

## Immobilization of a molecular cobalt cubane catalyst on porous BiVO<sub>4</sub> via electrochemical polymerization for efficient and stable photoelectrochemical water oxidation

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### Materials and Methods

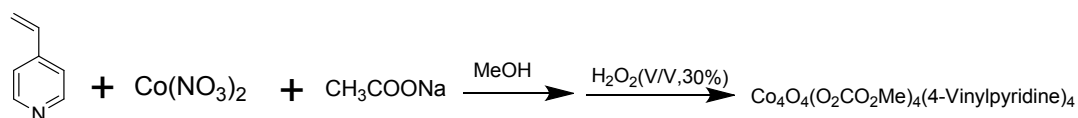
#### Materials.

Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, VO(acac)<sub>2</sub>, p-benzoquinone, o-phenylenediamine, salicylic aldehyde, 3,5-di-tert-butylsalicylaldehyde, Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, 4-vinylpyridine, tetrabutylammonium hexafluorophosphate and tetrabutyl titanate were purchased from Aldrich or Aladdin. All other reagents were commercially sourced and used without further purification. Glass slides coated with fluorine-doped tin oxide (FTO) purchased from Zhuhai Kaivo Optoelectronic Technology Co, Ltd. was cleaned by ultrasonication in ethanol, DI water, acetone and used as a substrate for the thin films. All other chemicals for the preparation of Co<sub>4</sub>O<sub>4</sub>(O<sub>2</sub>CMe)<sub>4</sub>(4-vinylpy)<sub>4</sub> and BiVO<sub>4</sub> are commercially available, and all solvents were reagent grade.

#### 1. Synthesis of 1.

Co<sub>4</sub>O<sub>4</sub>(O<sub>2</sub>CMe)<sub>4</sub>(4-vinylpy)<sub>4</sub> was prepared through a simple one pot reaction: Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.90 g, 10 mmol) and CH<sub>3</sub>COONa·3H<sub>2</sub>O (2.7 g, 20 mmol) were added in 30 mL methanol and heated to refluxing temperature, after 4-vinylpyridine (0.8 mL, 10 mmol) was added to the stirred reaction mixture. last a portion of 30% hydrogen peroxide (5 mL) was slowly dropped into the reaction mixture, continued for 4 h under refluxing conditions. The cooled

reaction mixture was concentrated in a rotary evaporator, and then the aqueous layer was separated out by adding dichloromethane to it. The light-pink aqueous layer was discarded, and the  $\text{CH}_2\text{Cl}_2$  layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . An olive-green compound precipitates on addition of petroleum ether to the dichloromethane solution. Fig S1 and Fig S2 are the  $^1\text{H-NMR}$  and MS of 1.  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ): 8.52 (d, 8H), 6.98 (d, 8H); 6.54 (q, 4H), 5.91 (d, 4H), 5.46 (d, 4H), 2.14 (s, 12H). MS (ESI):  $m/z^+ = 957.03$ .



Scheme S1. Structures and synthesis route of 1

## 2. Preparation of $\text{BiVO}_4$ electrode.

Briefly, Electrode position solutions was prepared as follow: 2.91 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 9.96 g KI were dissolved in 150 mL deionized water respectively before its pH was adjusted to 1.7 by adding  $\text{HNO}_3$ , then this solution was mixed with 60 mL of absolute ethanol (100%) containing 1.49 g *p*benzoquinone by stirred for a few minutes vigorously. A three-electrode cell was used for electrodeposition, with a FTO as the working electrode, an Ag/AgCl (3.5 M KCl) reference, and a platinum counter electrode. A CHI660 was used for electrodeposition studies. Deposition was carried out potentiostatically at -0.1 V vs Ag/AgCl for 5 min at 30 °C. All prepared films were rinsed by deionised water and then blow-dried with Nitrogen. 10 mL of a dimethyl sulfoxide (DMSO) solution containing 1.06 g vanadyl acetylacetonate ( $\text{VO}(\text{acac})_2$ ) was added onto the BiOI electrode. The BiOI electrodes were annealed at 450 °C (ramping rate = 2 °C/min) for 2 h. After annealing, the film was converted to crystalline  $\text{BiVO}_4$  and pure  $\text{BiVO}_4$  was obtained by dissolving the  $\text{V}_2\text{O}_5$  with 1 M KOH solution under stirring for several minates.

## 3. Preparation of $\text{Al}_2\text{O}_3/\text{BiVO}_4$ electrode

The  $\text{Al}_2\text{O}_3/\text{BiVO}_4$  electrode was synthesized as follow: the  $\text{BiVO}_4$  electrode was immersed into the solution containing 0.3 mL aluminum tri-sec-butoxide and 48.5 mL isopropanol, and maintained 0.5 h at 60 °C . After that, the electrode was taken out and heated in an oven at 200 °C for 1 h in air, obtaining the  $\text{Al}_2\text{O}_3$  thin layer coated  $\text{BiVO}_4$  electrode.

#### **4. Preparation of poly-1/BiVO<sub>4</sub> electrode**

The BiVO<sub>4</sub> electrode was carried into 0.5 mM 1 acetonitrile solution. Prior to the electrochemical polymerization, the solution was purged with nitrogen for about 20 min. An undivided three-electrode cell was used. Additional electrochemical polymerization was performed by applying -1.4 V vs. NHE (3.5 M KCl) for 50~150s. The obtained poly-1/BiVO<sub>4</sub> electrode was washed with acetonitrile, and drying at room-temperature.

#### **5. Preparation of poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode**

The as-prepared Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode was dropped into 10 mL acetonitrile contained 0.8 μL Vinylphosphonic acid for 2 h, then the electrode was taken out and blowed-dry by N<sub>2</sub>, obtaining the Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode. Next, the Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode was carried out 0.5 mM 1 acetonitrile solution, prior to the electrochemical polymerization, the solution was purged with nitrogen for 20 min. An undivided three-electrode cell was used. Additional electrochemical polymerization was performed by applying -1.4 V vs. NHE (3.5 M KCl) for 50~150s. The obtained poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode was washed with acetonitrile, and drying at room-temperature.

#### **6. Preparation of poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/Mo:BiVO<sub>4</sub> electrode**

The Mo:BiVO<sub>4</sub> electrode was prepared with the same methods of BiVO<sub>4</sub>, except for the solution contained vanadyl acetylacetonate was replaced by a mixture of VO(acac)<sub>2</sub> and MoO<sub>2</sub>(acac)<sub>2</sub> solution with the molar ratio of Mo:V=1:19 in dimethyl sulfoxide (DMSO) solution. And the poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/Mo:BiVO<sub>4</sub> electrodes was prepared as the same step 5 method.

#### **7. Preparation of poly-1/Vpa/TiO<sub>2</sub> electrode**

15 mL water, 15 mL concentrated HCl and 0.5 mL tetrabutyl titanate were mixed in a Teflon-lined stainless-steel autoclave and stirred for 15 min. The Kapton tape was also used to keep the exposed area of FTO glass to be 1 cm<sup>2</sup>. Then the FTO glass was put into the autoclave with the conductive side facing down. After, the autoclave was treated at 180 °C for 1 h. After the reactor cooled down naturally, the Kapton tape was torn off, and the FTO with white product was washed with water and alcohol, respectively, and dried naturally. Then the product was calcined in air at 500 °C for 2 h with the heating rate of 5 °C min<sup>-1</sup>. The prepared TiO<sub>2</sub> electrode was dropped into 10 mL acetonitrile contained 0.8 μL Vinylphosphonic acid for 2 h, then the electrode was taken out and blowed-dry by N<sub>2</sub>, obtaining the Vpa/TiO<sub>2</sub> electrode. the method for preparation of poly-

1/Vpa/TiO<sub>2</sub> electrodes is the same as route 4.

## Characterization

Scanning electron microscopy (SEM) images and energydispersive X-ray analysis (EDX) spectra of the films were obtained with a SU8000 Schottky field emission scanning electron microscope (SFE-SEM) equipped with a Rontec EDX system. Diffuse reflectance spectra of samples were obtained on a Lambda 35 UV-vis spectrophotometer, in which the sample electrode was placed in the centre of an integrating sphere to measure all light reflected and transmitted to accurately assess the absorbance. Element content was determined by an inductively coupled plasma mass spectroscopy (ICP, PE43008300). The evolved amount of oxygen and hydrogen were measured by GC (GC-6890A).

## Photoelectrochemical measurements

Electrochemical experiments were performed in a threeelectrode electrochemical cell with a CHI 660E instrument potentialstat (Shanghai Chenhua Instrument Co., Ltd.) at RT. In a three-electrode electrochemical system, the photoanodes were used as working electrodes, with an Ag/AgCl electrode (3 M KCl) as the reference electrode and a platinum wire as the counter electrode. The photoelectrodes were irradiated using a Xe lamp (CEL-HXF300C) equipped with an AM 1.5G-filtered illumination, and the light intensity was calibrated to 100 mW/cm<sup>2</sup>. The light irradiation came from the behind the photoelectrodes. J-V curves were obtained by linear sweep voltammetry with a scan rate of 20 mV/s. All measured potentials were converted to RHE. Generally, the electrolyte was a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 7). And the conversion between potentials vs. Ag/AgCl and vs. RHE is performed using the equation below

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

$$(E_{\text{Ag/AgCl}} (\text{reference}) = 0.1976 \text{ V vs. NHE at } 25 \text{ }^\circ\text{C})$$

The applied bias photon-to-current efficiency (ABPE) was calculated from the J-V curve,

where  $J$  is the photocurrent density,  $V_{\text{bias}}$  is the applied bias, and  $P_{\text{in}}$  is the incident illumination power density (AM 1.5G, 100 mW/cm<sup>2</sup>),

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

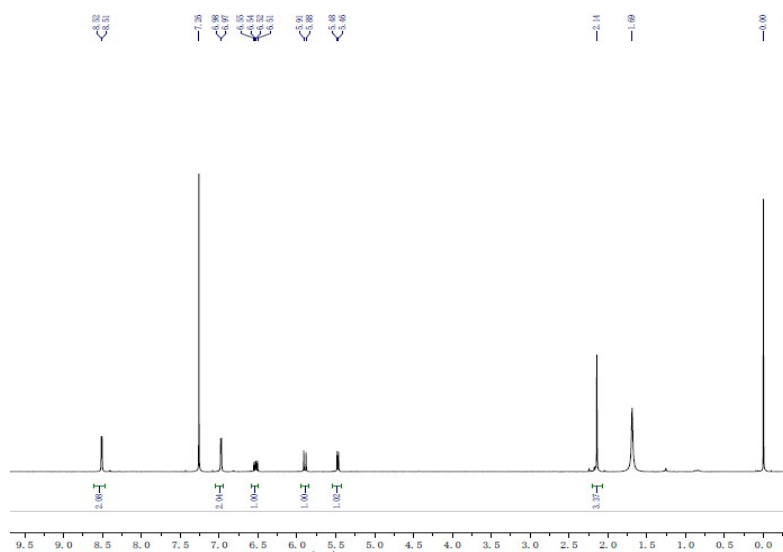
The photocurrent density arising from PEC water oxidation can be described as:  $J_{\text{H}_2\text{O}} = J_{\text{abs}} \times \eta_{\text{sep}} \times \eta_{\text{trans}}$ , where:  $J_{\text{abs}}$  is the photocurrent density when the absorbed photons completely convert into the current,  $\eta_{\text{sep}}$  is the charge separation efficiency of the photogenerated holes that refer to the bulk recombination, and  $\eta_{\text{trans}}$  is the charge injection efficiency of the surface reaching holes into the electrolyte. With Na<sub>2</sub>SO<sub>3</sub> as a hole scavenger, the surface recombination is eliminated,  $\eta_{\text{trans}} = 1$ , and the photocurrent density can be described as:  $J_{\text{Na}_2\text{SO}_3} = J_{\text{abs}} \times \eta_{\text{sep}}$ . So the  $\eta_{\text{trans}}$  can describe as  $\eta_{\text{trans}} = J_{\text{H}_2\text{O}} / J_{\text{Na}_2\text{SO}_3}$ .

Incident photon-to-current efficiency (IPCE) at each wavelength was determined by using illumination from a 300 W Xe arc lamp and neutral density filters to approximate the output of the sun. Monochromatic light was produced using an Oriel Cornerstone 130 monochromator with a 10-nm bandpass, and the output was measured with a photodiode detector. IPCE was measured at 0.6 V vs. RHE in 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 7) using the same three-electrode setup described above for photocurrent measurements.

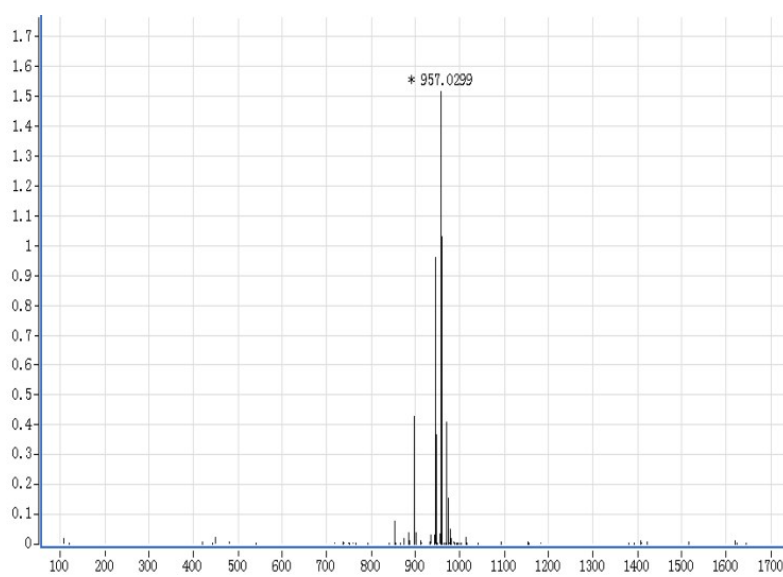
$$IPCE = \frac{1240 \times J}{\lambda \times P_{\text{in}}} \times 100\%$$

where  $J$  is the photocurrent density,  $\lambda$  is the incident light wavelength, and  $P_{\text{in}}$  is the measured irradiance.

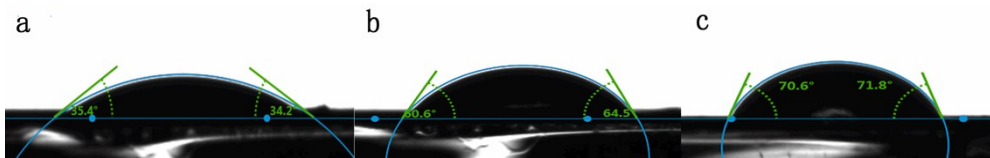
The evolved amount of O<sub>2</sub> and H<sub>2</sub> were measured by GC-6890A. Briefly, the poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode was inserted into undivided three-electrode cell containing 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution (pH 7), the solution was purged with nitrogen gas for about 30 min, so as to free air. then, illuminating through the FTO contact (back-side illumination) with 100 mW/cm<sup>2</sup> and applying 1.23 V vs. RHE (3.5 M KCl) for 4 h. The amount of H<sub>2</sub> and O<sub>2</sub> gas evolved was determined by taking 500  $\mu$ L of gas from the headspace of the cell using a syringe and injecting it into the gas-sampling loop of the GC every 30 min. Ar (Airgas, ultra high purity) was used as the carrier gas. Thermal conductivity detector (TCD) was used to quantify hydrogen and oxygen concentration.



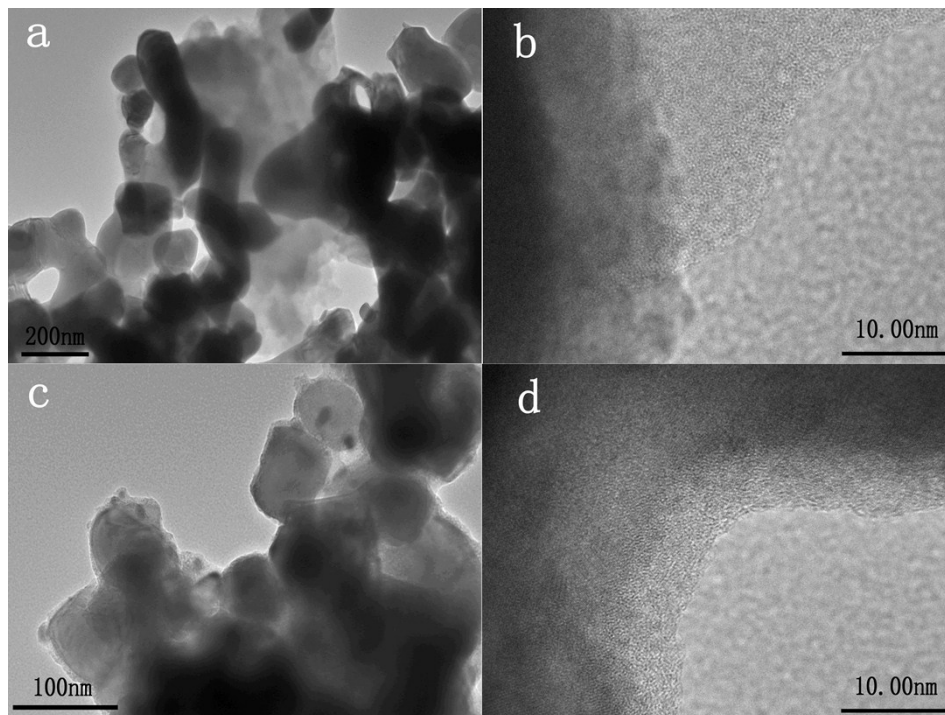
**Fig S1.**  $^1\text{H-NMR}$  spectrum of **1**



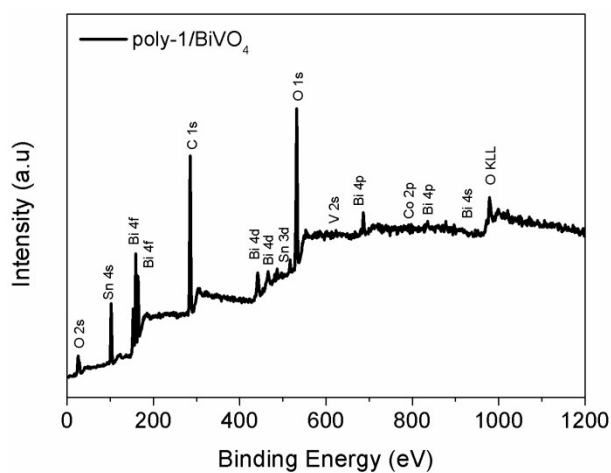
**Fig S2.** MS spectrum of **1**



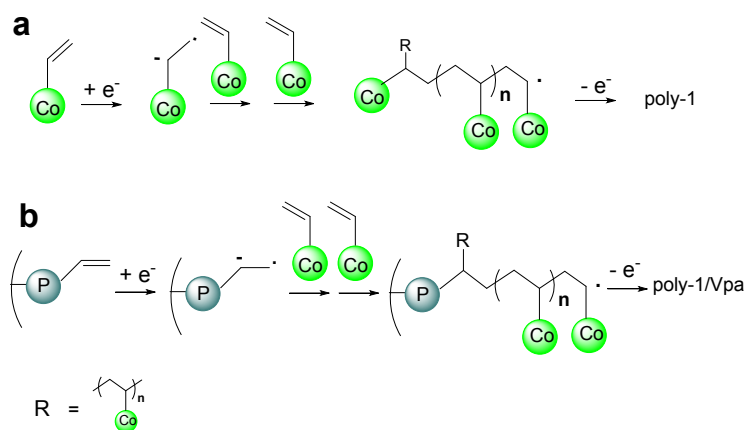
**Fig S3.** The contact angle images of (a)  $\text{BiVO}_4$ , (b) poly-1/ $\text{BiVO}_4$  and (c) poly-1/Vpa/ $\text{Al}_2\text{O}_3$ / $\text{BiVO}_4$ .



**Fig S4.** The high-resolution TEM images of poly-1/ $\text{BiVO}_4$  (a-b) and poly-1/Vpa/ $\text{Al}_2\text{O}_3$ / $\text{BiVO}_4$  electrodes (c-d).

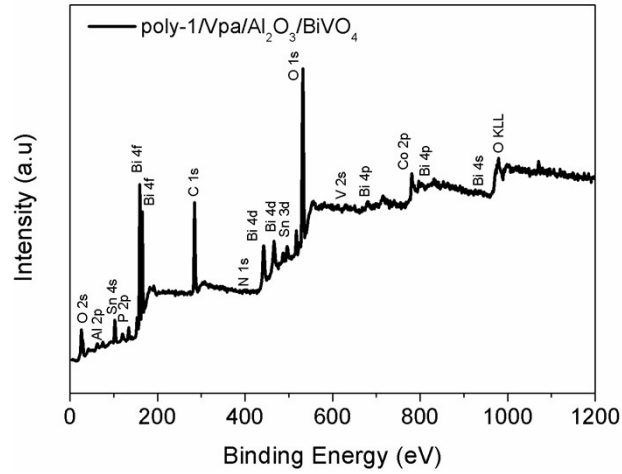


**Fig S5.** The XPS spectrum of poly-1/ $\text{BiVO}_4$  electrode.

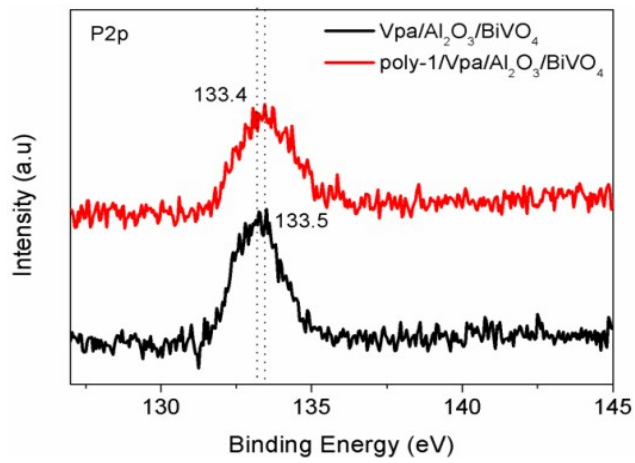


**Fig S6.** The electropolymerization mechanism of the poly-1/ $\text{BiVO}_4$  (a) and poly-1/Vpa/ $\text{Al}_2\text{O}_3$ / $\text{BiVO}_4$  (b) electrodes. (The mechanism of this electropolymerization process was reported by Meyer's group<sup>[1]</sup>)

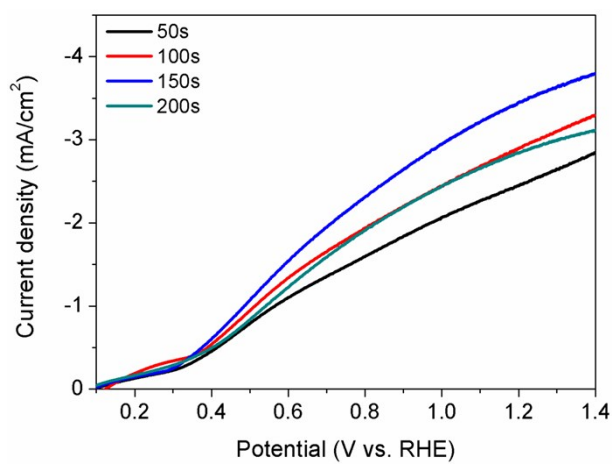




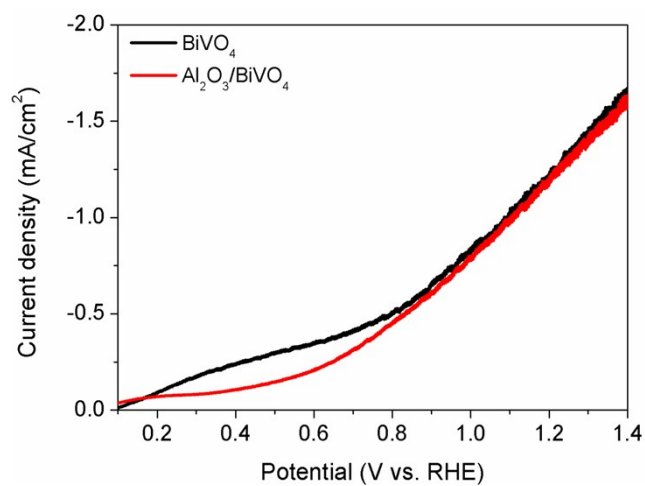
**Fig S7.** The XPS spectrum of poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode.



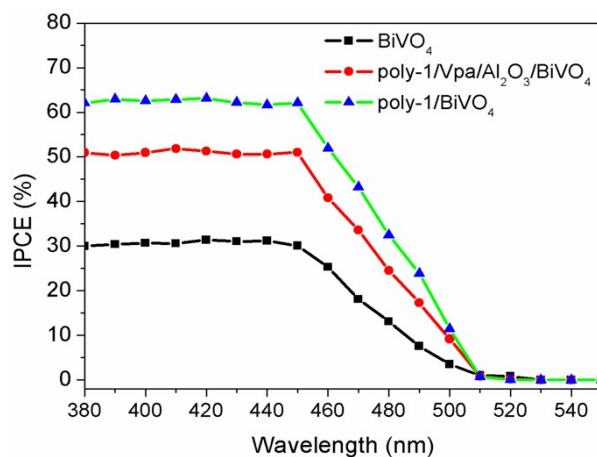
**Fig S8.** The HR-XPS spectra of P 2p of Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrodes.



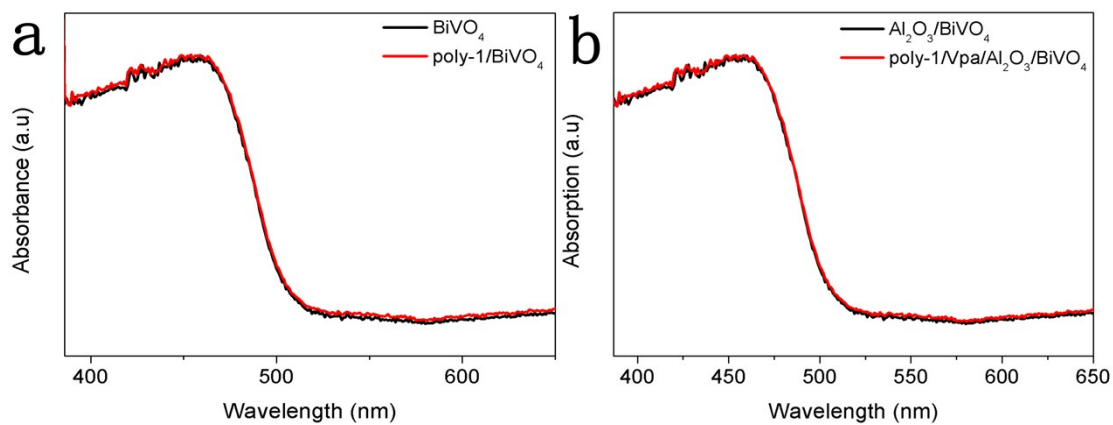
**Fig S9.** LSV curves of poly-1/BiVO<sub>4</sub> with different polymerization times.



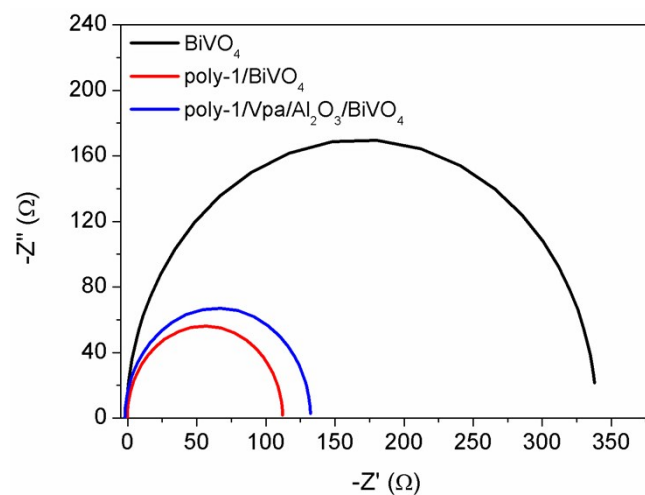
**Fig S10.** LSV curves of Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> and BiVO<sub>4</sub> electrodes.



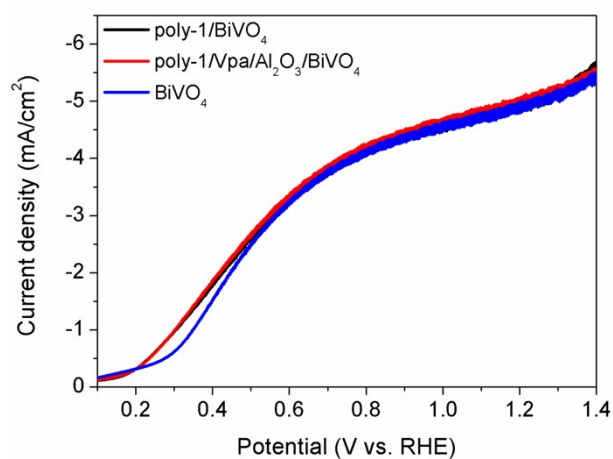
**Fig S11.** The IPCE values of BiVO<sub>4</sub>, poly-1/BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrodes.



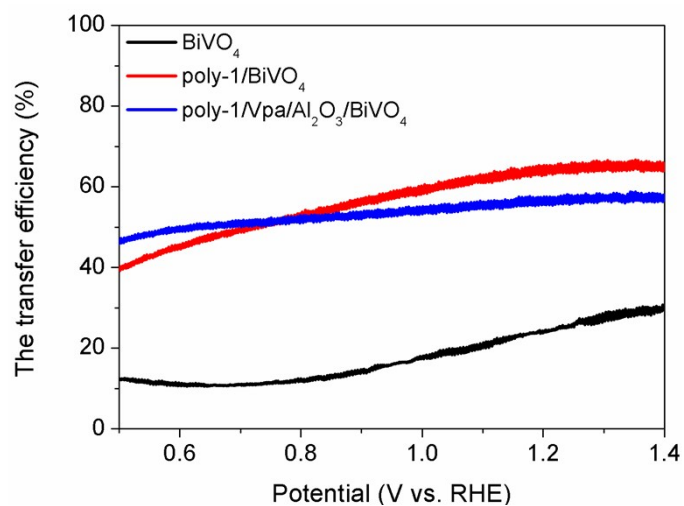
**Fig S12.** UV-vis absorption spectra of BiVO<sub>4</sub>, poly-1/BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrodes.



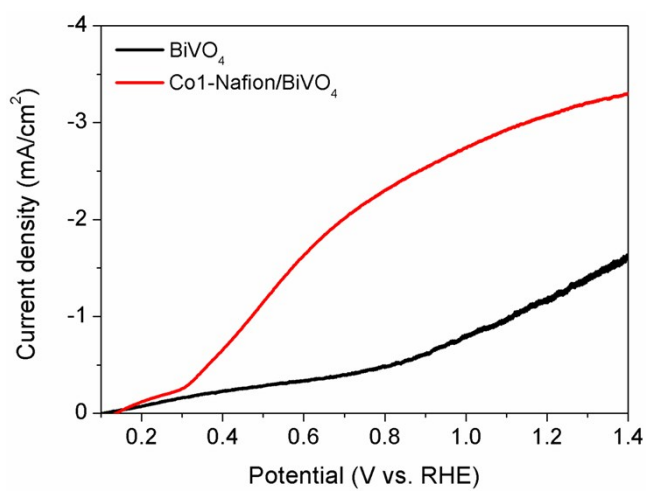
**Fig S13.** EIS spectra of the BiVO<sub>4</sub>, poly-1/BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrodes.



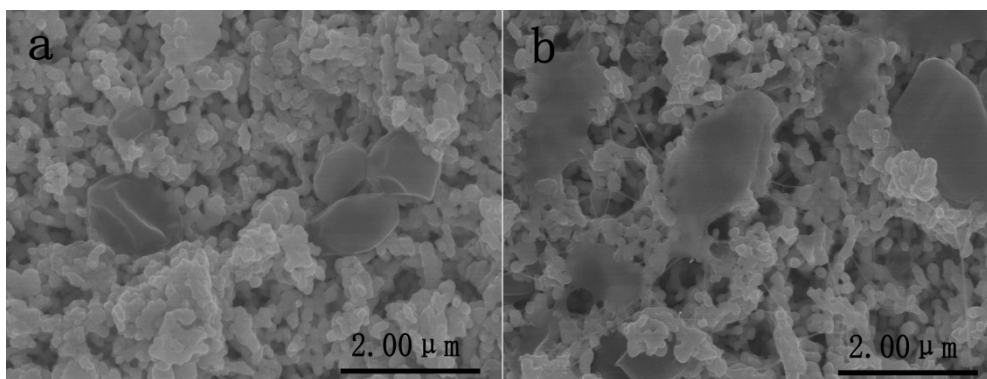
**Fig S14.** LSV curves of the BiVO<sub>4</sub>, poly-1/BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrodes.



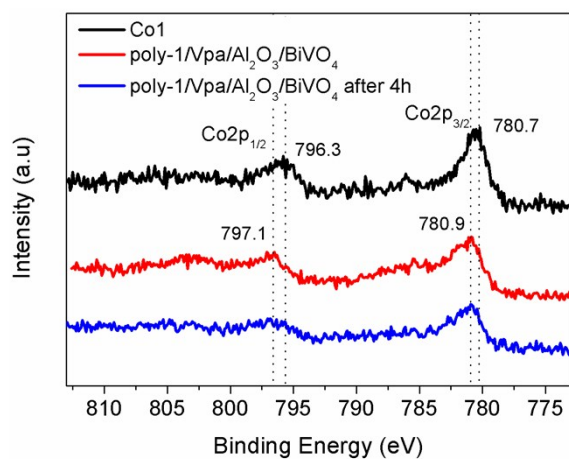
**Fig S15.** The charge transfer efficiencies of the  $\text{BiVO}_4$ ,  $\text{poly-1/BiVO}_4$  and  $\text{poly-1/Vpa/Al}_2\text{O}_3/\text{BiVO}_4$  electrodes.



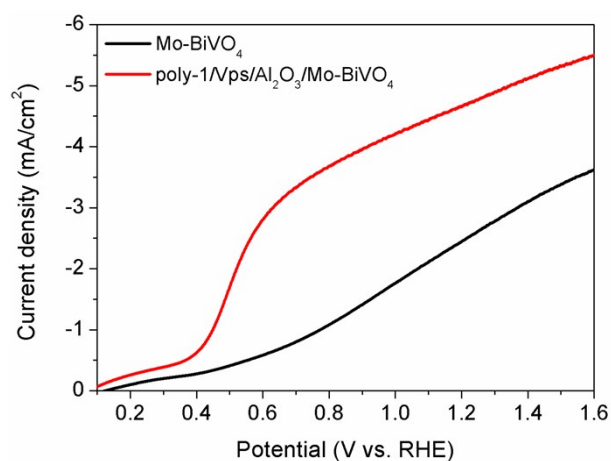
**Fig S16.** LSV curves of  $\text{BiVO}_4$  and  $\text{Co1-Nafion/BiVO}_4$  electrodes.



**Fig S17.** SEM images of poly-1/BiVO<sub>4</sub> (a) and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> (b) electrodes after 4 h i-t measurement at 1.23 V vs. RHE.



**Fig S18.** The HR-XPS spectra of Co 2p of Co catalyst and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/BiVO<sub>4</sub> electrode before and after 4 h irradiation.



**Fig S19.** LSV curves of Mo:BiVO<sub>4</sub> and poly-1/Vpa/Al<sub>2</sub>O<sub>3</sub>/Mo:BiVO<sub>4</sub> electrodes.

## References

- 1 a) Zhen Fang, S. Keinan, L. Alibabaei, Hanlin Luo, A. Ito and T. J. Meyer, *Angew. Chem. Int. Ed.*, 2014, **53**, 4872-4876; b) D. A. Torelli, D. P. Harrison, A. M. Lapidés and T. J. Meyer, *ACS Appl. Mater. Interfaces.*, 2013, **5**, 7050-7057.