O_4 (a) and Mn 2p XPS spectra of MnO_x (b) deposited by photo-deposition and impregnation method (P.D., photo-deposition method; imp, impregnation method).

Scheme S1: The thermaldynamic analysis of water oxidation reaction using IO_3^- as sacrifical reagent.

The reaction can be divided into two half reactions, one is water oxidation, the other is the reduction of IO_3^- to I^-. Both of them can be summarized as the following equations.

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \tag{1}$$

$$4H^+ + \frac{2}{3}IO_3^- + 4e^- \rightarrow \frac{2}{3}I^- + 2H_2O \tag{2}$$

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

$$\frac{2}{3}IO_3^- \rightarrow \frac{2}{3}I^- + O_2 \tag{3}$$

The Enthalpies and Gibbs Energies of IO_3^- (aq), I^- (aq) and O_2(g) are obtained from Lange's handbook of chemistry (The16th edition, inorganic chemistry section, page 1253).

$\Delta_f H^{\Theta}$ (IO_3^-) =-221.3 kJ/mol, $\Delta_f G^{\Theta}$ (IO_3^-) =-128.0 kJ/mol, S^{Θ} (IO_3^-) =118.4 J/mol.K

$\Delta_f H^{\Theta}$ (I^-) =-56.8 kJ/mol, $\Delta_f G^{\Theta}$ (I^-) =-51.6 kJ/mol, S^{Θ} (I^-) =118.4 J/mol.K

$\Delta_f H^{\Theta}$ (O_2) =0 kJ/mol, $\Delta_f G^{\Theta}$ (O_2) =0 kJ/mol, S^{Θ} (O_2) =205.1 J/mol.K

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

$$\Delta G = 2/3\Delta_f G^{\Theta}\,(I^-) + 0 - 2/3\Delta_f G^{\Theta}\,(IO_3^-) = 50.9\ \text{kJ/mol}$$

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.

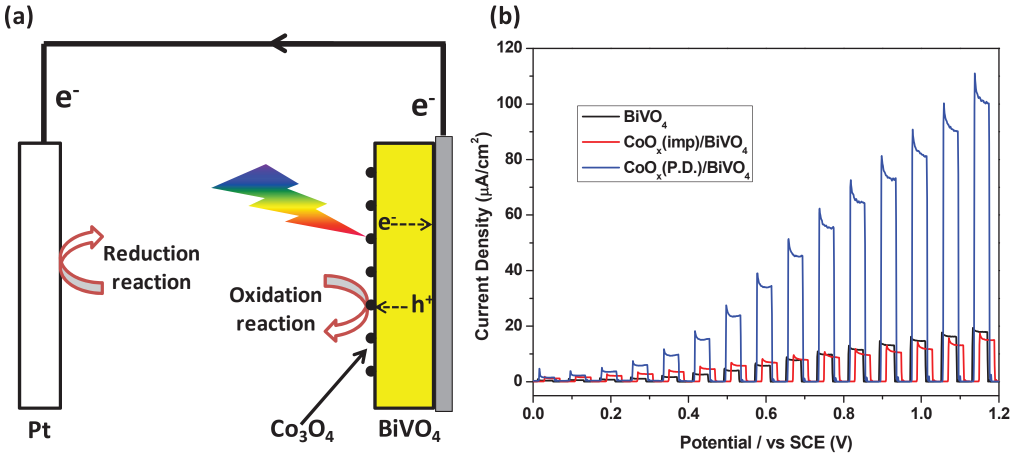

Figure S8. The photoelectrochemical performances of $Co_3O_4/BiVO_4$ deposited by impregnation and photo-deposition method, respectively.

Reaction conditions: 0.5 M Na_2SO_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; λ≥420 nm) was used as the light source.

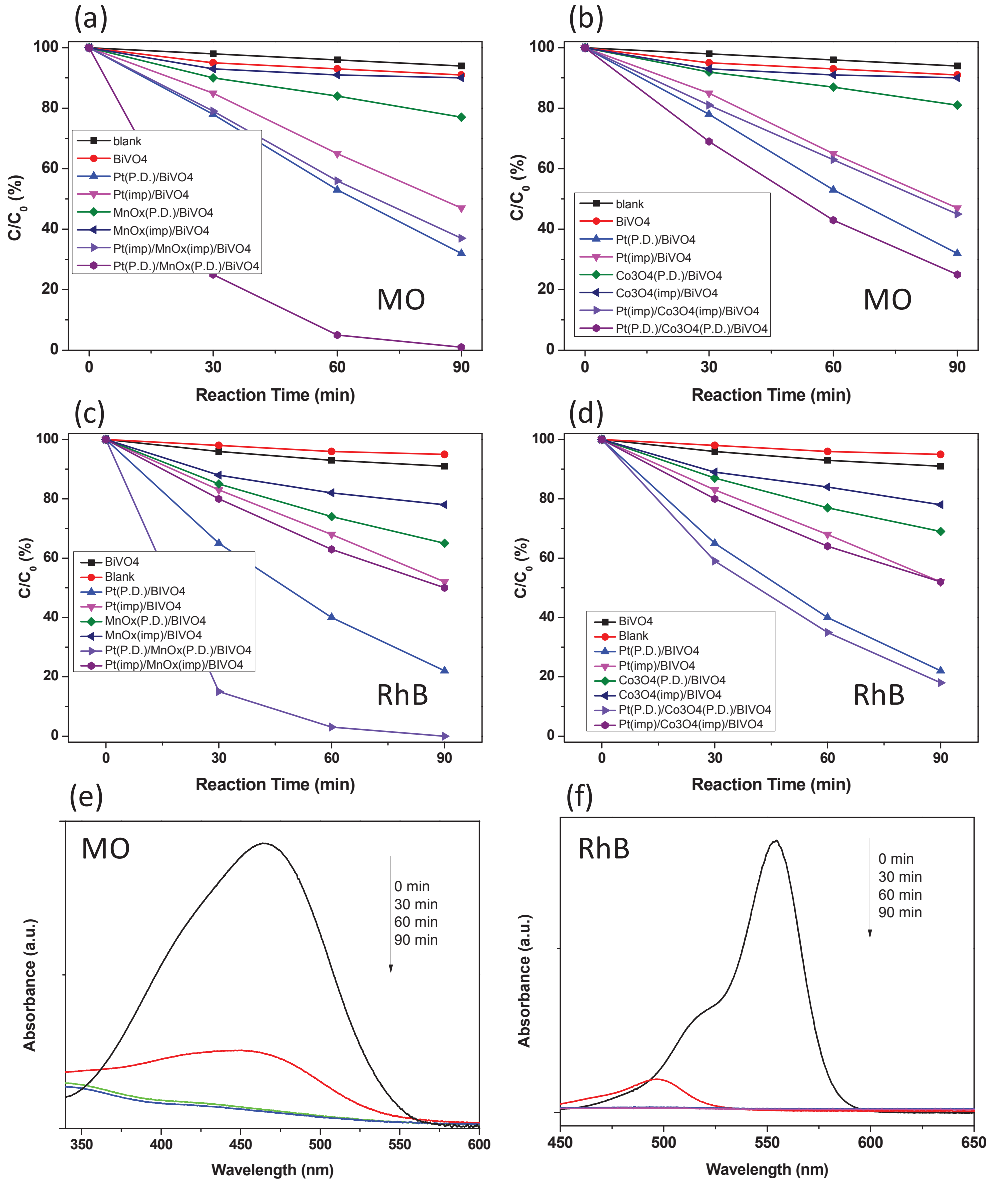

Figure S9. Photocatalytic degradation performances of $BiVO_4$ with cocatalytsts deposited by different methods. (a) $Pt/MnO_x/BiVO_4$ for degradation of methyl orange (MO); (b) $Pt/Co_3O_4/BiVO_4$ for degradation of MO; (c) $Pt/MnO_x/BiVO_4$ for degradation of rhodamine B (RhB) ; (d) $Pt/Co_3O_4/BiVO_4$ for degradation of RhB; (e) The UV-vis spectra of MO after reaction using Pt(P.D.)/MnO_x(P.D.)/$BiVO_4$ as photocatalyst; (d) The UV-vis spectra of RhB after reaction using Pt(P.D.)/MnO_x(P.D.)/$BiVO_4$ as photocatalyst.

Reaction conditions: 50 mg Cat., 100 mL dye solution with concentration of 10 mg/L, O_2 bubble, 300 W Xe lamp (λ≥420 nm), top irradiation.

Scheme S2. The reaction processes of photocatalytic degradation (oxidation) of environmental pollutants.

$$semiconductor + h\nu \rightarrow e^- + h^+$$

$$Dye_{ads} + h^+ \rightarrow Dye_{ads}{}^{*+}$$

$$O_2 + e^- \rightarrow O_2{}^-$$

$$O_2{}^- + H^+ \rightarrow HOO\cdot \rightarrow \cdot OH$$

$$Dye_{ads}{}^{*+} + O_2{}^-(or \cdot OH) \rightarrow peroxylated\ or\ hydroxylated\ intermdiates \rightarrow\rightarrow degraded\ or\ mineralized\ products$$

Table S1. The amount of CO absorption for Pt/$BiVO_4$ and Co_3O_4/$BiVO_4$ with different deposition methods of cocatalysts.

Photocatalyst	Active metal surface area (m^2/g)	Monlayer uptake (μmol/g)
$BiVO_4$	$4.5*10^{-5}$	$9.5*10^{-4}$
Pt(P.D.)/$BiVO_4$	$2.0*10^{-3}$	$4.2*10^{-2}$
Pt(imp)/$BiVO_4$	$2.5*10^{-3}$	$5.2*10^{-2}$
Co_3O_4(P.D.)/$BiVO_4$	$6.5*10^{-4}$	$1.6*10^{-2}$
Co_3O_4(imp)/$BiVO_4$	$7.6*10^{-4}$	$2.1*10^{-2}$

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_3O_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.

1. R. G. Li, F. X. Zhang, D. E. Wang, J. X. Yang, M. R. Li, J. Zhu, X. Zhou, H. X. Han and C. Li, *Nat. Commun.* 2013, **4**, 1432. DOI: 10.1038/ncomms2401.