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Electronic Supplementary Information

Photocatalytic Water Oxidation by Combination of $BiVO_4$-RGO and Molecular Cobalt Catalyst

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Experimental Section

Materials

4-methoxypyridine, 4-tert-butylpyridine, 4-bromopyridine hydrochloride and 4-cyanopyridine were purchased from Energy Chemicals. Cobalt(II) complexes [Co(salophen)] (**2**, salophen = (*N,N'*-bis(salicylaldehyde)-1,2-phenylenediamine) and $[Co(bpy)_2(OH_2)_2](ClO_4)_2$ (**3**, bpy = 2,2'-bipyridine) were synthesized according to the reported methods.[1,2] $Bi(NO_3)_3$ $5H_2O$ (99.0%) and pyridine (99.9%) were purchased from Aladdin Chemicals. Graphite powder and V_2O_5 (99.0%) were purchased from Sinopharm Chemicals. All other chemicals are commercially available.

General methods

SEM micrographs and EDX analysis were conducted with a Nova NanoSEM 450 instrument. X-ray diffraction was collected with a D/max-2400 diffractometer. UV-vis diffuse reflectance spectra measurement was performed on an Evolution 200 spectrophotometer (Thermo, USA). The photoluminescence (PL) emission spectra were measured on a fluorescence spectrometer (FluoroMax-4P, France) at an

excitation wavelength of 400 nm. ^{1}H NMR spectra were recorded at 298 K using a Bruker DRX-400 instrument operating at 400 MHz. UV-vis absorption measurement was taken with an Agilent 8453 spectrophotometer.

Preparation of $BiVO_4$-RGO composite

$BiVO_4$-RGO composite was prepared according to a method reported in literatre.[3] In detail, $Bi(NO_3)_3$ $5H_2O$ (10 mmol), V_2O_5 (5 mmol) and graphene oxide (0.162g, GO was prepared based on the Hummer's method[4]) were mixed in 0.75 M HNO_3 solution (50 mL). The suspension was stirred for 2 days at room temperature and the obtained greenish $BiVO_4$-GO precursor was collected by filtration and dried at 110℃. 1mg/mL of $BiVO_4$-GO in solvent-grade ethanol was employed as a typical concentration, which was irradiated by visible light ($\lambda > 420$ nm) using a 300 W xenon lamp installed a cut-off filter. The suspension was stirred constantly during irradiation and was bubbled with argon for 3 hours. Finally, the $BiVO_4$-RGO powders obtained by filtration and dried overnight was characterized by SEM, XRD and DRS (See Figures S2~4).

Synthesis of $Co_4O_4(O_2CMe)_4(py)_4$, (1-H).

Complex **1-H** was synthesized according to a literature procedure.[5] $Co(NO_3)_2$ $6H_2O$ (2.90 g, 10 mmol) and CH_3CO_2Na $3H_2O$ (2.70 g, 20 mmol) were stirred in methanol (30 mL) and heated to refluxing temperature, and pyridine (0.8 mL, 10 mmol) was added to the stirred reaction mixture. A portion of 30% H_2O_2 (5 mL) was added to the reaction mixture dropwise and stirred under refluxing condition for 4 hours. The cooled reaction mixture was concentrated in a rotary evaporator and then the aqueous layer was separated out by adding CH_2Cl_2 to it. The light-pink aqueous layer was discarded and the CH_2Cl_2 layer was dried over anhydrous Na_2SO_4, and then filtered. After the solvent was removed on a rotary evaporator, the residue was purified by column chromatography on silica gel with dichloromethane-methanol (15:1, V:V) as eluent to obtain the dark green product. Yield: 724 mg (34%).

^{1}H NMR (400 MHz, D_2O): δ 8.13 (d, 8H), 7.63-7.66 (t, 4H), 7.14 (d, 8H), 2.01 (s, 12H). ESI-MS: *m/z* = 852.67 $[M]^+$ (calcd: 851.93).

$Co_4O_4(O_2CMe)_4(4\text{-}OMepy)_4$, (**1-OMe**), $Co_4O_4(O_2CMe)_4(4\text{-}t\text{-}Bupy)_4$, (**1-t-Bu**), $Co_4O_4(O_2CMe)_4(4\text{-}Brpy)_4$, (**1-Br**) and $Co_4O_4(O_2CMe)_4(4\text{-}CNpy)_4$, (**1-CN**) were also prepared following the reported methods[5]. The main procedure was similar with preparing complex **1-H** except using 4-methoxypyridine, 4-tert-butylpyridine, 4-bromopyridine hydrochloride and 4-cyanopyridine to replace pyridine, respectively.

Photocatalytic oxygen evolution

In a typical reaction, $BiVO_4$-RGO was dispersed in an aqueous solution containing cobalt complex **1-X** (0.25 mM) and $AgNO_3$ (15 mM) in a 50 mL Schlenk bottle without any pH adjustment. The solution was deaerated by bubbling argon for 30 min. This hybrid system was irradiated with a 300W xenon lamp equipped with a 420 nm cut-off filter at room temperature. The amount of evolved O_2 was sampled by syringe from the headspace of cuvette and analyzed by a Techcomp GC 7890T instrument equipped with a 5 Å molecular sieve column and a thermal conductivity detector with argon carrier gas. For the photocatalytic reactions operated at different pH values, nitric acid was added to the aqueous solution to adjust the pH values.

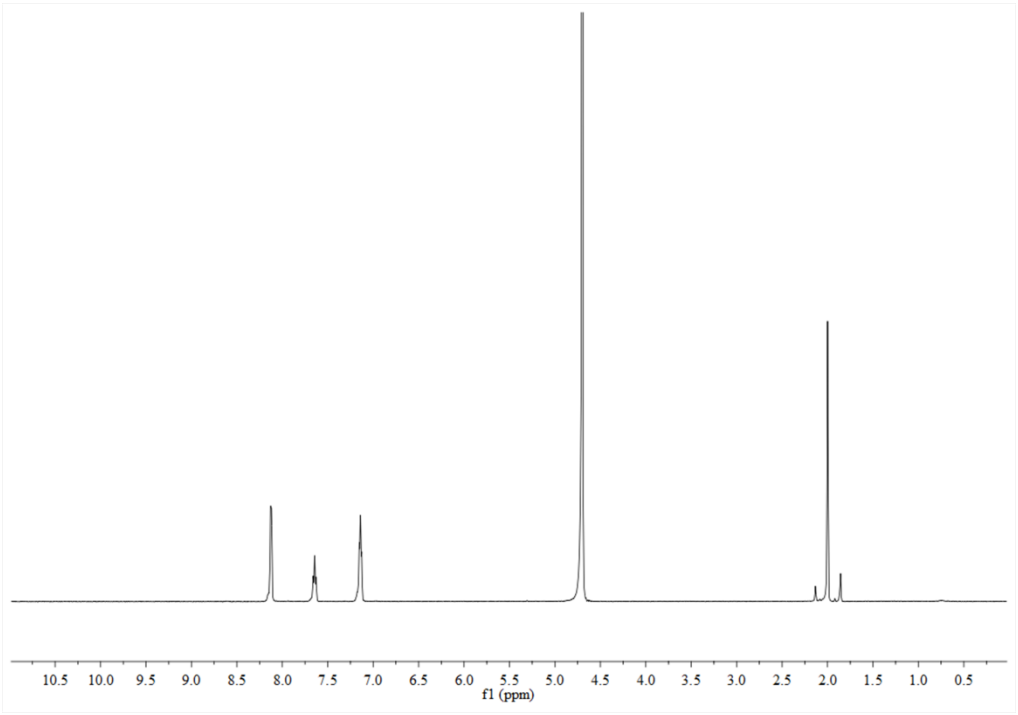

Figure S1. ^1H NMR spectrum of **1-H** in D_2O

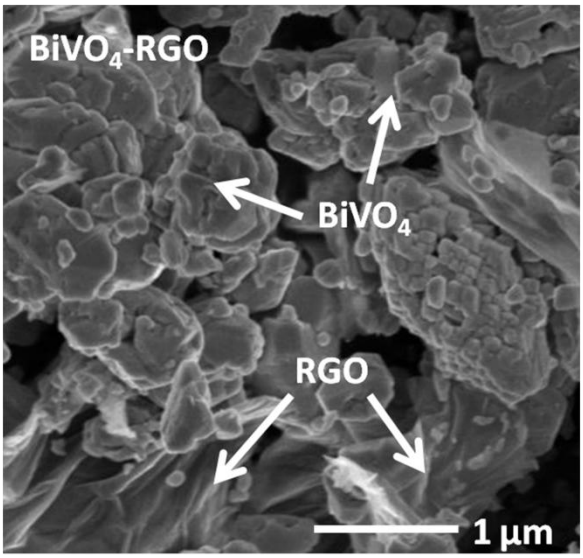

Figure S2. SEM image of $BiVO_4$-RGO composite.

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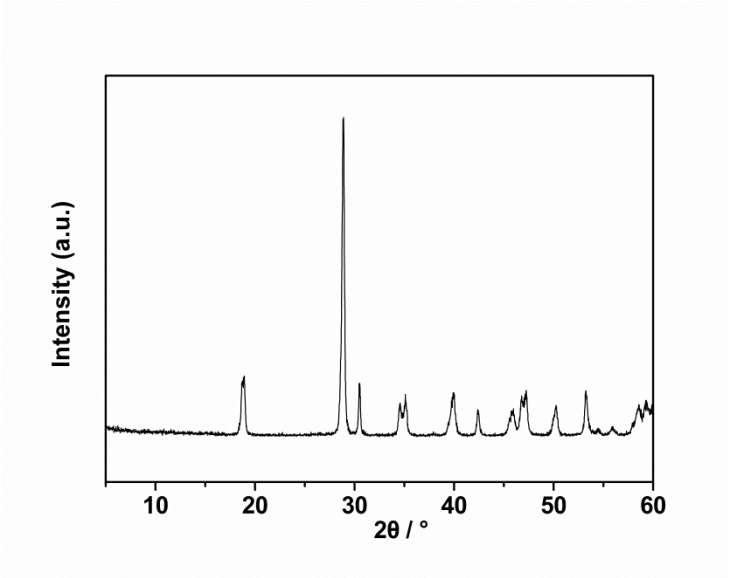


Figure S3. Powder XRD pattern of $BiVO_4$-RGO composite.

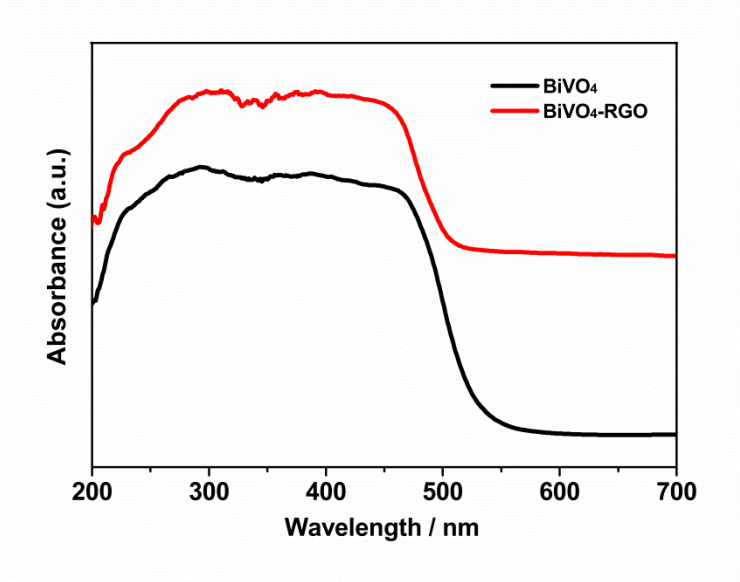


Figure S4. UV-vis diffuse reflectance spectra of $BiVO_4$-RGO and $BiVO_4$.

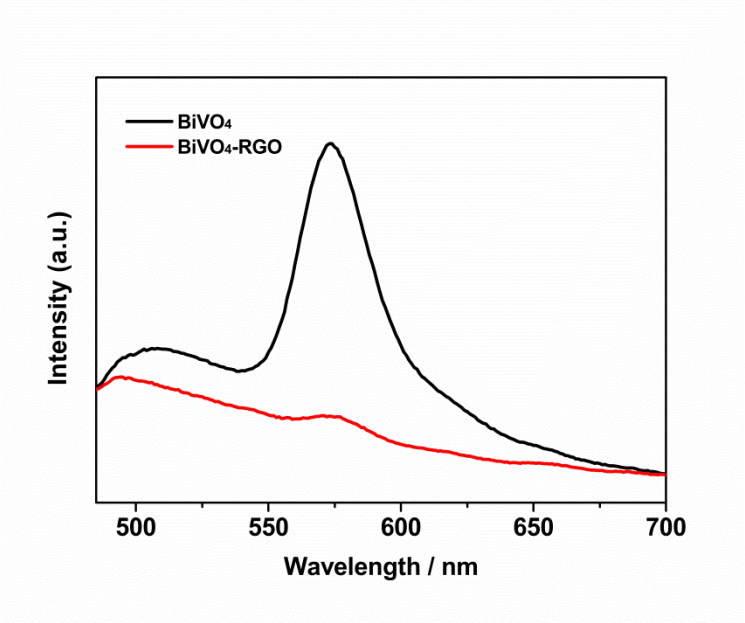


Figure S5. PL spectra of $BiVO_4$-RGO and $BiVO_4$.

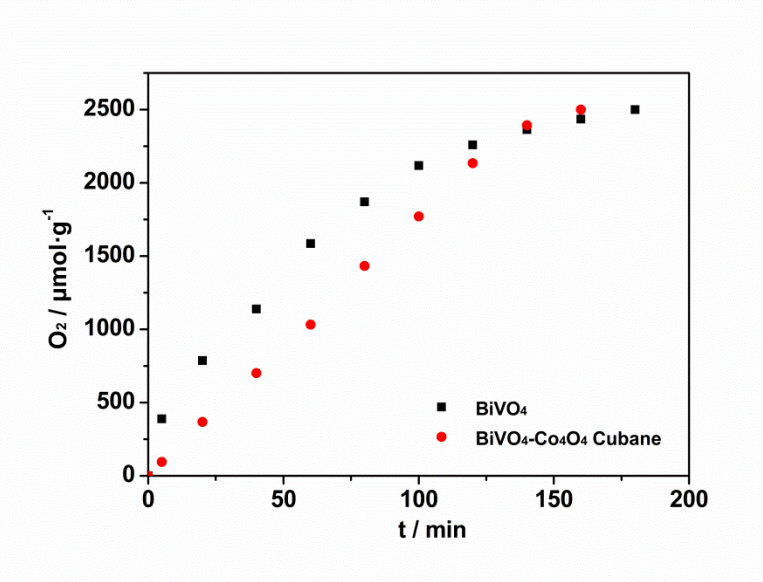


Figure S6. Time courses of the amount of evolved oxygen under visible light (λ > 420 nm) irradiation of $BiVO_4$ (15 mg) (black) and a mixture of $BiVO_4$ (15 mg)/**1-H** (0.25 mM) (red), respectively, in aqueous $AgNO_3$ (15 mM) solutions; light source, 300 W Xe lamp equipped with a 420 nm cut-off filter.

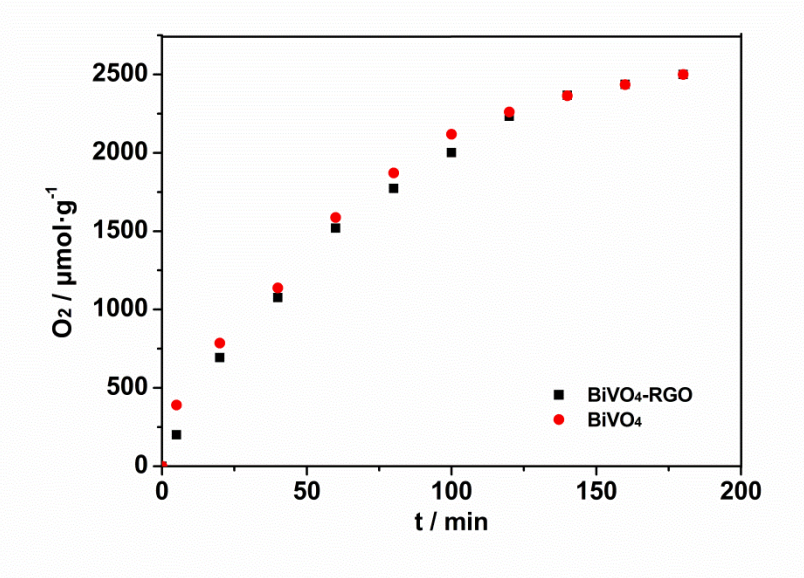


Figure S7. Time courses of the amount of evolved oxygen under visible light (λ > 420 nm) irradiation of $BiVO_4$-RGO (15 mg) (black) and $BiVO_4$ (15 mg) (red), respectively, in aqueous $AgNO_3$ (15 mM) solutions; light source, 300 W Xe lamp equipped with a 420 nm cut-off filter.

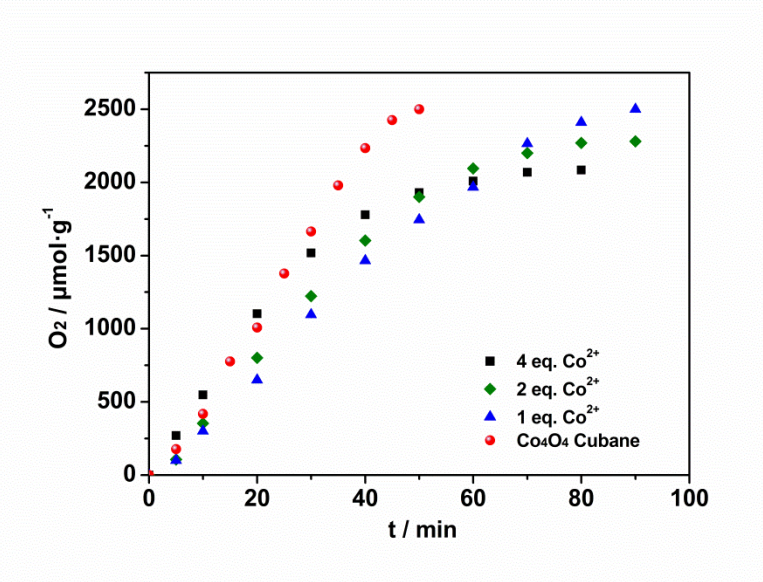


Figure S8 Time courses of oxygen evolution by $BiVO_4$-RGO (15 mg) in aqueous $AgNO_3$ (15 mM) solution under visible light ($\lambda > 420$ nm) irradiation in the presence of **1-H** (2.5×10^{-4} M) and different concentrations of $Co(NO_3)_2$, respectively. Red: 2.5×10^{-4} M **1-H**; blue: 2.5×10^{-4} M Co^{2+}; green: 5×10^{-4} M Co^{2+}; black: 10^{-3} M Co^{2+}.

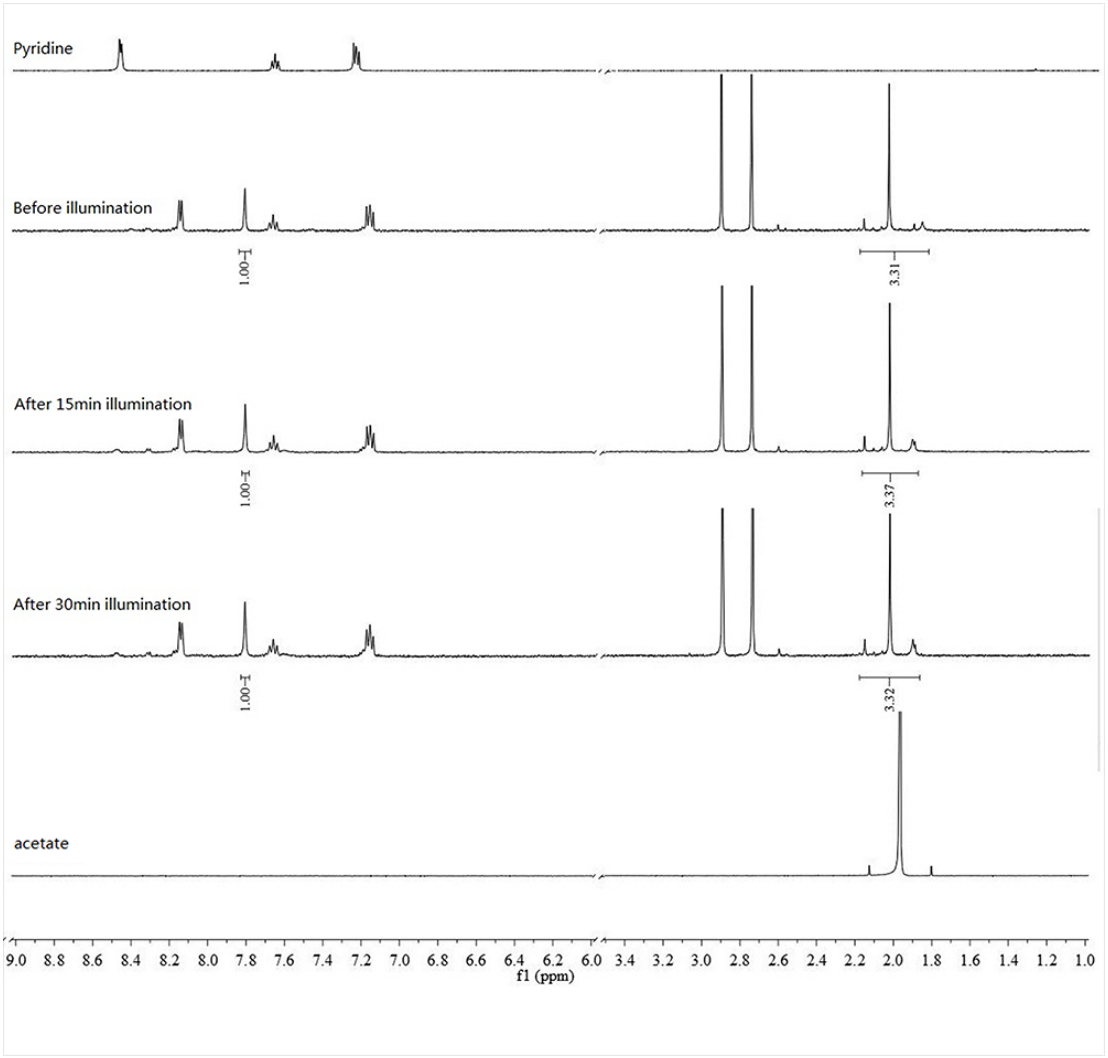


Figure S9. ^{1}H NMR spectra of **1-H** in D_2O containing $BiVO_4$-RGO and $AgNO_3$ under irradiation at t = 0, t = 15 min and t = 30 min. ^{1}H NMR spectra of free pyridine and acetate in D_2O are also shown.

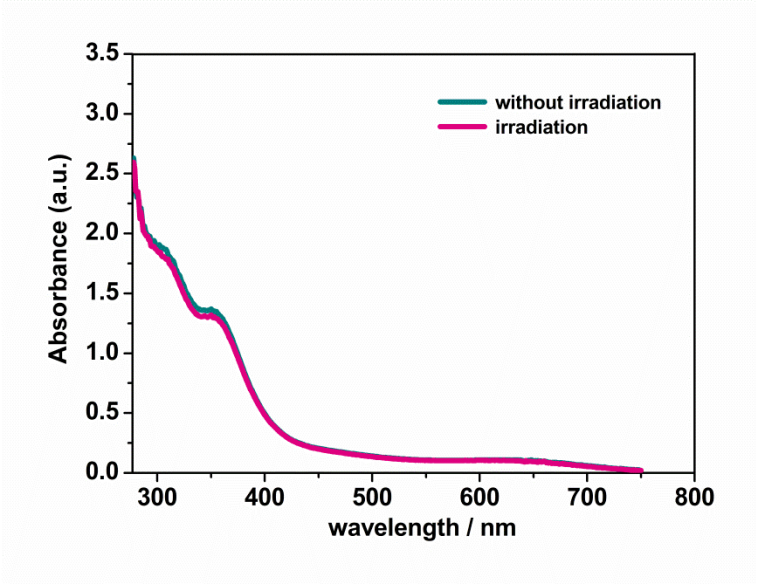


Figure S10. UV-vis spectra of **1-H** in water before and after photocatalytic water oxidation.

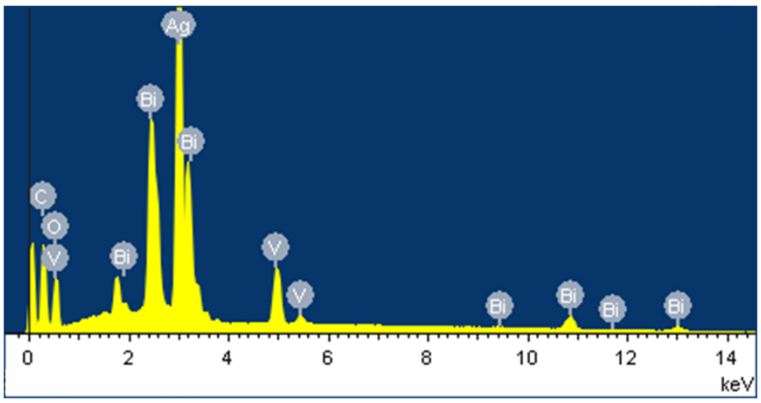


Figure S11. EDX spectra of $BiVO_4$-RGO composite after the photocatalytic reaction.

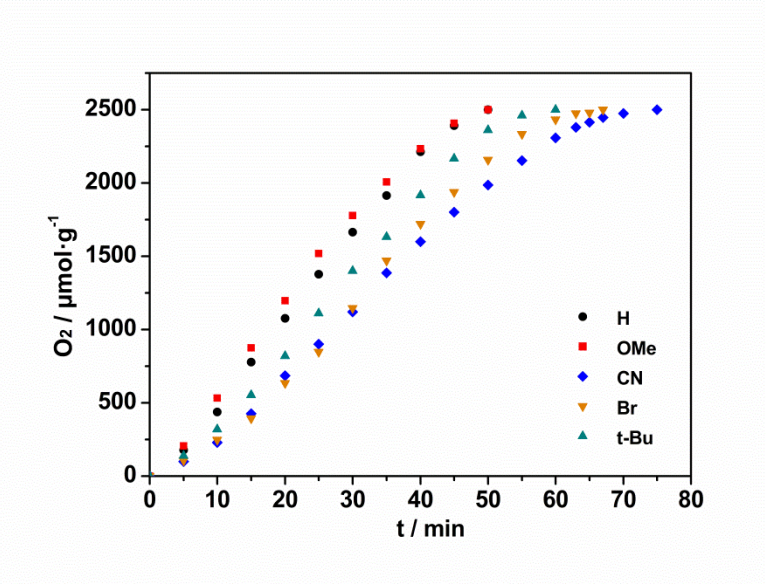
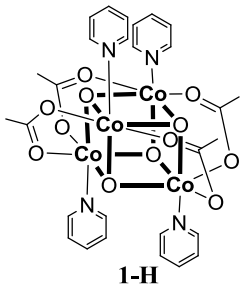
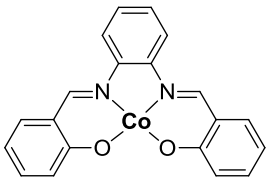


Figure S12. Time courses of oxygen evolution under visible light (λ > 420 nm) irradiation of mixtures of **1-X** (2.5 × 10^{-4} M) and $BiVO_4$-RGO (15 mg) in the presence of $AgNO_3$ (15 mM)

Table S1. The O_2 evolution rate of different cobalt catalyst in the hybrid system.[a]



1-H



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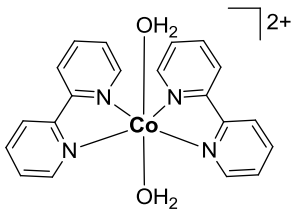

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Entry	Catalyst	O_2 evolution rate (μmol g^{-1} min^{-1})[b]
1	--	13.9
2	**1-H**	55.6
3	**2**	34.1
4	**3**	20.4

[a] Reaction conditions: 15 mg $BiVO_4$-RGO, 2.5×10^{-4} M cobalt complex, 10 mL H_2O, 300 W Xe lamp equipped with a 420 nm cut-off filter. [b] O_2 evolution rate = the total amount of O_2 evolved / the total time consumed.

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