Supporting Information

A Heterogeneous Cobalt Cubane Polymer Co-catalyst for Cooperative Water Oxidation

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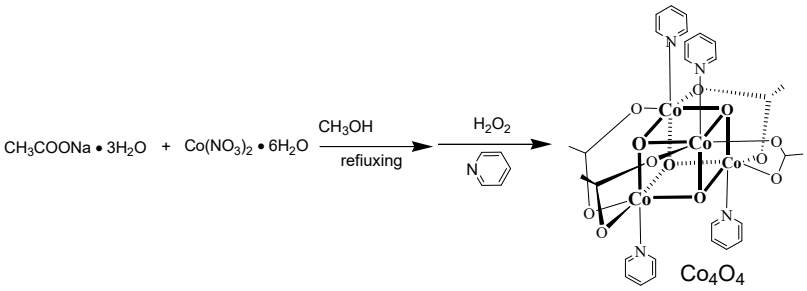
Experimental Section

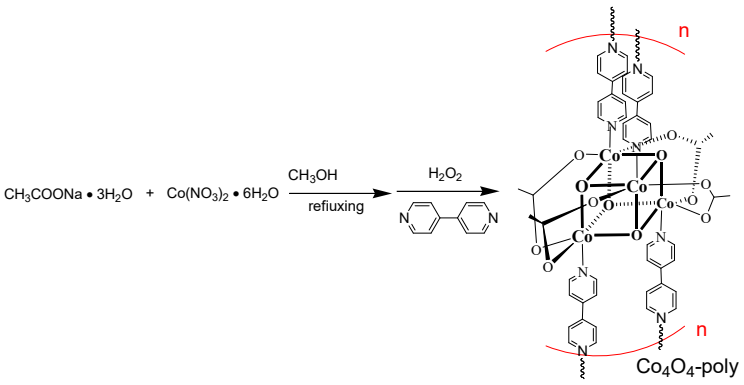
Synthesis of Co_4O_4 molecules water oxidation co-catalyst.

Cobalt cubane (Co_4O_4) molecules was synthesized by reported work. $Co(NO_3)_2 \cdot 6H_2O$ (10 mmol) and $CH_3COONa \cdot 3H_2O$ (10 mmol) were initially dissolved in a 250 mL two-necked flask containing 30 mL of methanol and then heated to reflux temperature. Subsequently, 10 mmol of pyridine and 5 mL of hydrogen peroxide (30%) were added separately to the reaction mixture. The mixture was stirred for 4 hours at reflux temperature. Following this, the cooled reaction mixture underwent concentration using a rotary evaporator, and the aqueous layer was separated by the addition of CH_2Cl_2. Anhydrous sulfuric acid was subsequently introduced to the CH_2Cl_2 solution to eliminate residual water, followed by further concentration to approximately 5 ml. Chromatographic separation was carried out employing a silica gel column with elution using CH_3OH and CH_2Cl_2 (V : V, 1:15). The resulting separated solution was further concentrated to yield a yellow-green powder with a 31% yield, which was then subjected to vacuum-drying for subsequent use.



Synthesis of Co_4O_4-ploy water oxidation co-catalyst.

$Co(NO_3)_2 \cdot 6H_2O$ (10 mmol) and $CH_3COONa \cdot 3H_2O$ (10 mmol) were first dissolved in a 250 mL two-necked flask containing 30 mL of methanol, and the mixture was then heated to reflux temperature. Subsequently, 10 mmol of 4,4'-bipyridine and 5 mL of hydrogen peroxide (30%) were added separately to the reaction mixture. The stirring persisted for 4 hours at reflux temperature, resulting in the formation of a distinct brown-yellow precipitate in the solution. This turbid suspension underwent suction filtration to eliminate CH_3OH and the aqueous solution, ultimately yielding a brown-yellow precipitate. Subsequent washing with water, CH_2Cl_2 and CH_3OH was carried out sequentially to remove any remaining $Co(NO_3)_2$, CH_3COONa, and 4,4'-bipyridine ligand. The final precipitate, obtained with a yield of 45%, underwent vacuum drying for subsequent use.



Fabrication of $BiVO_4$ photoanode.

In brief, 2.91 g of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 150 mL of deionized water containing 9.96 g of KI. The pH of the solution was adjusted to 1.7 by the addition of HNO_3. Subsequently, 60 mL of absolute ethanol containing 1.49 g of p-benzoquinone was introduced into the solution with vigorous stirring. Electrodeposition was performed using a CHI660 with a three-electrode setup, maintaining

the process at -0.1 V vs. Ag/AgCl for 5 minutes to create a layer of BiOI. Following this, 100 μL of a DMSO solution containing 0.23 M vanadium acetone oxide was applied onto the BiOI surface, and the sample was annealed at 450 ℃ (ramping rate = 2 ℃/min) for 2 hours. After annealing, the resulting photoanodes were immersed in 1 M NaOH solution under stirring for 30 minutes to dissolve V_2O_5. The $BiVO_4$ photoanode obtained was rinsed with deionized water and subsequently dried using nitrogen.

Fabrication of Co_4O_4/$BiVO_4$ and Co_4O_4-poly/$BiVO_4$ photoanode.

Weigh equal amounts of substances Co_4O_4 and Co_4O_4-ploy, dispersing them individually in methanol using ultrasonication to achieve even distribution. Next, apply equal volumes of the catalyst solutions separately onto a $BiVO_4$ electrode. Allow them to naturally air dry, rinse with water prior to use, and then dry them using nitrogen gas.

Photocatalytic performance measurement

The photocatalytic O_2 evolution reactions was carried out in a Labsolar-6A reactor (Beijing Perpectlight) and evacuation system using a 300 W Xe lamp (Ushio-CERMAX LX300) with an optical cut-off filter ($\lambda \geqslant 420$ nm). The photocatalyst (0.1 g) was dispersed in 100 mL aqueous solution contained $NaIO_3$ (5.0 mM) in a pyrex reaction cell and thoroughly degassed by evacuation in order to drive off the air inside. The evolved O_2 was quantified using an online gas chromatograph with argon (Ar) as the carrier gas. Samples were collected at 30-minute intervals to compare the O_2 production of different photocatalysts.

Photoelectrochemical (PEC) measurement.

PEC experiments were conducted in a three-electrode electrochemical cell using a CHI 660E instrument potentialstat (Shanghai Chenhua Instrument Co., Ltd.) at 25°C. The three-electrode system consisted of the as-prepared photoanode as the working electrode, a platinum tablet as the counter electrode, and a Ag/AgCl electrode as the reference electrode. A Xe lamp (CEL-HXF300C) equipped with an AM 1.5G-filter was used for photoanode irradiation, and the light intensity was calibrated to 100 mW/cm^2. The light irradiation was applied from behind the photoanode. J-V curves were obtained via linear sweep voltammetry at a scan rate of 20 mV/s. Typically, a 0.1 M phosphate buffer solution (PBS, pH 7) served as the electrolyte. The conversion between potentials vs. Ag/AgCl and vs. RHE was performed using the equation:

E (vs. RHE) = E (vs. Ag/AgCl) + 0.0591 V × pH + $E_{Ag/AgCl}$ (reference)

The applied bias photon-to-current efficiency (ABPE) was calculated from the J-V curve, where J is the photocurrent density, V_{bias} is the applied bias, and P_{in} is the incident illumination power density (AM 1.5G, 100 mW/cm^2),

$$ABPE = \frac{J \times (1.23 - V_{bia})}{P_{in}} \times 100\%$$

The photocurrent density arising from PEC water oxidation can be described as:

$$J_{H_2O} = J_{abs} \times \eta_{sep} \times \eta_{inj}$$

Here, J_{abs} denotes the photocurrent density when absorbed photons are fully converted into current, η_{sep} represents the charge separation efficiency of photogenerated holes, referring to bulk recombination, and η_{inj} signifies the charge transfer efficiency of surface-reaching holes into the electrolyte. By using Na_2SO_3 as a hole scavenger, surface recombination is eliminated (η_{inj} = 1), and

the photocurrent density can be described as:

$$J_{Na_2SO_3} = J_{abs} \times \eta_{sep}$$

So the η_{inj} can be described as:

$$\eta_{inj} = \frac{J_{H_2O}}{J_{Na_2SO_3}}$$

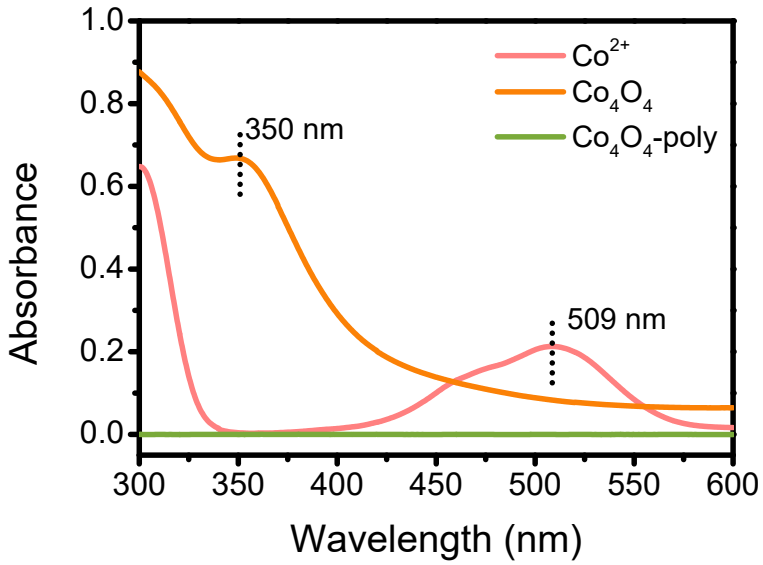


Figure S1. UV-vis spectra of water solutions containing Co^{2+} ions, Co_4O_4 molecules and Co_4O_4-poly (filtered the precipitate).

As shown in **Figure S1**, the water solution containing Co_4O_4 molecules exhibits obvious peaks at 350 nm. In contrast, the water solution containing Co_4O_4-poly, when the precipitate is filtered, shows almost no absorbance. This further confirms that Co_4O_4-poly lacks Co^{2+} ions and other soluble impurities.

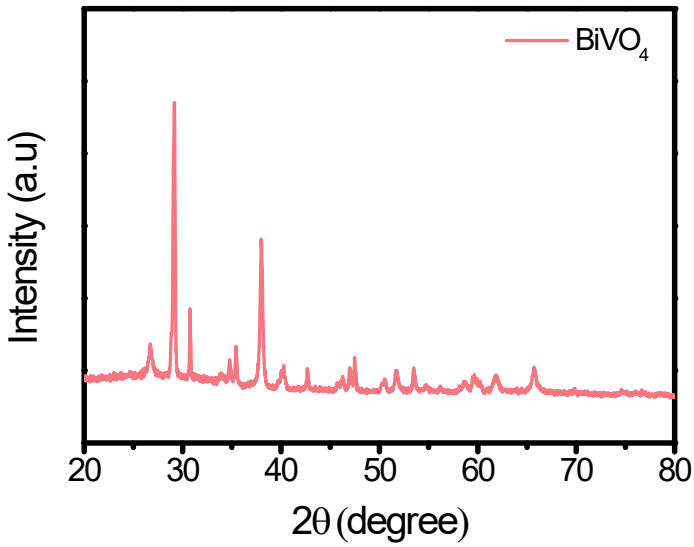


Figure S2. XRD pattern of $BiVO_4$.

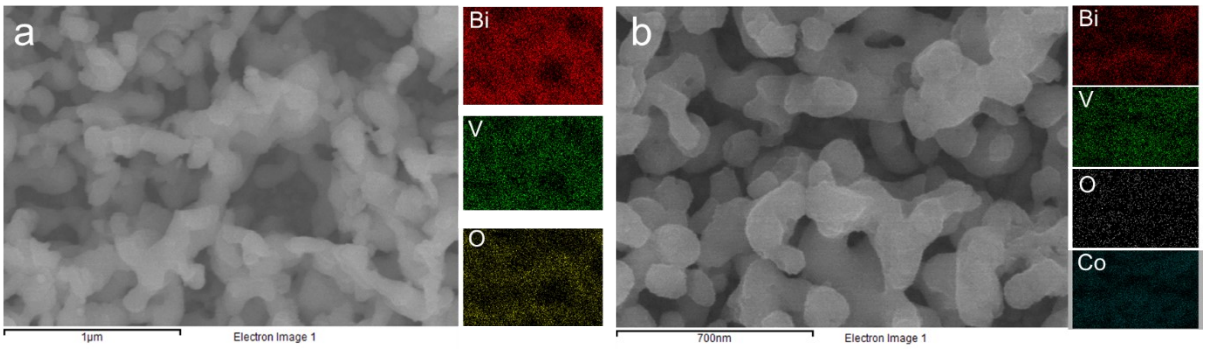


Figure S3. SEM and EDS-mapping images of (a) $BiVO_4$ and (b) $Co_4O_4/BiVO_4$.

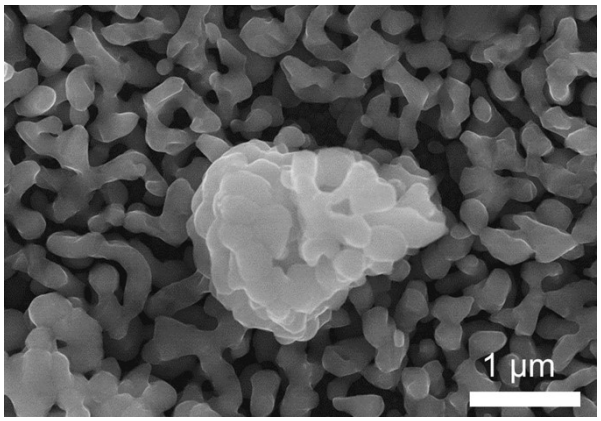


Figure S4. SEM image of Co_4O_4-poly/$BiVO_4$.

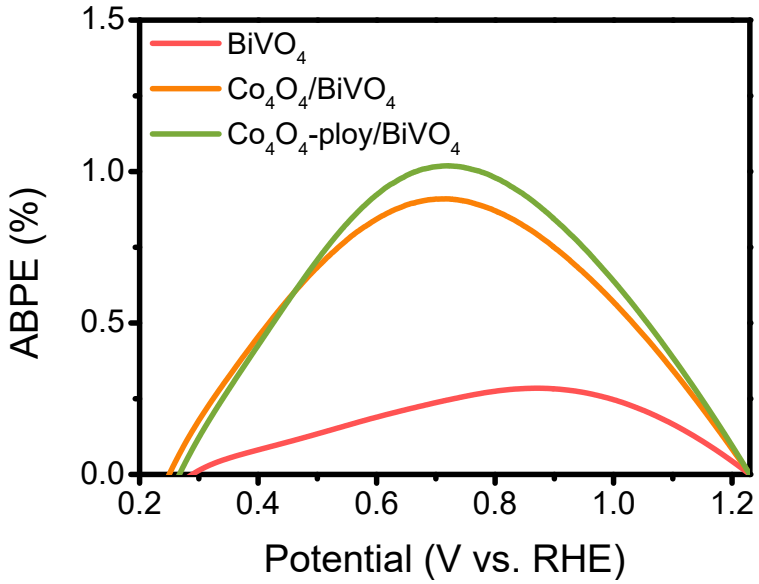


Figure S5. ABPE values of $BiVO_4$-based photoanods.

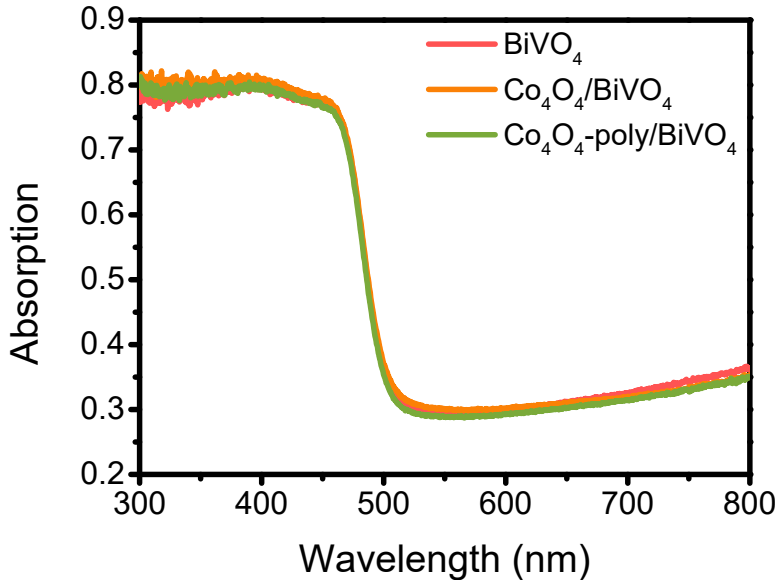


Figure S6. UV-vis spectra of $BiVO_4$-based photoanods.

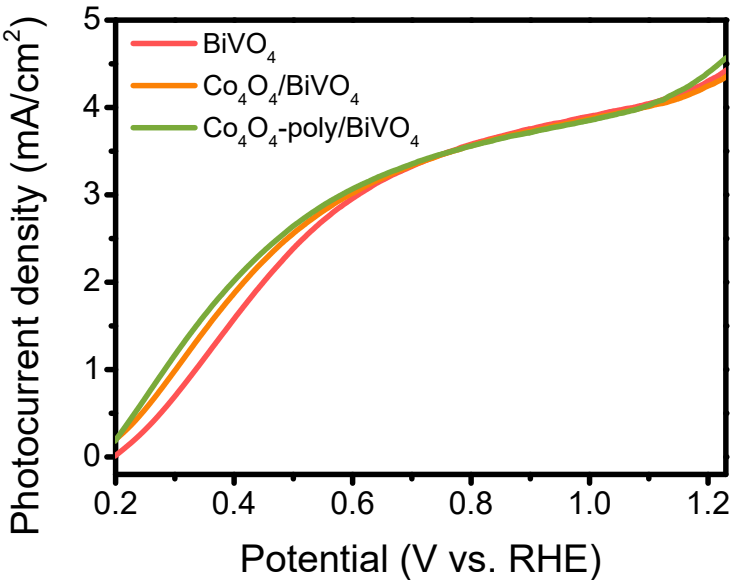


Figure S7. The LSV curves of $BiVO_4$-based photoanodes in Na_2SO_3.

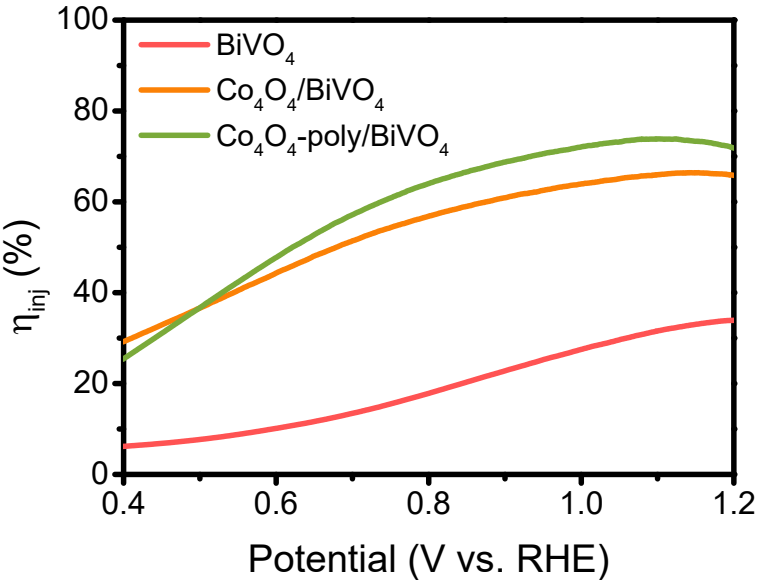


Figure S8. The charge injection efficiencies of $BiVO_4$-based photoanodes.

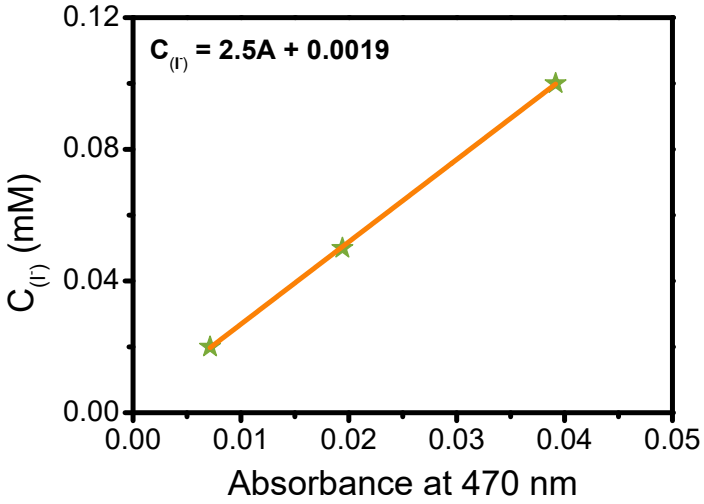


Figure S9. Calibration carve for the quantitative analysis of I- ion. (I_3^- ions, characterized by yellow absorbance (peak top: 470 nm), were generated by adding 5 mL of HNO_3 to 5 mL of sample solutions.)

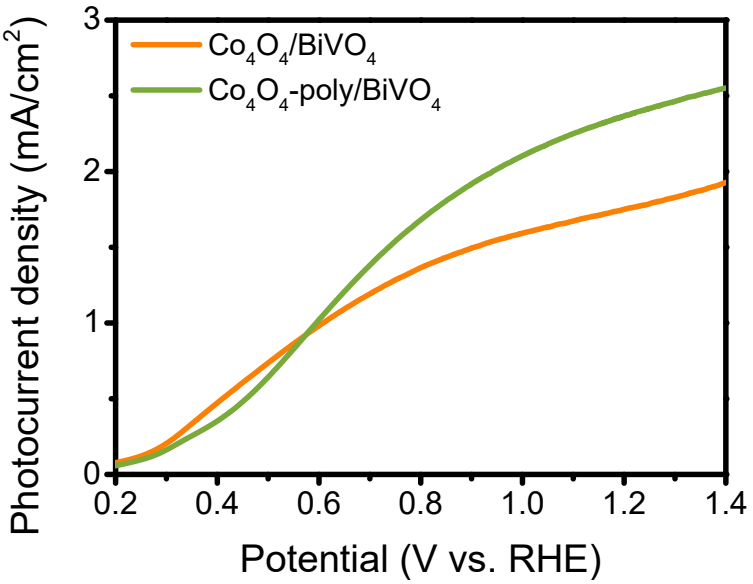


Figure S10. The LSV curves of $BiVO_4$-based photoanodes in D_2O.

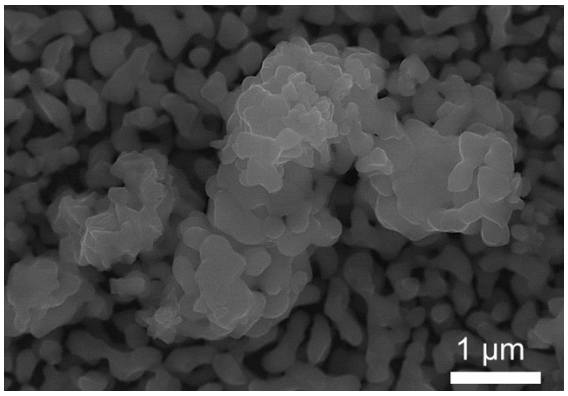


Figure S11. SEM image of Co_4O_4-poly/$BiVO_4$ after prolonged electrolysis.

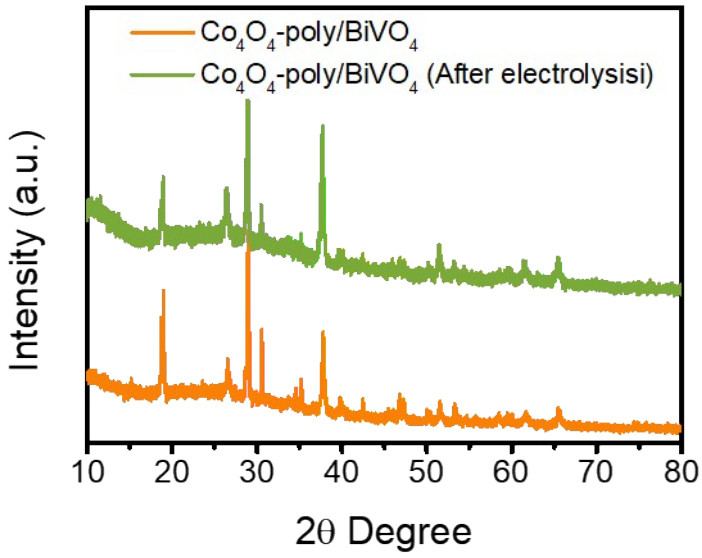


Figure S12. XRD patterns of Co_4O_4-poly/$BiVO_4$ before and after prolonged electrolysis.

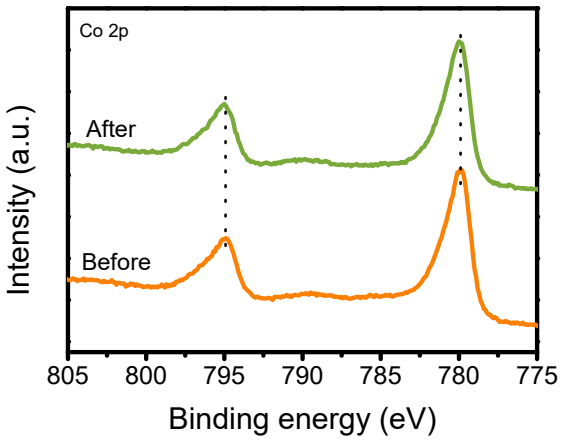


Figure S13. HR-XPS spectra of Co 2p for Co_4O_4-poly/$BiVO_4$ before and after prolonged electrolysis.

Table S1. PEC water oxidation performances of recently reported molecule/semiconductor hybrid photoanodes.

Photoanodes	Electrolyte	Photocurrent density (mA/cm^2 @ 1.23 V_{RHE})	References
(Co_4O_4)1h/$BiVO_4$	0.5 M borate buffer (pH 9.3)	5.0	[1]
Fe-PBI/$BiVO_4$	0.2 M borate buffer (pH 8.2)	1.3	[2]
Co_4O_4/$BiVO_4$	0.5 M borate buffer (pH 8)	3.3	[3]
Co2/$BiVO_4$	0.1 M PBS (pH 7.0)	4.3	[4]
Cobim/BVO-20	0.5 M Na_2SO_4 (pH 7)	3.1	[5]
Ni_4O_4/$BiVO_4$	0.2 M PBS (pH 7)	3.9	[6]
poly-1/Vpa/Al_2O_3/$BiVO_4$	0.1 M PBS (pH 7.0)	2.8	[7]
Co_4O_4-poly/$BiVO_4$	**0.1 M PBS (pH 7.0)**	**3.2**	**This work**

References

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