Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information for

Highly conformal deposition of an ultrathin cobalt acetate on bismuth vanadate nanostructure for solar water splitting

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Reagents and Materials

Analytical grade $CoSO_4$, glacial acetic acid, CH_3COONa, KH_2PO_4, K_2HPO_4 (all from Sigma Aldrich) were used as received. All solutions were prepared in ultrapure water. The acetate buffer solution of pH 7.0 was prepared by mixing 0.1 M CH_3COONa and 0.1 M glacial acetic acid solutions. Similarly, the phosphate buffer solution was prepared by titrating 0.1 M KH_2PO_4 solution against 0.1 M K_2HPO_4 solution until the pH reached 7.0. Fluorine-doped tin oxide (FTO)-coated glass plate (15 Ω/sq.) of thickness 2.2 mm was used as the substrate.

The borate buffered (KB) solution used in stability measurement was prepared by dissolving 1.0M H_3BO_3 (Showa, 99.5%) in deionized water and adjusting the pH to be 9.3 using KOH (Duksan, 85%)

Fabrication of Porous $BiVO_4$ Photoelectrode

In the first step, nanoporous $BiVO_4$ (BVO) was grown on an FTO-coated glass following a previously reported method. Briefly, 0.97 g of $Bi(NO_3)_3$ was dissolved in 50 mL of a pH 1.7 HNO_3 solution. After the mixture was vigorously stirred for 30 min, 3.32 g KI was added to the solution at room temperature and the mixture was stirred for another 15 min. This solution was mixed with 20 mL of absolute ethanol containing 4.6 mmol of *p*-benzoquinone. Electrodeposition was carried out in a typical three-electrode system at –0.1 V vs Ag/AgCl for 5 min to obtain the BiOI electrode, which was rinsed with ethanol and dried at 60 °C in the air. $BiVO_4$ electrodes were prepared by placing 65 μL of a dimethyl sulfoxide solution containing 0.2 M vanadyl acetylacetonate ($VO(acac)_2$) on the BiOI electrodes, followed by heating in a muffle furnace at 450 °C (ramping rate 2 °C/min) for 2 h. After being cooled to room temperature, the electrodes were soaked in 1 M NaOH solution for 15 min to remove the excess V_2O_5. The obtained pure $BiVO_4$ electrodes were rinsed with deionized water and dried in air (denoted as BVO).

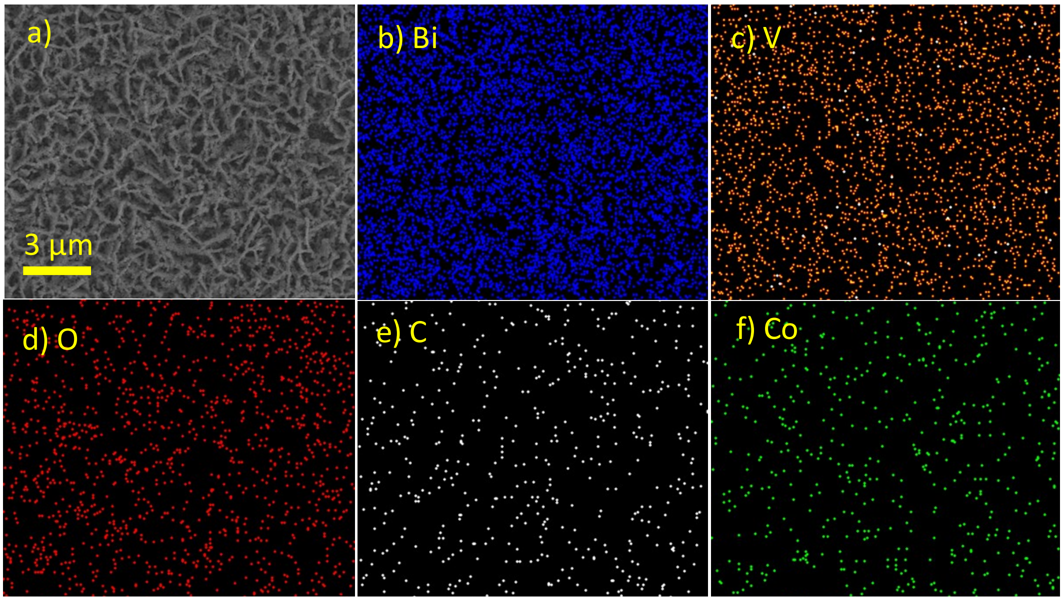

Figure S1 SEM and EDS mapping of Co-Ac on BVO surface. a) SEM image of the examined area. EDS mapping of b) Bi, c) V, d) O, e) C and f) Co.

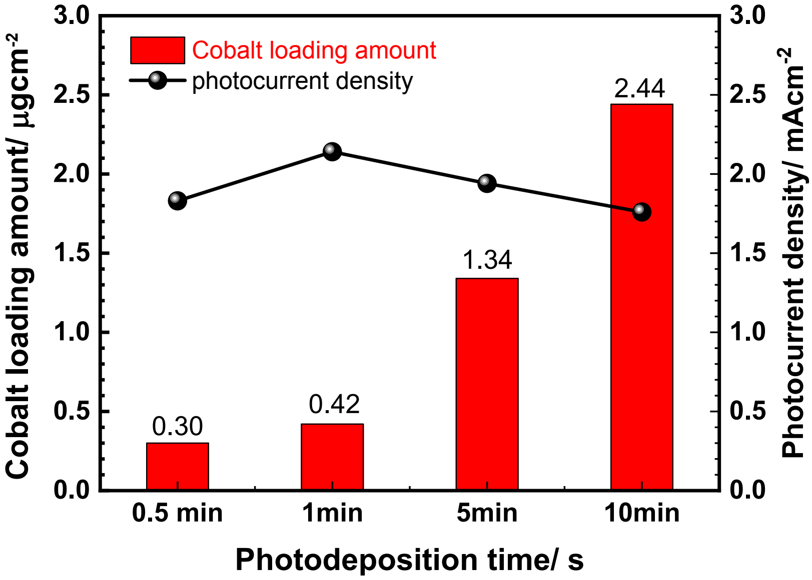

Figure S2 Relationship among photodeposition time, photocurrent density of BVO/Co-Ac and cobalt loading amount (detected by ICP-AES)

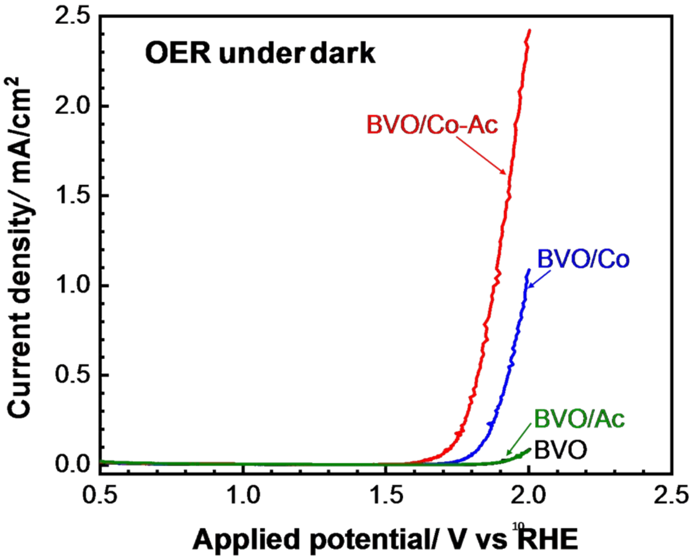

Figure S3 Current (*J*)–potential (*V*) curves of BVO and BVO/Co-Ac in KPi (pH 7) under dark condition.

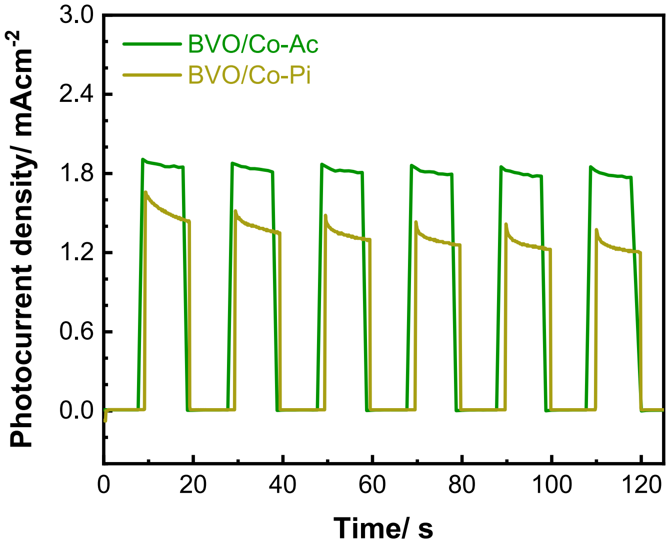

Figure S4 Transient *J*–*t* measurements of BVO/Co-Ac and BVO/Co-Pi performed with chopped light at 1.23 V in KPi (pH 7)

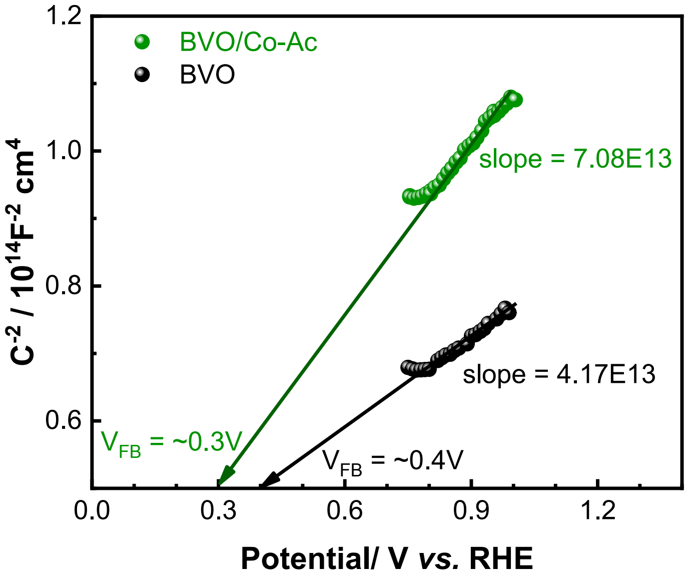

Figure S5 M-S plots collected at a fixed frequency of 1 kHz of BVO (blue) and BVO/Co-Ac (red) under dark condition

Upon Co-Ac modification, the flat band potential is derived to be ca. 0.3V vs. RHE, indicating that Co-Ac deposition has no significant effect on the band bending at the surface but mainly on the promotion of surface reaction kinetic.

Table S1 EIS parameters obtained by fitting experimental data with Randle circuit

Sample	**Onset potential (V)**	**Applied potential (V)**	**R_{ct} (Ω)**	**CPE (μMho)**
BVO	0.3	0.5	828	55
BVO/Co-Ac	0.7	0.9	149	72

**Potential (V) is referred to reversible hydrogen electrode (RHE)*

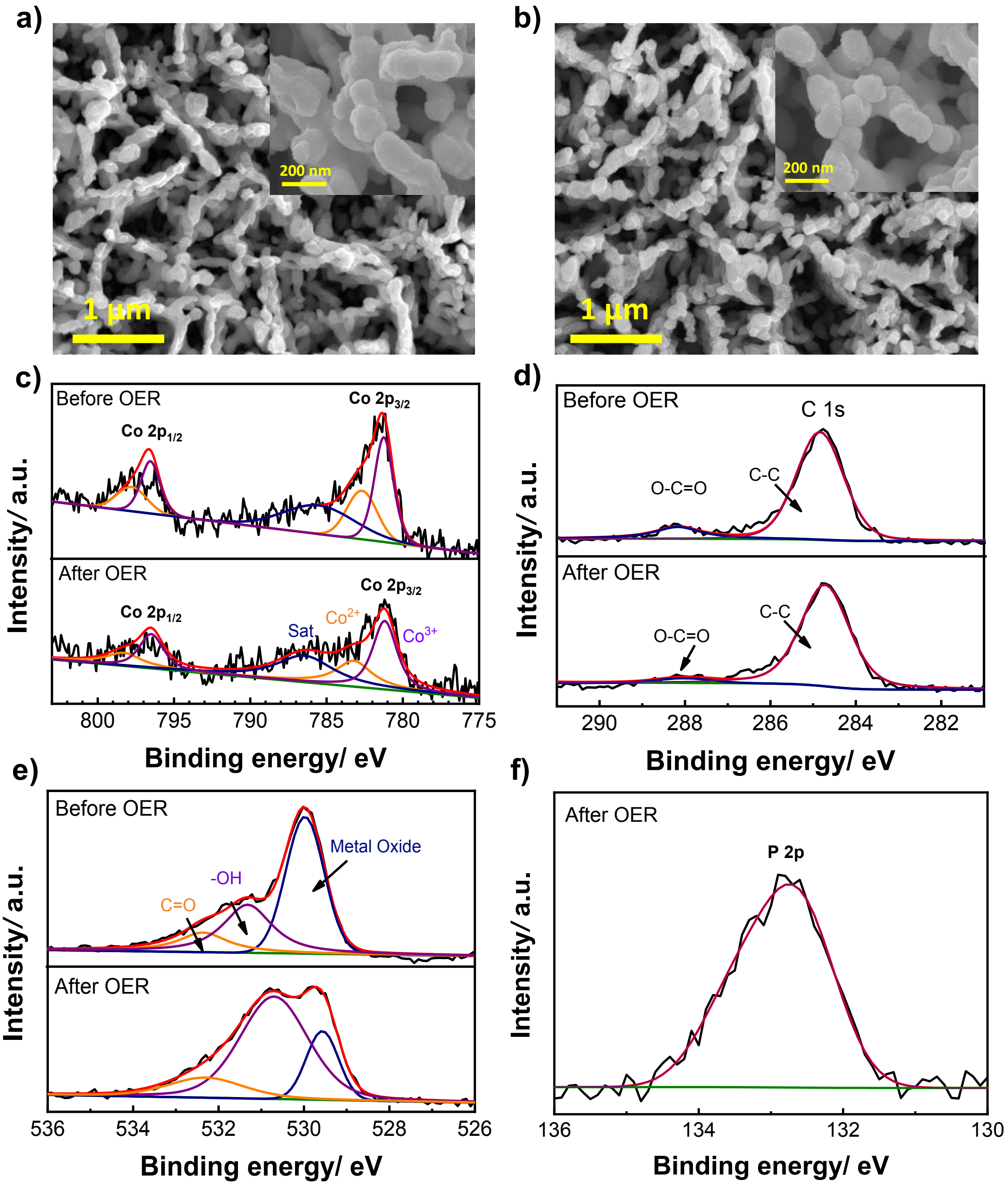

Figure S6 (a, b) SEM images; BVO/Co-Ac after stability in phosphate (pH 7) and borate (pH 9.4) buffer under AM 1.5 G light illumination; (c-f) XPS spectra BVO/Co-Ac before after stability in KPi buffer.

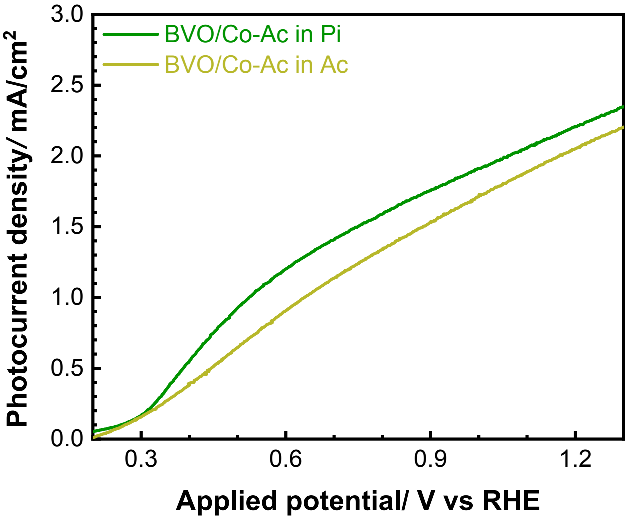

Figure S7 (a) *J–V* curves of BVO/Co-Ac in phosphate (pH 7) and acetate (pH 7) buffer.

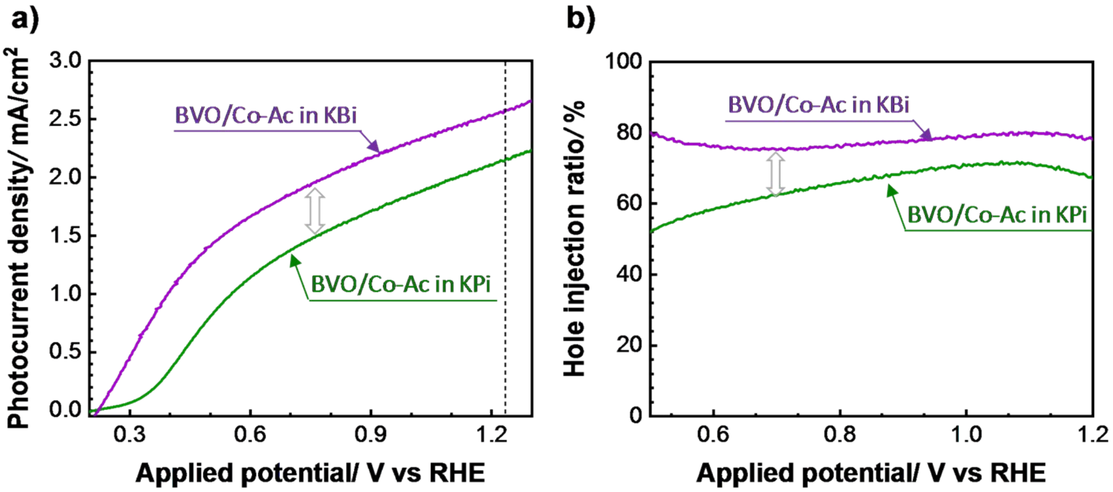

Figure S8 (a) *J–V* curves and (b) calculated charge injection efficiency of BVO/Co-Ac in phosphate (pH 7) and borate (pH 9.4) buffer under AM 1.5 G light illumination.

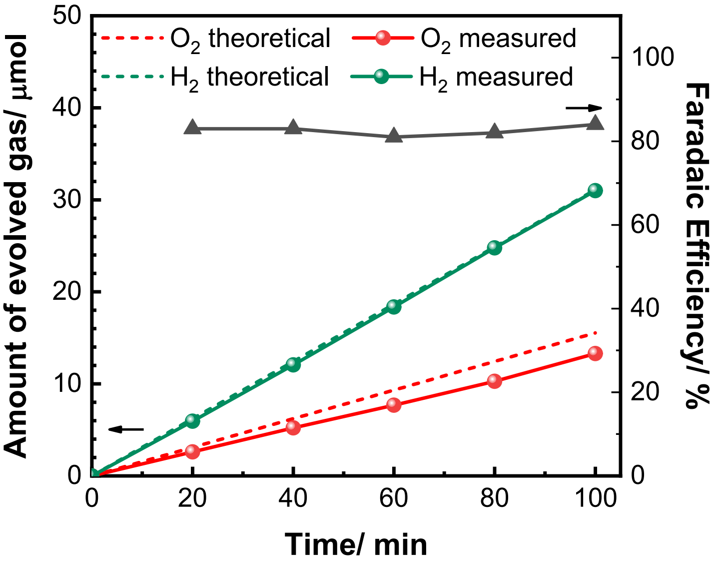

Figure S9 Amount evolved O_2 (red dot) and H_2 (green dot) and Faradaic efficiency of O_2 produced from water oxidation for the BVO photoanode in borate buffer. Red and green dashed lines are the theoretical amount of O_2 and H_2, respectively.