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Visible Light Driven Overall Water Splitting with Cocatalyst/$BiVO_4$ Photoanode Assisted with the Minimized Bias

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Experimental details

1. Materials

All chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water (Millipore Milli-Q purification system, resistivity > 18 MΩ·cm). The FTO (fluorine-doped tin oxide) conductive glass was purchased from Nippon Sheet Glass Company (Japan) and was ultrasonic cleaned with acetone, ethanol and deionized water for 20 min each in sequence prior to use.

2. Fabrication of $BiVO_4$ and $CoB_i/BiVO_4$ electrodes

$BiVO_4$ electrodes were prepared by electrodeposition followed by an annealing procedure similar with that reported by Seabold et al.[1] Typically, 3.5 g $VOSO_4.xH_2O$ (≥ 98.5%, Shanghai Chemical) and 2.4 g $Bi(NO_3)_3.6H_2O$ (≥ 99%, Sinopharm Chemical) were dissolved in 425 mL 0.75 M HNO_3 solution. The pH value was raised to 5.1 with 102.5 g sodium acetate (≥ 99%, Tianjin Kemiou Chemical) and then adjusted to 4.7 with concentrated HNO_3 (65% ~ 68%, Tianjin Kemiou Chemical) and H_2O. A CH Instruments 760D potentiostat was used for the electrodeposition and all subsequent electrochemical studies. The electrodeposition was carried out potentiostatically at 1.9 V vs. Ag/AgCl for 40 min at 70 °C without stirring in a three-electrode cell with FTO working electrode, Ag/AgCl (saturated KCl) reference electrode and Pt counter electrode (2 cm × 4 cm). The solution seemes to be slightly turbid after electrodeposition at 70 °C. The adhension of the deposited film to FTO is better when the solution is heated and the solution turned completely turbid if the temprature is higher than 70 °C. The as-deposited films were rinsed and then annealed at 500 °C for 1 h in air with a ramping rate of 2 °C min^{-1}. Then it was immerged in 1 M KOH solution under stirring for 20 min to remove the V_2O_5 impurity.

$BiVO_4$ electrodes were loaded with CoB_i cocatalyst via electrodeposition method carried out in 0.2 M sodium borate buffer solution (pH 9) containing 30 μM Co^{2+}. Fresh solution was prepared for each experiment by dissolving $Co(NO_3)_2.6H_2O$ (≥ 99%, Sinopharm Chemical) to 0.2 M sodium borate solution (H_3BO_3 and $Na_2B_4O_7.10H_2O$, ≥99.5%, Sinopharm Chemical). The sodium borate buffer was prepared by mixing 800 mL 0.05 M $Na_2B_4O_7$ solution with 200 mL 0.2 M H_3BO_3 solution. A small amount of precipitate was observed following the dissolution of Co^{2+} source. Prior to use, this solution was passing through a 0.45 μm syringe filter to remove the microprecipitates. From the cyclic voltammetric scans of the solution, Co^{2+} was oxidized at 0.59 V vs. SCE (Fig. S1). So the deposition of CoB_i was carried out in a three-electrode cell at 0.59 V with $BiVO_4$ working electrode, saturation mercury reference electrode (SCE) and Pt counter electrode (2 cm × 4 cm). The loading amount of CoB_i was controled by the deposition time and the electric charge passed per geometric area, the deposition amount of CoB_i on $BiVO_4$ was 10 μC cm^{-2} (the corresponding depostion time was around 5 s and loading amount of Co was 0.01 wt % determined by ICP) unless otherwise stated. For comparison, CoB_i were electrodeposited on FTO substrate via the same procedure.

The I-t profile for the electrodeposition of $BiVO_4$ and CoB_i were given in Fig. S2.

For comparison, CoPi cocatalyst was loaded on $BiVO_4$ electrode via PEC deposition as described previously which was reported to be the most efficient loading method for CoPi cocatalyst[2,3]. The loading amount of CoPi was also optimized..

3. Characterizations of the electrodes

The prepared samples were characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer using Cu Kα radiation (operating voltage: 40 kV, operating current: 200 mA, scan rate: 5° min^{-1}). The UV−visible diffuse reflectance spectra (Fig. S3c) were recorded on a UV-visible spectrophotometer (JASCO V-550) and calibrated by Kubelka-Munk method. The morphologies and energy dispersive X-ray (EDX) of the electrodes were examined by a Quanta 200 FEG scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (accelerating voltage of 20 kV). X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG ESCALAB MK2 spectrometer with monochromatized Al Kα excitation (12.0 kV, 240 W).

4. PEC measurements

The photocurrents, EIS (Electrochemical Impedance Spectroscopy), IPCE (Incident Photon-to-current Efficiency), MS (Mott-Schottky) measurement were performed in a three-electrode setup with Pt counter electrode (2 cm × 3 cm) and SCE reference electrode with a scanning rate of 20 mV s^{-1}. For photocurrent measurement, the light source was a 300 W Xe lamp with an optical filter (Kenko, L-42; $\lambda > 420$ nm) unless otherwise stated, the light intensity at the surface of the electrode is 400 mW cm^{-2}. Prior to measurement, the areas of electrodes were fixed by insulating cement.

The EIS was recorded on an IM6ex electrochemical workstation (Germany, Zahner Company) from 100 mHz to 10 kHz at 0.4 V vs. SCE using a 140 W Xe lamp with an optical filter ($\lambda > 420$ nm) as light source.

The MS plots were measured on a PARSTAT2273 electrochemical workstation (Princeton Applied Research) in 0.2 M sodium borate (pH 9) electrolyte.

IPCE was measured using a monochromator (CROWNTECH QEM24-D 1/4 m Double) and the light intensity of each wavelength was measured using a hand-held optical power meter (Newport 70260, USA). IPCE values were calculated according to equation (1)[4]:

$$\mathrm{IPCE}(\lambda) = \frac{\text{electron flux}}{\text{photon flux}} = \frac{N_A\, j(\lambda)/F}{P_i(\lambda)/E(\lambda)} \tag{1}$$

where $j(\lambda)$ is the measured photocurrent (A), $P_i(\lambda)$ is the incident light intensity (W) for each wavelength, NA is the Avogadro constant, F is the Faraday constant and $E(\lambda)$ is the photon energy calculated by hc/λ.

5. Measurements of H_2 and O_2 evolution and Applied Bias Photon-to-current Efficiency

PEC water splitting reactions were carried out in a two-electrode cell connected to a closed gas circulation and evacuation system (Fig. S5). Typically, $BiVO_4$ (2 cm × 3 cm) working electrode and Pt counter electrode (3 cm × 3.5 cm) with a distance of 2 cm were immerged in 85 mL electrolyte. The system was thoroughly degassed and then irradiated by a 300 W Xe ($\lambda > 420$ nm) from the backside of $BiVO_4$ electrode. The electrochemical cell was maintained at 15 ± 2 °C by a cooling water bath during the reaction. Evolved O_2 and H_2 were analyzed by an online gas chromatograph with thermal conductivity detector (Agilent GC 7890, 5A zeolite column and Ar carrier gas).

The measurement of ABPE (Applied Bias Photon-to-current Efficiency) was performed in the same two-electrode system as mentioned above under simulated AM 1.5G solar light irradiation (100 mW cm^{-2}, Newport Sol3A Class AAA Solar simulator). The ABPE value was calculated according to the equation (2)[4,5]:

$$\mathrm{ABPE} = \left[\frac{j\,(\mathrm{mA/cm^2}) \times (1.23\,\mathrm{V} - V_b)}{P_i\ (\mathrm{mW/cm^2})}\right]_{\mathrm{AM1.5G}} \times 100\% \tag{2}$$

in which j (mA cm^{-2}) is the measured photocurrent density, V_b is the bias between the working electrode and counter electrode and P_i is the incident light intensity (100 mW cm^{-2}).

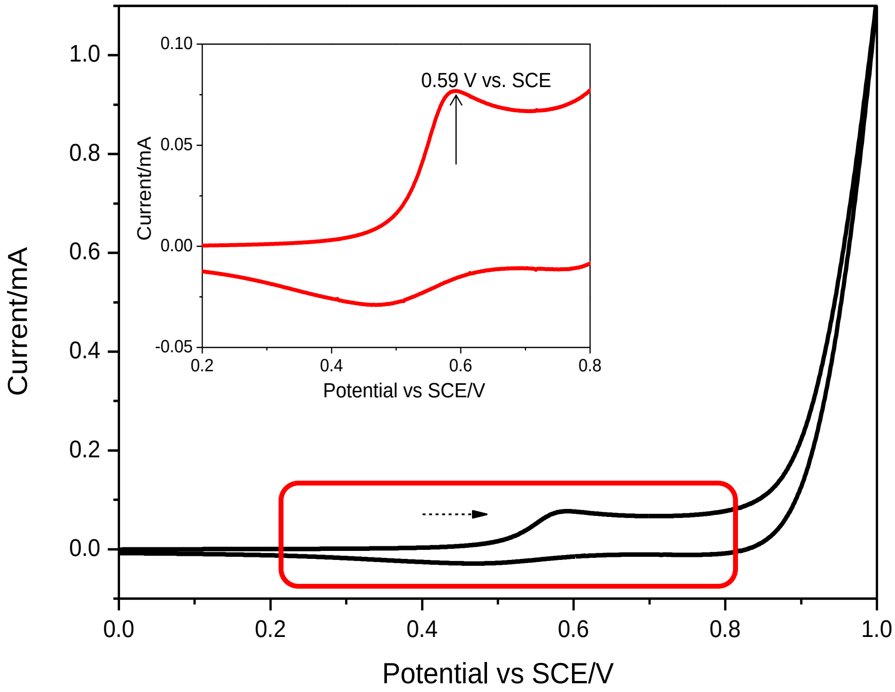

Fig. S1 Cyclic voltammetric scan of 0.2 M sodium borate solution at pH 9 containing 30 μM Co^{2+} in a three-electrode cell with a FTO working electrode, saturation mercury electrode (SCE) reference electrode and Pt counter electrode.

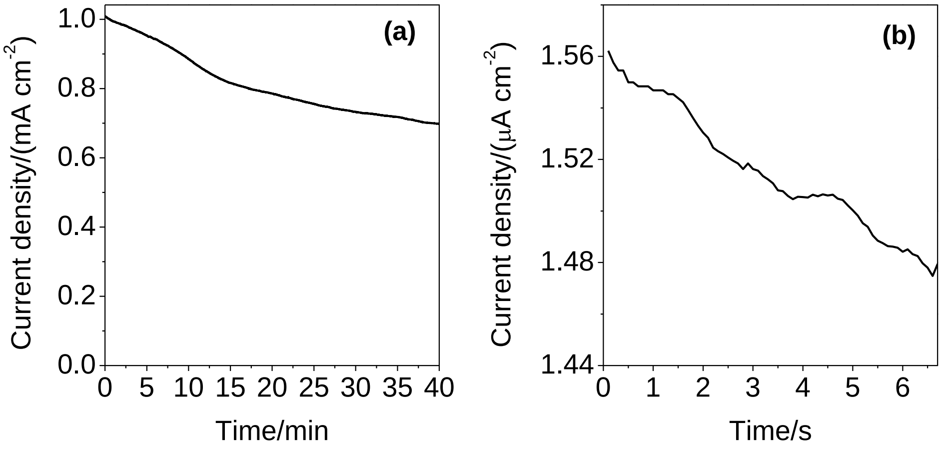

Fig. S2 The current-time profile for electrodeposition process of (a) $BiVO_4$ and (b)CoB_i

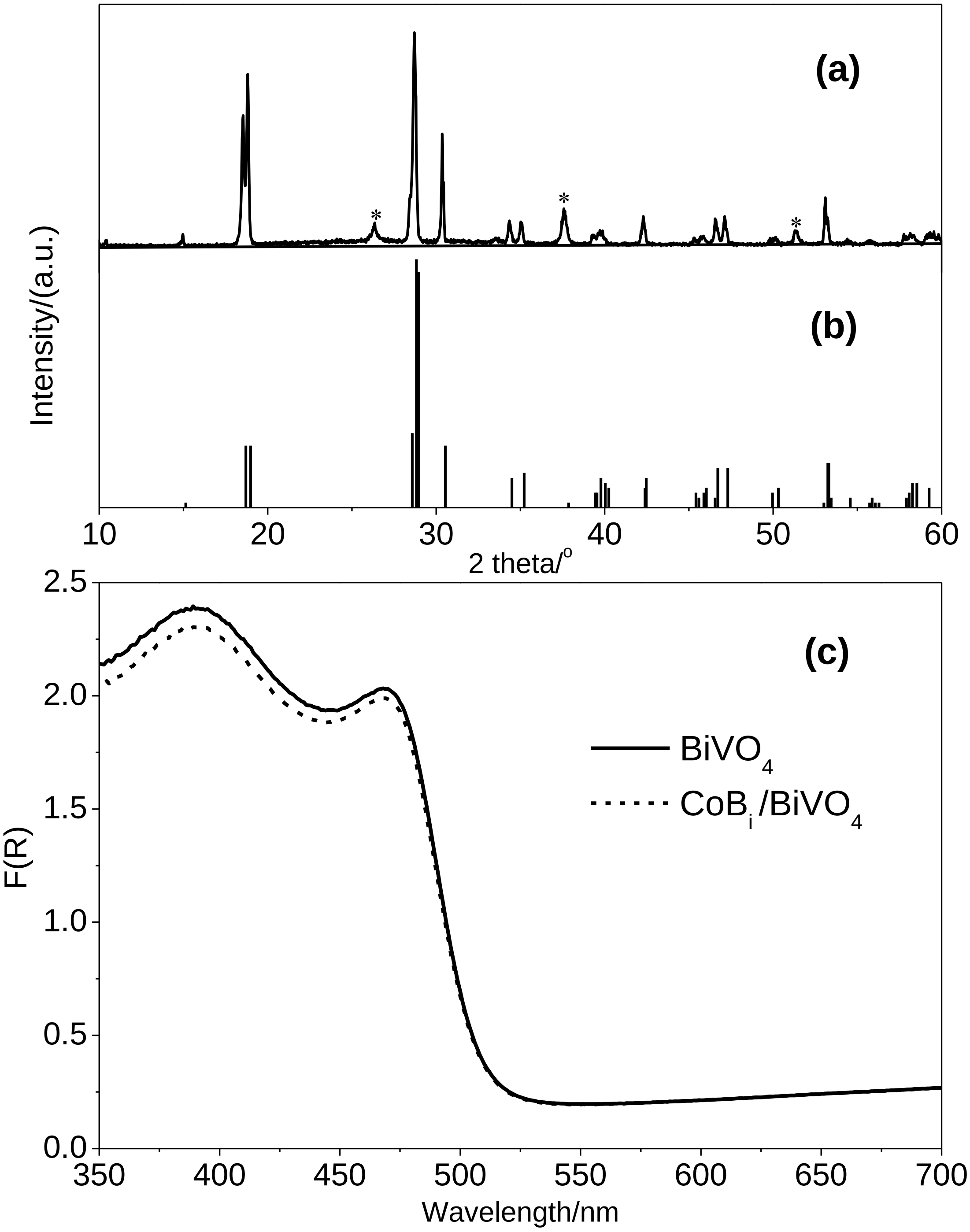

Fig. S3 (a) The XRD pattern of $BiVO_4$ electrode on FTO substrate (the peaks noted by * are FTO signals), (b) standard monoclinic $BiVO_4$ XRD pattern (PDF# 14-0688), and (c) UV-visible diffusion spectra of $BiVO_4$ and $CoB_i/BiVO_4$ electrodes.

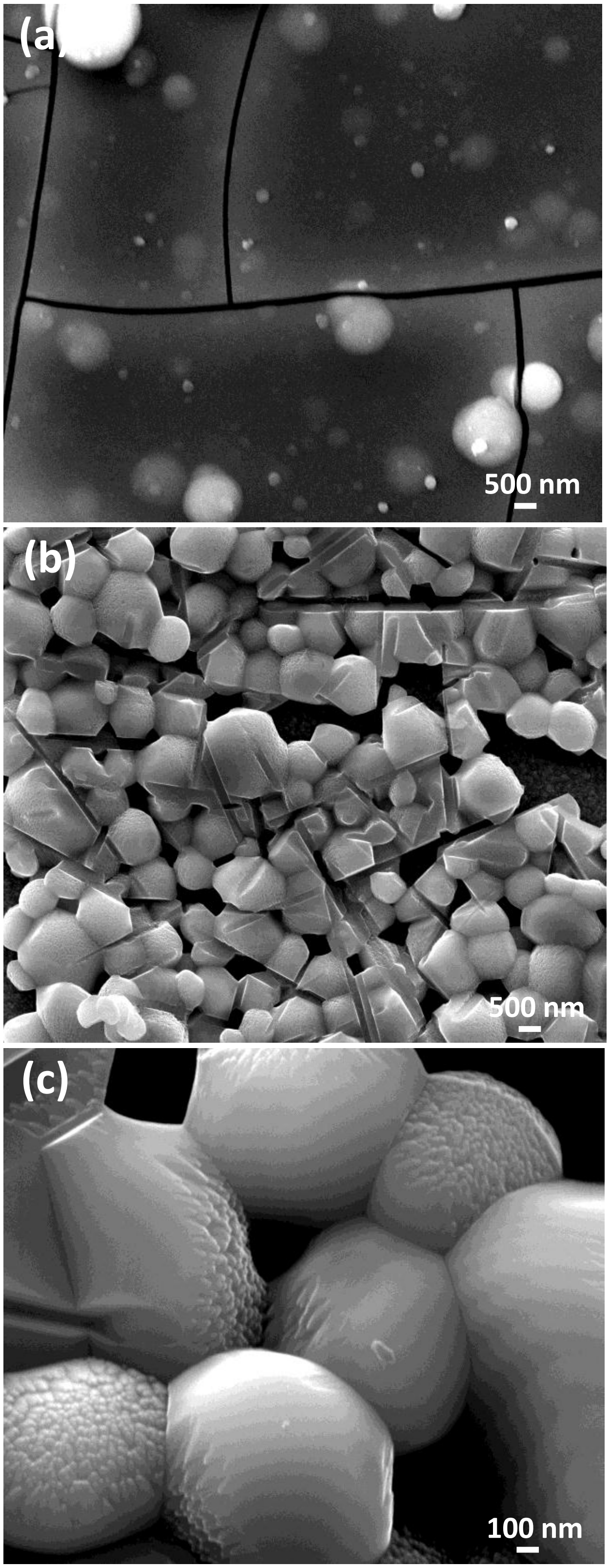

Fig. S4 SEM images of the electrodeposited film before (a) and after calcination (b, c)

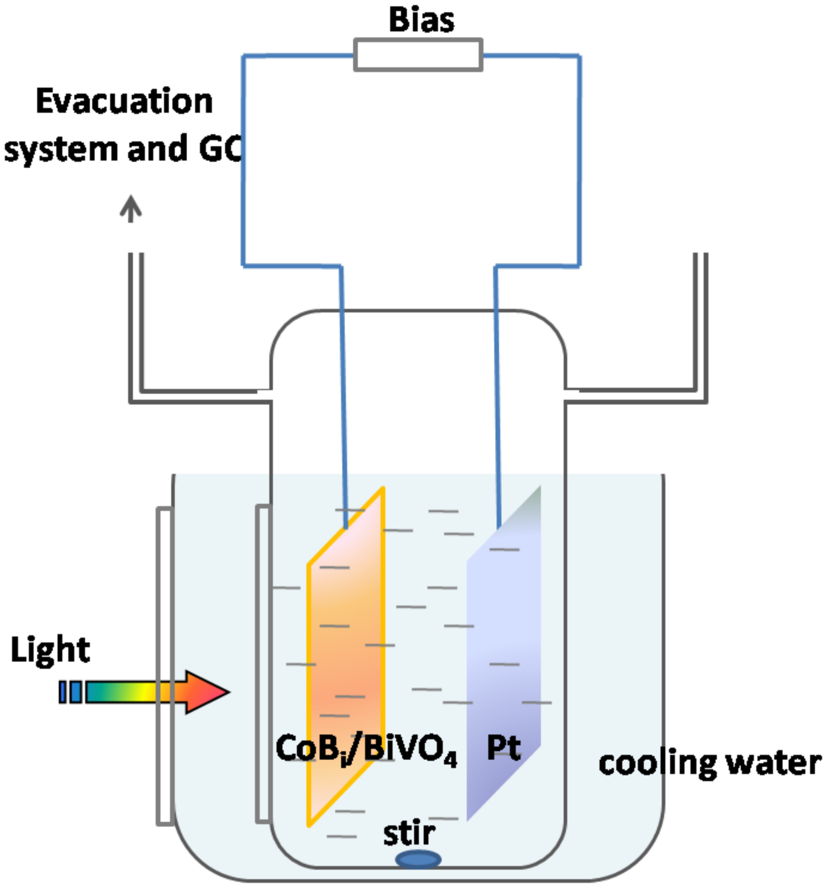

Fig. S5 A scheme of the setup for the PEC water spliting reaction and gas evolution determination

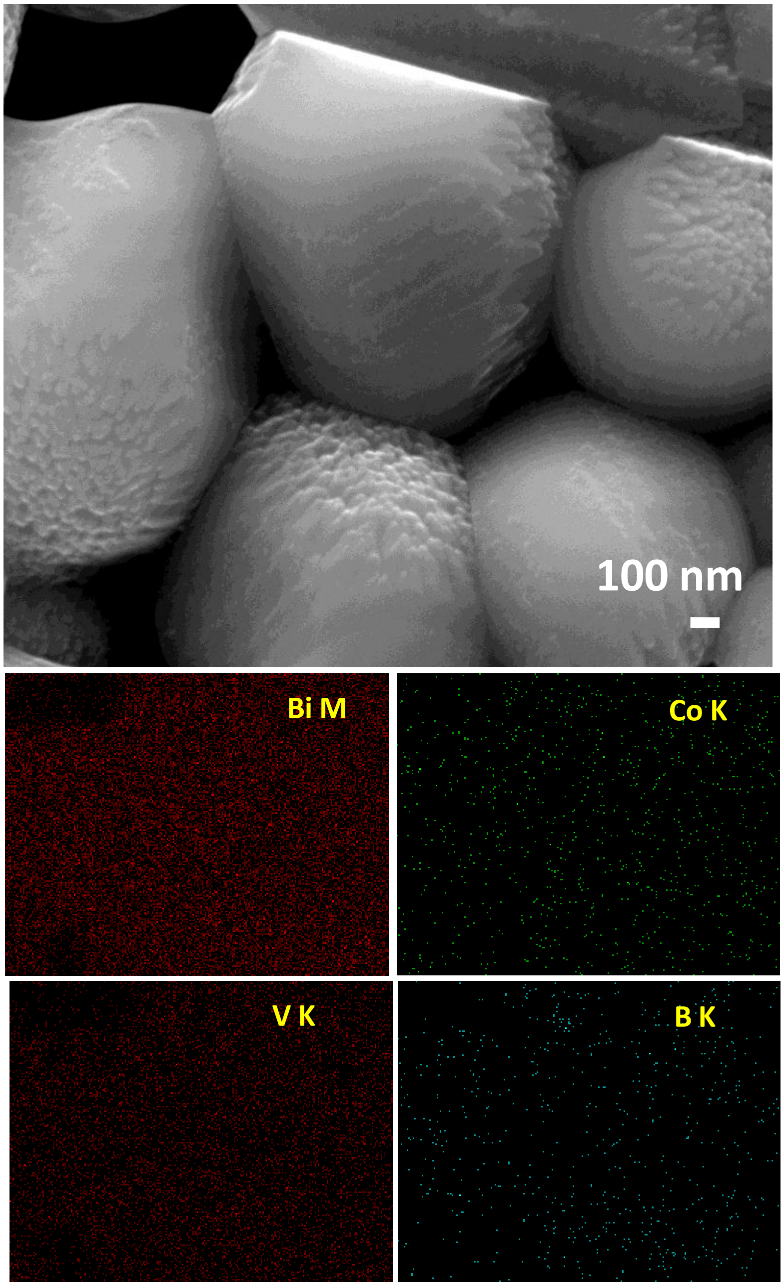

Fig. S6. SEM images of $CoB_i/BiVO_4$ electrode and the corresponding EDX maps investigated in the Bi M, V K, Co K, B K transition.

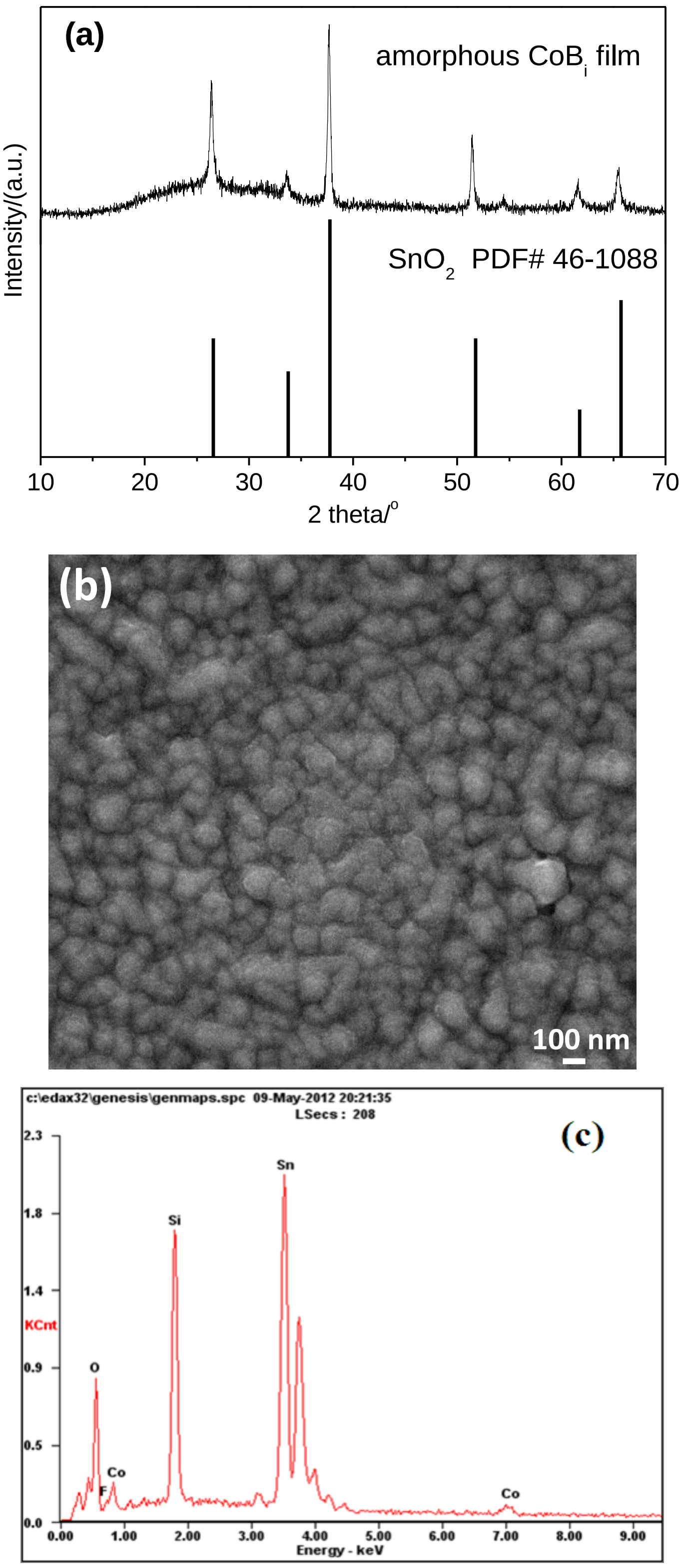

Fig. S7 (a) XRD pattern, (b) SEM image and EDX histogram of CoB$_i$ film electrodeposited on FTO substrate

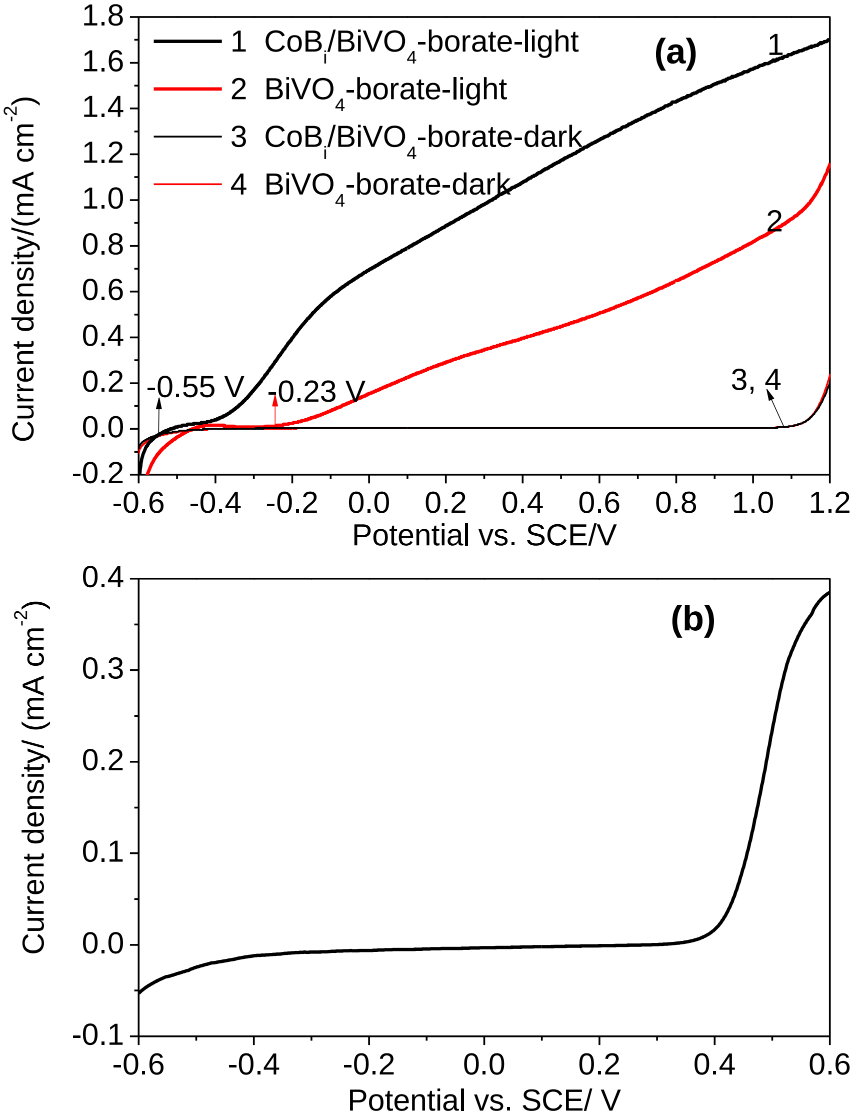

Fig. S8 (a) LSV scans of $BiVO_4$ and $CoB_i/BiVO_4$ photoanodes under Am 1.5G illumination without a shuttle and (b) LSV scan of CoB_i film under 300 W Xe lamp (λ > 420 nm) chopped light irradiation; Scanning rate: 20 mV s^{-1}; Electrolyte: 0.2 M sodium borate (buffered at pH 9)

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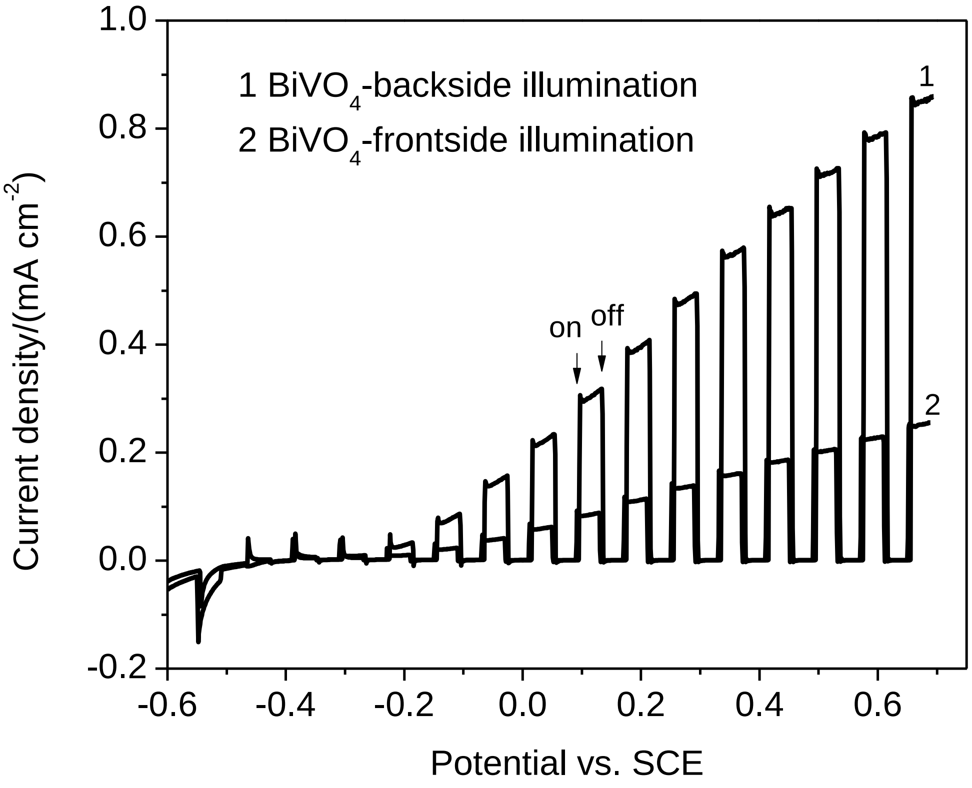

Fig. S9 (a) LSV scans of bare BiVO$_4$ photoanode under frontside and backside irradiation. Electrolyte: 0.2 M sodium borate electrolyte (pH 9); Light source: 300 W Xe lamp (λ > 420 nm); (b) A scheme of the setup for PEC water splitting reactions.

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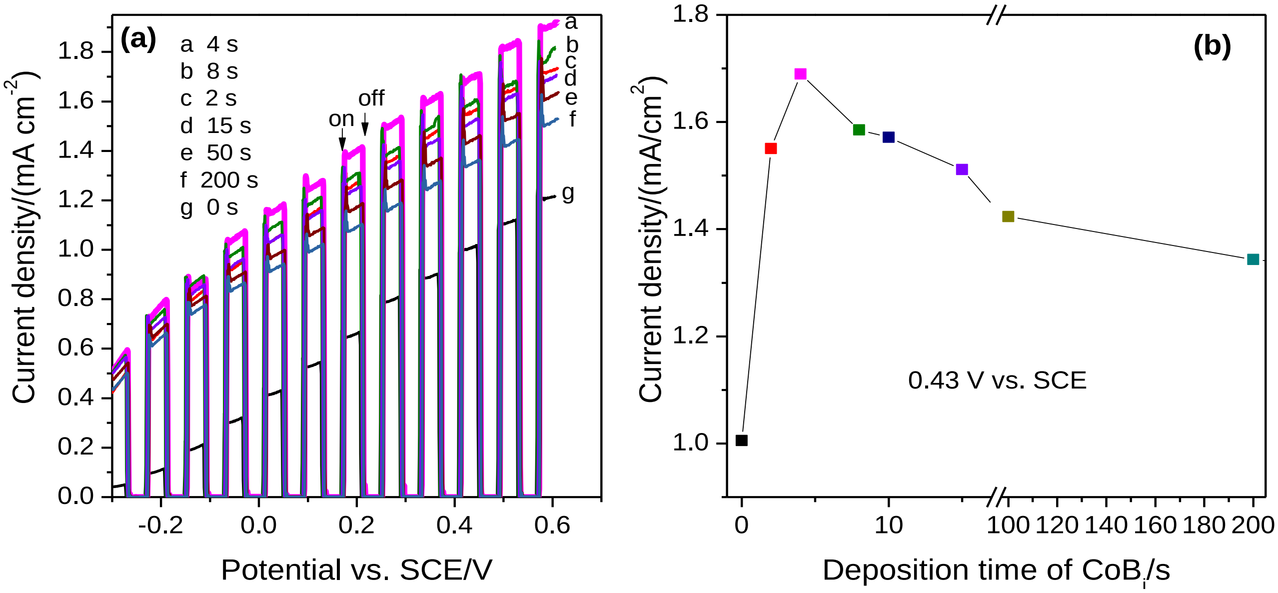

Fig. S10 (a) LSV scans of $CoB_i/BiVO_4$ photoanode with different deposition times of CoB_i under chopped light illumination and (b) the comparison of the photocurrent density at 0.43 V vs. SCE with different deposition time of CoB_i. Electrolyte: 0.2 M sodium borate electrolyte (pH 9); Light source: 300 W Xe lamp (λ > 420 nm).

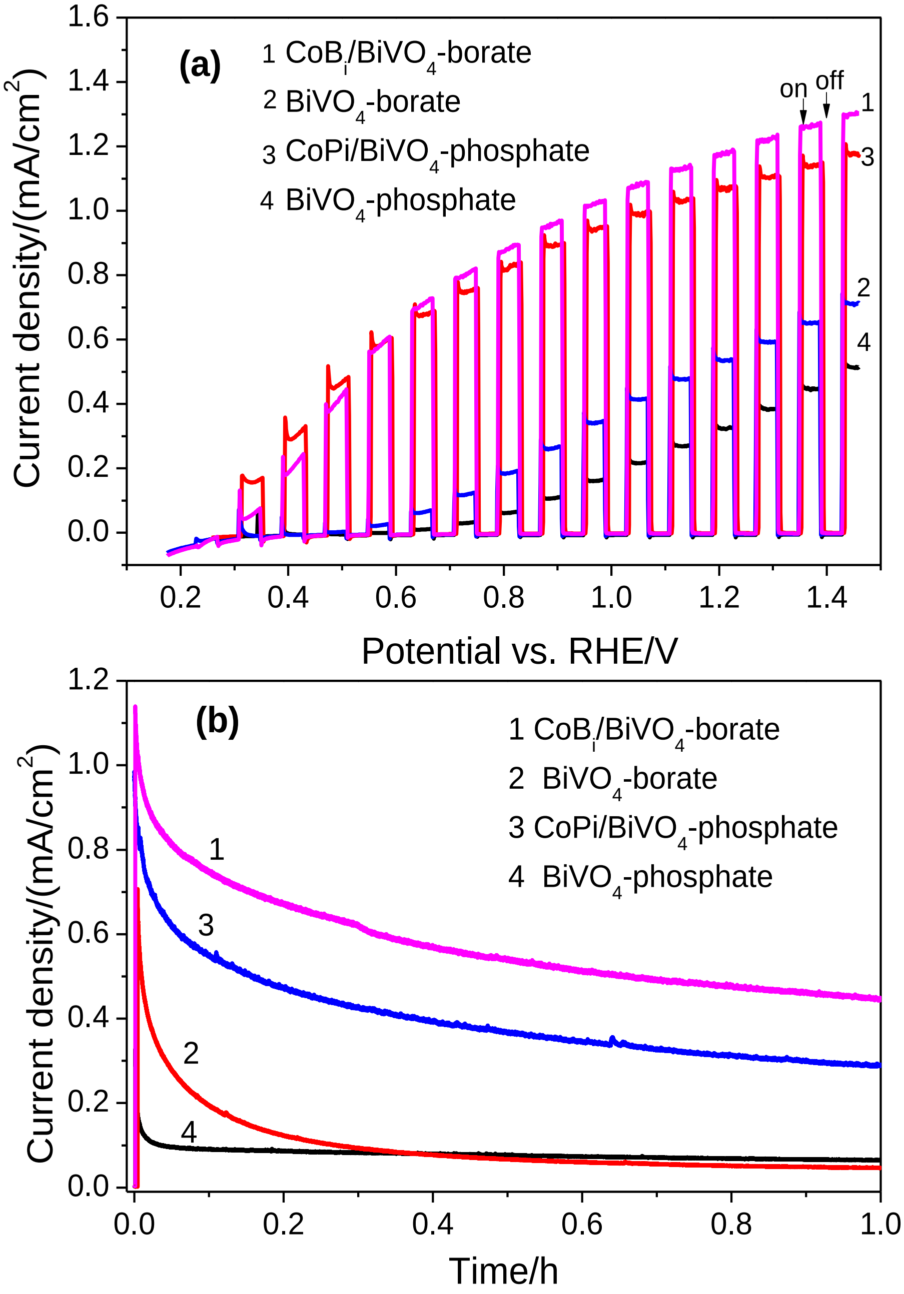

Fig. S11 (a) Linear sweep voltammetric scans and (b) amperometric i-t curves at 1.175 V vs. RHE of bare $BiVO_4$ and CoPi/$BiVO_4$ electrodes in 0.2 M sodium phosphate (buffered at pH 7), and bare $BiVO_4$ and CoB_i/$BiVO_4$ electrodes in 0.2 M sodium borate (buffered at pH 9) electrolyte; Light source: 300 W Xe lamp (λ > 420 nm); Scanning rate: 20 mV/s.

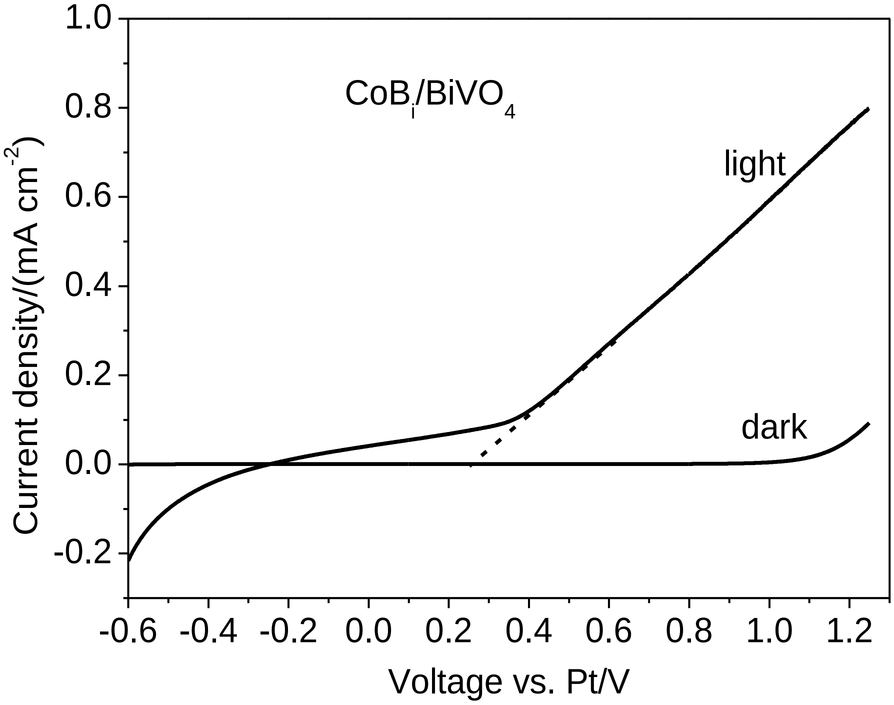

Fig. S12 LSV scans of CoB$_i$/BiVO$_4$ photoanode in a two-electrode system with Pt as counter electrode and reference electrode. Electrolyte: 0.2 M sodium borate electrolyte (pH 9); Light source: 300 W Xe lamp ($\lambda > 420$ nm).

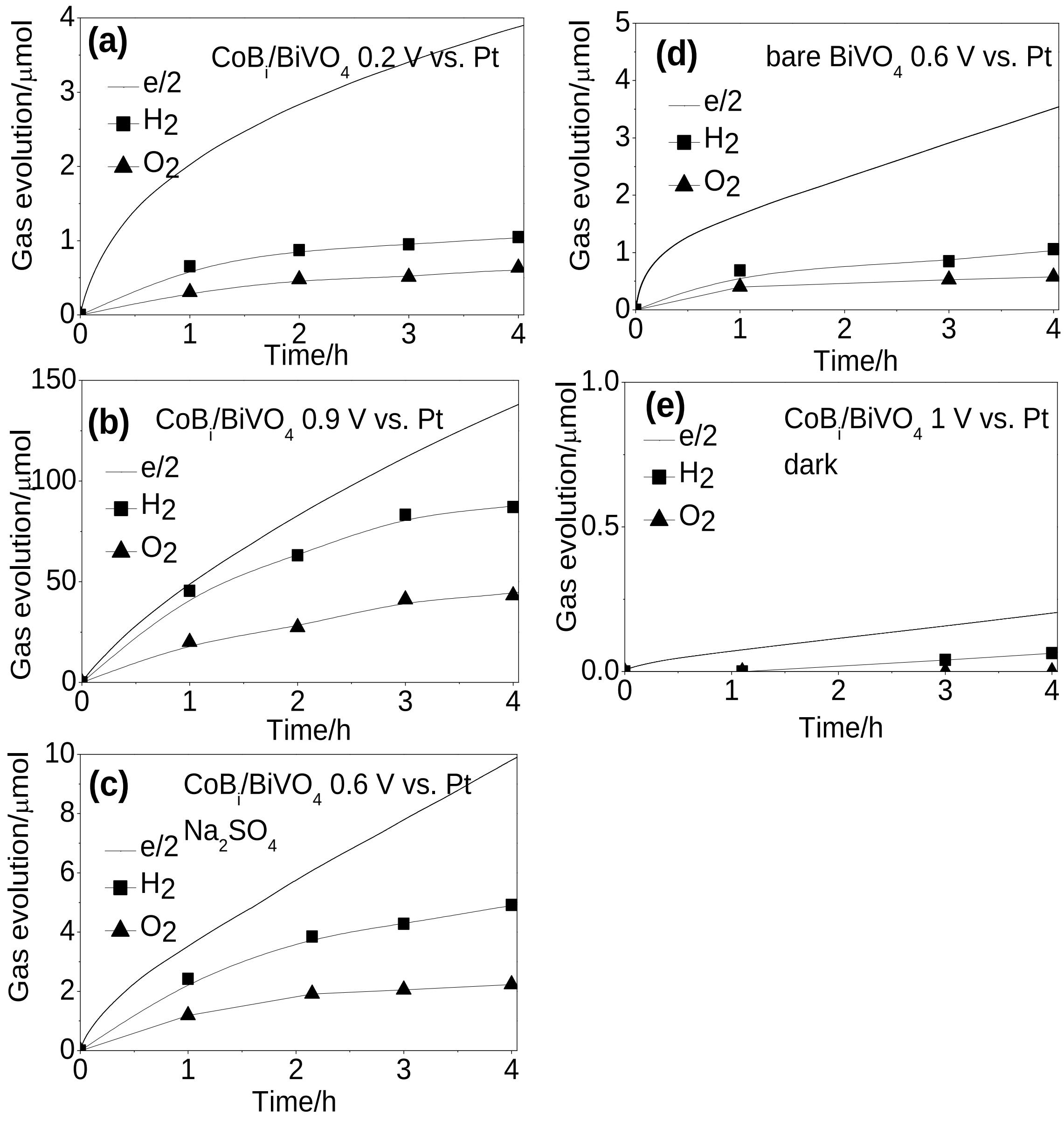

Fig. S13 Time courses of gas evolution (square dots: H_2, triangular dots: O_2) and the theoretical H_2 evolution amounts e/2 (solid lines) with CoB$_i$/BiVO$_4$ electrode under (a) 0.2 V, (b) 0.9 V vs. Pt in 0.2 M sodium borate (pH 9) and the control experiments of (c) CoB$_i$/BiVO$_4$ in 0.2 M Na_2SO_4 (pH 9), (d) bare BiVO$_4$ and (e) CoB$_i$/BiVO$_4$ in dark condition under a bias of 1 V in 0.2 M sodium borate (pH 9). Light source: 300 W Xe lamp (λ > 420 nm).

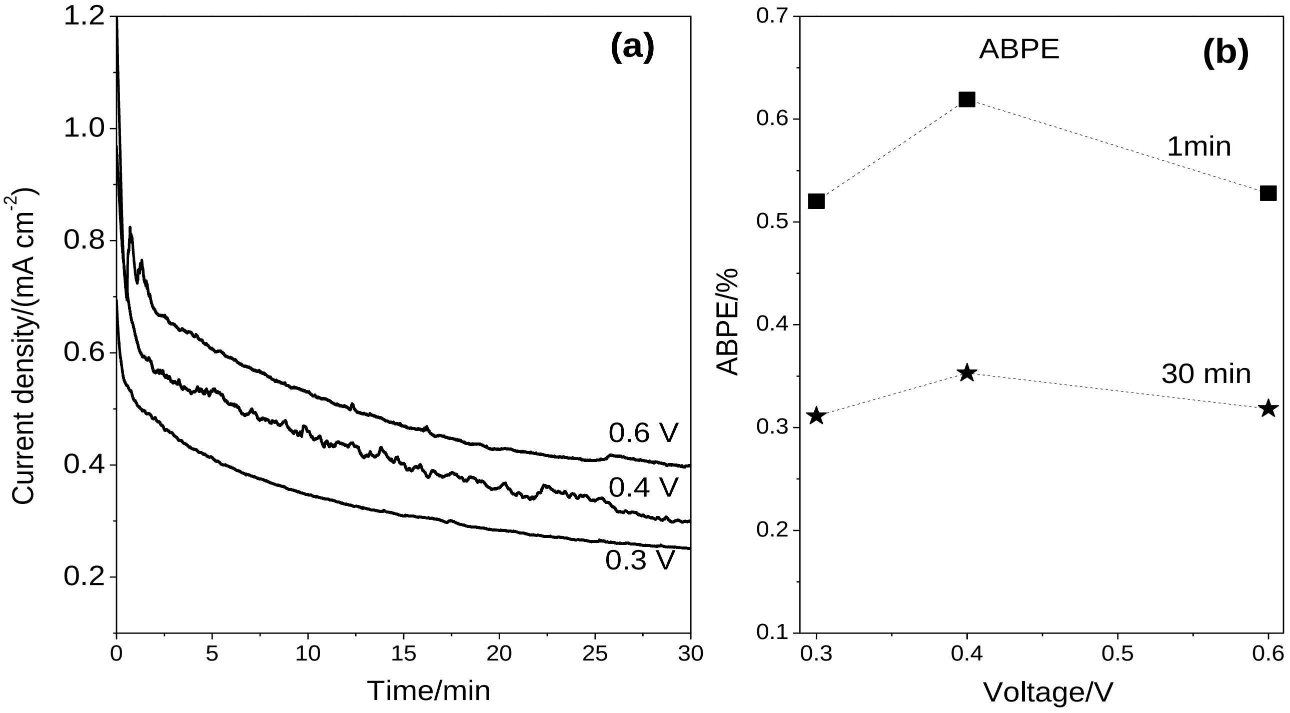

Fig. S14 Amperometric i-t curves of $CoB_i/BiVO_4$ photoanode under different biases vs. Pt counter electrode in 0.2 M sodium borate electrolyte (pH 9) and the corresponding ABPE (Applied Bias Photon-to-current Efficiency) calculated by the average photocurrent during 1 min and 30 min illumination. Light source: AM 1.5G sun light simulater.

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