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Supporting Information

Simple preparation of highly active water splitting FTO/$BiVO_4$ photoanode modified with tri-layers water oxidation catalysts

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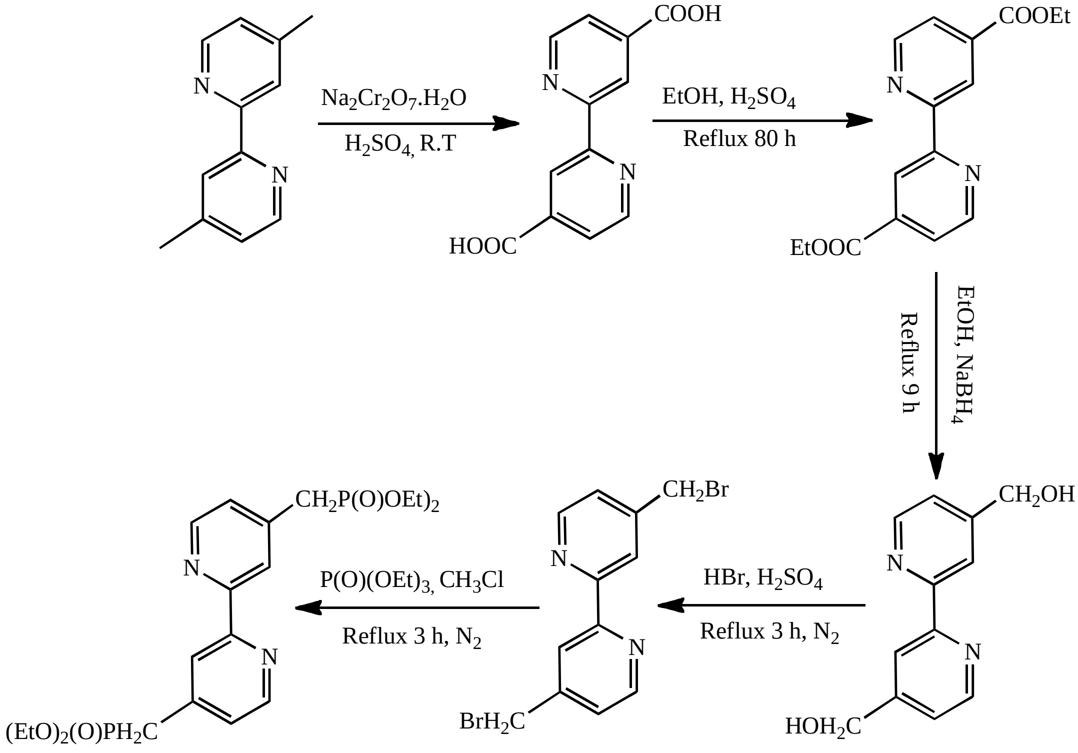
Materials. The FTO conducting glass sheet (fluorine doped SnO_2, 30 cm x 30 cm, sheet resistance: 7 Ω/square, transmission, 90% in the visible region) was obtained from SPD Laboratory, Inc. $Bi(NO_3)_3{\cdot}5H_2O$ (99.9 %) and NH_4VO_3 (99.9%) were purchased from Kanto Chemical Co. 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI triflate), 4,4\`-bismethyl-2,2\`-bipyridine, $CoCl_2$, $FeSO_4$, $NiSO_4$, KH_2PO_4 (≥ 99%), K_2HPO_4 (≥ 99%), Na_2SO_3, KOH (≥ 86%), $HClO_4$, and $NaClO_4$ (99.99%,) were purchased from Sigma-Aldrich Co. All reagents were used as received without further purification. Mill-Q water (18 M Ω.cm) was used for solutions preparation.

Instruments and characterization. UV-visible spectra were determined with a Shimadzu UV-2501PC spectrometer. The electrochemical measurements were carried out on an Autolab Potentiostat/Galvanostat model PGSTAT128N. Particle morphologies and sizes were observed by scanning electron microscopy, Field Emission Hitachi Model S-4300 scanning electron microscope operated at 15 KV accelerating voltage and 15 mm working distance. The X-ray diffraction patterns (XRD) of the sample were collected by Rigaku Co. XRD patterns were recorded from 15° to 60° in 2θ at a step size of 0.05° and a scan rate of 0.25°/min. Gas chromatographic analyses were done with a Shimadzu GC-8A equipped with a capillary column (0.53 mm ID x 15 m) with a Molecular Sieve 5A layer at 40 ^oC using Ar as a carrier gas. XP spectra were obtained using a Ulvac Phi 5000 VersaProbe CU X-ray Photoelectron Spectrometer with a Multipak data treatment system. The photoelectrons emitted by a monochromated Al K□ (1486.6 eV; 350 W) radiation were collected with path energy of 23.5 eV through a hemispherical analyzer. The pressure in the analyzing chamber was below 1 x 10^{-9} Torr during the measurements. All spectra in XPS were calibrated to C 1s = 284.6 eV. The photocurrent under monochromic light and the IPCE spectrum were measured with a monochromator light source M10-T, Bunkoukeiki Co., Ltd. The intensity of the applied monochromic light was calibrated by a reference silicon cell, S1337-1010BQ, Hamamatsu Photonics K. K. In the measurements of photocurrent and evolved O_2 and H_2, a 300-W Xenon lamp, MX-302, Asahi Spectra Co., Ltd. was used as the light source using a 420 nm cut off filter. The light intensity was calibrated to a100 mW cm^{-2} using a reference silicon cell, BS-520, Bunkoukeiki Co., Ltd.

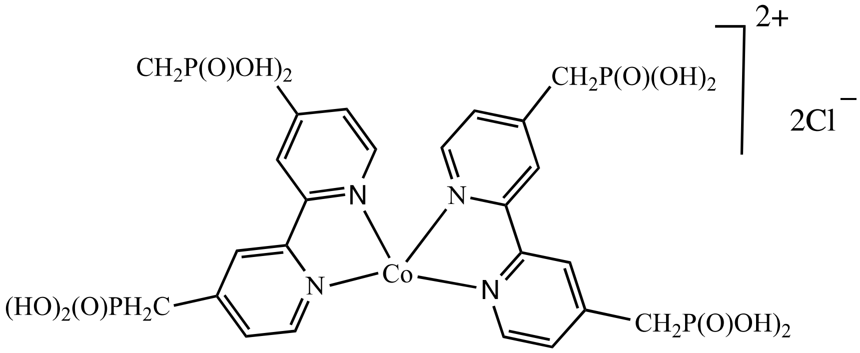
Preparation of $[Co(bpy\text{-}P)_2]Cl_2$ water oxidation catalyst. First, the ligand 4,4`-Bis(diethylmethylphosphonate)-2,2`-bipyridine (bpy-PEt) was prepared by following reported procedures[1] according to the following chart:



4,4`-Bis(diethylmethylphosphonate)-2,2`-bipyridine

^{1}H NMR (400 MHz, $CDCl_3$): δ8.59 (d, 2H), 8.35 (t, 2H), 7.33 (dd, 2H), 4.08 (m, 8H), 3.22 (d, 4H), 1.29 (t, 12H). MALDI-TOF-MS: m/z = 456.6 (found), 456.41 (calcd.). Then, the ligand (0.7 g, 1.54 mmol), anhydrous $CoCl_2$ (0.1 g, 0.77 mmol), and dry ethanol (15 ml) were charged into a Schlenk tube. The orange solution was refluxed under N_2 overnight. The solvent was then removed under vaccuo, and the orange red residue was further purified over Sephadex using CH_2Cl_2 as eluent. The Matrix

Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass, UV-vis spectra, and elemental analysis are consistent with the formation of a pure [Co(bpy-PEt)$_2$]Cl$_2$ complex. The ethyl phosphonate of the complex was hydrolyzed to the corresponding phosphonic acid by mixing the complex (100 mg in 10 mL CH_3OH) with Conc. HCl (12 M, 10 mL) and overnight refluxing. The free phosphonic acid containing complex, [Co(bpy-P)$_2$]Cl$_2$ was further purified on the Sephadex column using CH_3OH as eluent. The MALDI-TOF, UV-vis, and elemental analysis confirm its purity. The chemical structure of the complex is presented below:



[Co(bpy-P)$_2$]Cl$_2$

Electrocatalytic water oxidation performance of [Co(bpy-P)$_2$]Cl$_2$ anchored to metal oxide electrodes. To the best of our knowledge, only one report uses a bipyridine ligand covalently anchored to a graphene modified electrode as an efficient way to bind several metal ions including Co^{2+}, Ni^{2+}, Fe^{3+} and Cu^{2+} to the surface of the electrode and uses the assembly as efficient water oxidation catalysts.[2] Phosphonic acid, on the other hand, is a well-known anchor group that previously used to provide a strong chemical attachment of Ru terpyridine water oxidation catalysts (WOCs) and Ru bipyridine dyes to metal oxide electrodes such as TiO_2, FTO, and ITO. Here we used the phosphonic acid as a linker to attach the Co bipyridine WOC ([Co(bpy-P)$_2$]Cl$_2$) to the FTO/EMI s-m $BiVO_4$ photoanode. The anchoring and the electrochemical performance of the catalyst were first investigated on a Ti/TiO_2 electrode prepared by a reported procedures.[3] The modification of the catalyst on the Ti/TiO_2 electrode was achieved by soaking the electrode in a 1 mM catalyst solution in EtOH. The electrode modified with the catalyst was then washed with EtOH several times and allowed to dry at r.t for a couple of hours before further characterization and electrochemical measurements. Figure S5 shows the results of such investigations that indicate the high activity of the catalyst for water oxidation.

Preparation of $BiVO_4$ colloidal solution. $Bi(NO_3)_3{\cdot}5H_2O$ (1.502 g, 3 mmol), NH_4VO_3 (0.362 g, 3 mmol), and MeOH (5.1 mL) were mixed and sonicated for several hours at room temperature to form a yellow colloidal solution of $BiVO_4$. EMI triflate ionic liquid (0.9 mL) was then added to the solution to form the desired EMI triflate containing $BiVO_4$ colloidal solution.

Preparation of FTO/EMI s-m $BiVO_4$ photoanode. A FTO sheet was cut down to rectangular plates of 5.0 cm x□3.0 cm, sonicated in acetone and de-ionized water for 15 min each, and then dried in an oven at 60 °C. An adhesive NITOFLON® tape No. 973UL (Nitto Denko Co., Ltd) was attached on the plate (2 layers of tape) in such a way that 1.0 cm x 5.0 cm of the plate remained uncovered. The EMI triflate containing $BiVO_4$ colloidal paste solution (200 μL) was spread over the uncovered 1.0 cm x 5.0 cm of the plate then justified with a glass tube using a doctor Blading technique. The EMI triflate containing $BiVO_4$ layer was allowed to dry in few minutes, the tape was then removed, and the FTO/ EMI triflate containing $BiVO_4$ layer was sintered in an oven at 450 °C for 2 hours under air. After cooling down, the FTO/ EMI triflate containing $BiVO_4$ was washed strongly with tap water to leave a strongly attached $BiVO_4$ layer on the FTO electrode called FTO/EMI s-m $BiVO_4$. The FTO/EMI s-m $BiVO_4$ was cut into suitable pieces (0.5 cm x 1.0 cm) for the characterization and measurements.

Preparation of FTO/EMI s-m $BiVO_4$/FeOOH photoanode. FeOOH water oxidation catalyst was photodeposited on the FTO/EMI s-m $BiVO_4$ photoanode using the same procedures reported by Kim, T. W. et al.[4] The photodeposition was achieved at 0.25 V vs. Ag/AgCl in a three-electrode cell composed of a FTO/EMI s-m $BiVO_4$ working electrode, a Pt counter electrode, and a Ag/AgCl (3 M KCl) reference electrode and filled with an air free 0.1 M $FeSO_4$ solution of pH adjusted to 7.0 by adding NaOH. A 300 W Xe lamp with an adjusted power intensity of 100 mW/cm^2 was used as the light source. The light was illuminated through the FTO contact (back-side illumination). The photodeposition was continued until a total charge of 45 mC/cm^2 was consumed that took about 15 min. After photodeposition, an electrodeposition of FeOOH was performed in the same solution at 1.2 V vs. Ag/AgCl for 1 min.

Preparation of FTO/EMI s-m $BiVO_4$/FeOOH/NiOOH photoanode. NiOOH water oxidation catalyst was photodeposited on the FTO/EMI s-m $BiVO_4$/FeOOH photoanode using the same procedures reported by Kim, T. W. et al.[4] The photodeposition was achieved at 0.11 V vs. Ag/AgCl in a three-electrode cell composed of a FTO/EMI s-m $BiVO_4$/FeOOH working electrode, a Pt counter electrode, and a Ag/AgCl (3 M KCl) reference electrode and filled with an air free 0.1 M $NiSO_4$ solution of pH adjusted to 7.0 by adding NaOH. A 300 W Xe lamp with an adjusted power intensity of 100 mW/cm^2 was used as the light source. The light was illuminated through the FTO contact (back-side illumination). The photodeposition was continued until a total charge of 22 mC/cm^2 was consumed that took about 10 min. After photodeposition, an electrodeposition of NiOOH was performed in the same solution at 1.2 V vs. Ag/AgCl for 1 min.

Preparation of FTO/EMI s-m $BiVO_4$/FeOOH/NiOOH/Co(bpy-P)$_2$ photoanode. The FTO/EMI s-m $BiVO_4$/FeOOH/NiOOH photoanode was immersed into a 1mM ethanolic solution of the Co(bpy-P)$_2$ water oxidation catalyst and removed immediately. The photoanode was allowed to dry at the r.t then heated at 120 ^oC for a couple of hours.

Photoelectrochemical and electrochemical measurements. The photocurrent measurements were performed under an argon atmosphere using a conventional three-electrode cell. The working electrode was FTO/EMI s-m $BiVO_4$, FTO/EMI s-m $BiVO_4$/FeOOH, FTO/EMI s-m $BiVO_4$/FeOOH/NiOOH, or FTO/EMI s-m $BiVO_4$/FeOOH/NiOOH/Co(bpy-P)$_2$. A Pt wire and an Ag/AgCl (3 M NaCl) were the counter and reference electrodes, respectively. While all measurements were carried out using a Ag/AgCl (3 M KCl) reference electrode, the results in this study are presented against the reversible hydrogen electrode (RHE) for ease of comparison with H_2 and O_2 redox levels and other reports that used electrolytes with different pH conditions. The conversion between potentials vs. Ag/AgCl and vs. RHE is performed using the equation:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.059\ \text{pH} + E(\text{Ag/AgCl})$$

$$E(\text{Ag/AgCl}) = 0.198 \text{ V vs. NHE at } 25\ ^{o}\text{C}$$

All measurements were made in a neutral 0.1 M potassium phosphate, K-Pi buffer solution of pH = 7.0 and in 0.1M K-Pi containing 0.5 M Na_2SO_3 as a hole scavenger, as noted in the main text at 25°C. A solar simulator (OTENTO-SUN II, Bunkoukeiki Co., Ltd.) was used as an AM 1.5 light source. The power of the simulated light was calibrated to a 100 mW/cm^2 using a certified reference silicon cell (BS-520, Bunkoukeiki Co., Ltd.). Illumination through the FTO side (backside illumination) was used. All illuminated areas were 0.28 cm^2 by masking with Teflon tape. Photocurrents were measured either while sweeping the potential to the positive direction with a scan rate of 10 mV/s or while applying a constant bias under AM 1.5G illumination (100 mW cm^2).

Incident photon-to-current efficiency, IPCE (%) at each wavelength was determined using the following equation:

$$\text{IPCE}\ (\%) = \frac{1240 \ \text{x}\ J_{\text{ph}} \text{ x } 100}{\text{P}_{\text{light}} \text{ x } \lambda}$$

where J_{ph}, P_{light}, and λ refer to the photocurrent density in mA/cm^2, incident photon flux in mW/cm^2, and wavelength in nm, respectively. IPCE was measured at 1.23 V vs. RHE in 0.1 M K-Pi solution (pH 7) using the same three-electrode setup described above for photocurrent measurements. Absorbed photon-to-current efficiency (APCE) at 1.23 V *vs.* RHE was obtained by dividing the IPCE (%) by the light harvesting efficiency (LHE) at each wavelength using the following equations.

$$\text{APCE}\ (\%) = \frac{\text{IPCE}\ (\%)}{\text{LHE}}$$

$$\text{where, LHE} = 1\text{-}\ 10^{-A(\lambda)} \quad (A(\lambda)\text{: absorbance at wavelength } \lambda)$$

In order to calculate the maximum photocurrent density (J_{max}) that can be achieved by $BiVO_4$ assuming 100% IPCE, the National Renewable Energy Laboratory (NREL) reference solar spectral irradiance at AM 1.5G (radiation energy, W/m^2.nm) *vs.* wavelength (nm) was first converted to the solar energy spectrum in terms of the number of photons ($s^{-1}.m^{-2}.nm^{-1}$) *vs.* wavelength (nm). Then, the total number of photons in the wavelength range of 280-530 nm (absorption range of the current EMI s-m $BiVO_4$, band gap = 2.4 eV) were summated and converted to current density (7.7 mA/cm^2). In order to calculate the photocurrent density that can be achieved with 100% APCE (J_{abs}), the LHE at each wavelength was multiplied during each step of the number pf photons calculation.

Photoelectrolysis and oxygen and hydrogen measurements. Bulk electrolysis was performed in a gas tight one-compartment cell: The cell was filled with 0.1 M K-Pi solution. The solution was degased by Ar for 20 min. A FTO/EMI s-m $BiVO_4$ (0.28 cm^2) and Ag/AgCl (3 M NaCl) working and reference electrodes were inserted close to each other and a Pt foil (20 cm^2) was used as a counter electrode.

Product analysis.

O_2 and H_2 gas calibration curve constructions: The electrolysis cell was filled with 0.1 M K-Pi solution (10 mL), the solution was then purged with Ar gas for 30 min then the cell was closed and different known amounts of O_2 and H_2 gases were introduced to the headspace then 500 μl of the headspace gas was taken with a gas-tight syringe and analyzed the samples on a GC. The areas of the H_2 peak (at 0.9 min retention time) and that of O_2 (at 1.3 min retention time) were used for calibration of H_2 and O_2, respectively.

The calibration curves for H_2 and O_2 were then used to determine the generated O_2 and H_2 gases produced from the bulk electrolysis experiments.

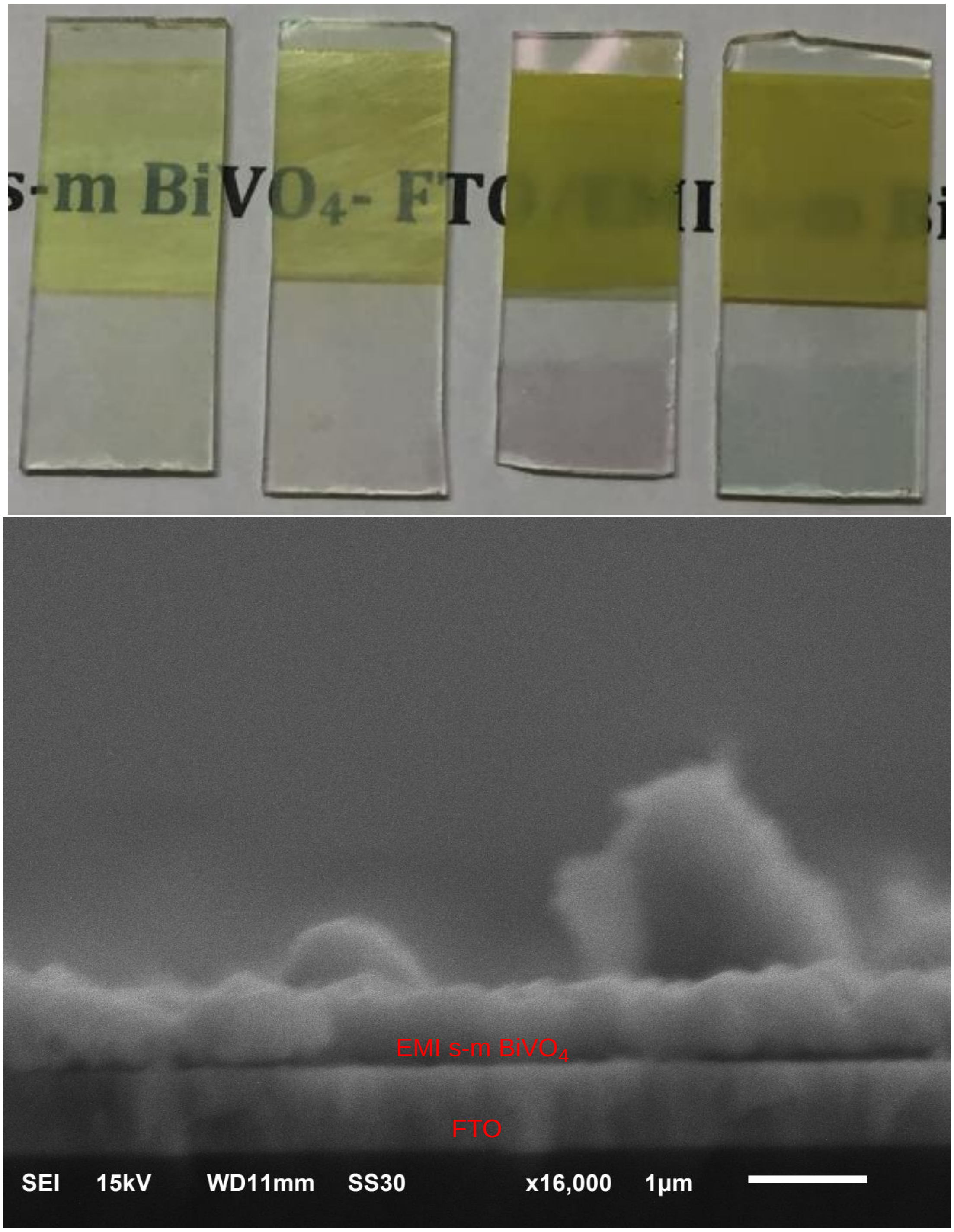


Figure S1. Actual photos of FTO/EMI s-m $BiVO_4$ photoanodes with different transparency (top) and SEM image (cross section, bottom) of the most active FTO/EMI s-m $BiVO_4$ photoanode.

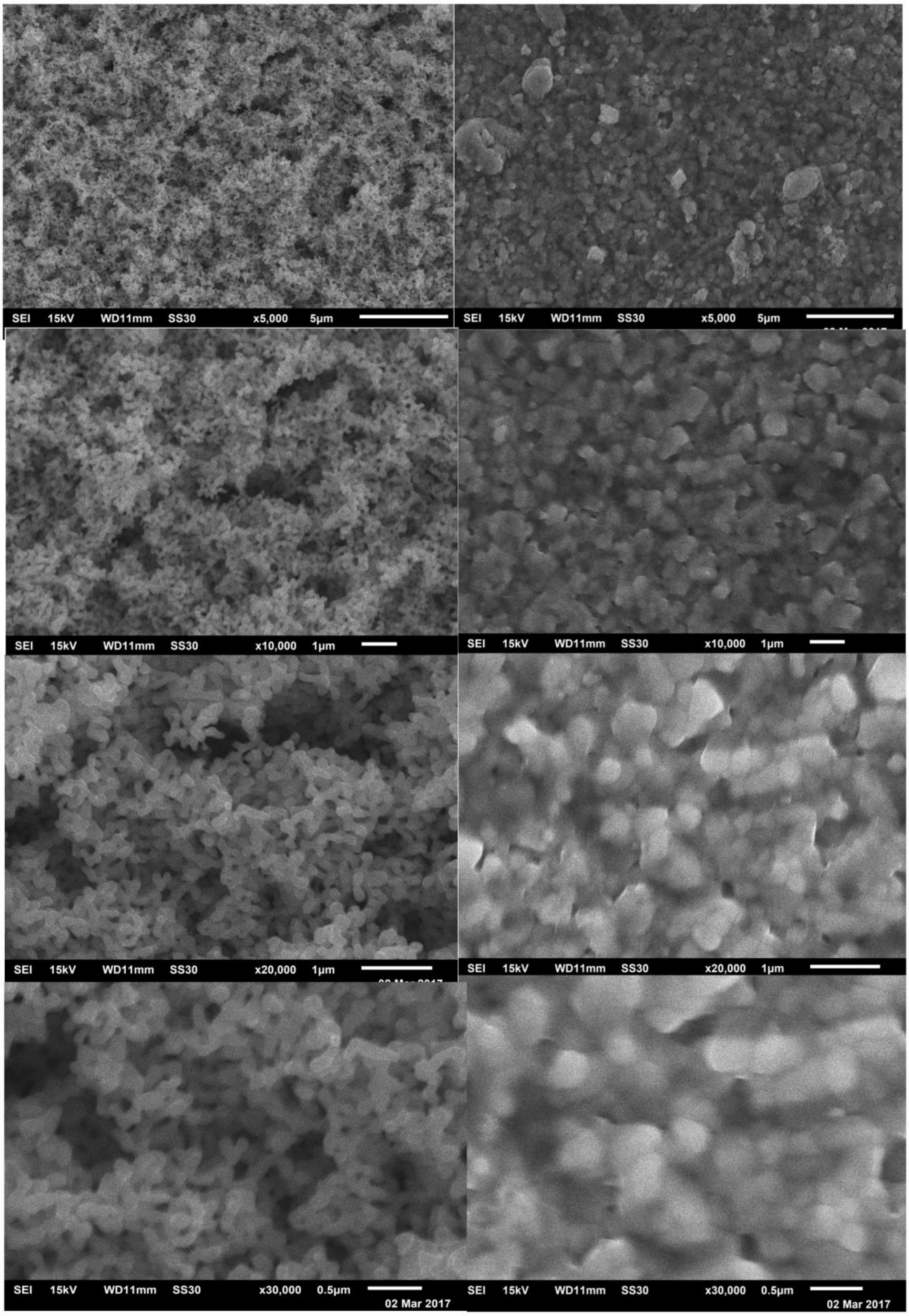


Figure S2. Top view SEM images of FTO/EMI s-m $BiVO_4$ (right) and EMI free FTO/$BiVO_4$ (left) photoanodes at different magnification.

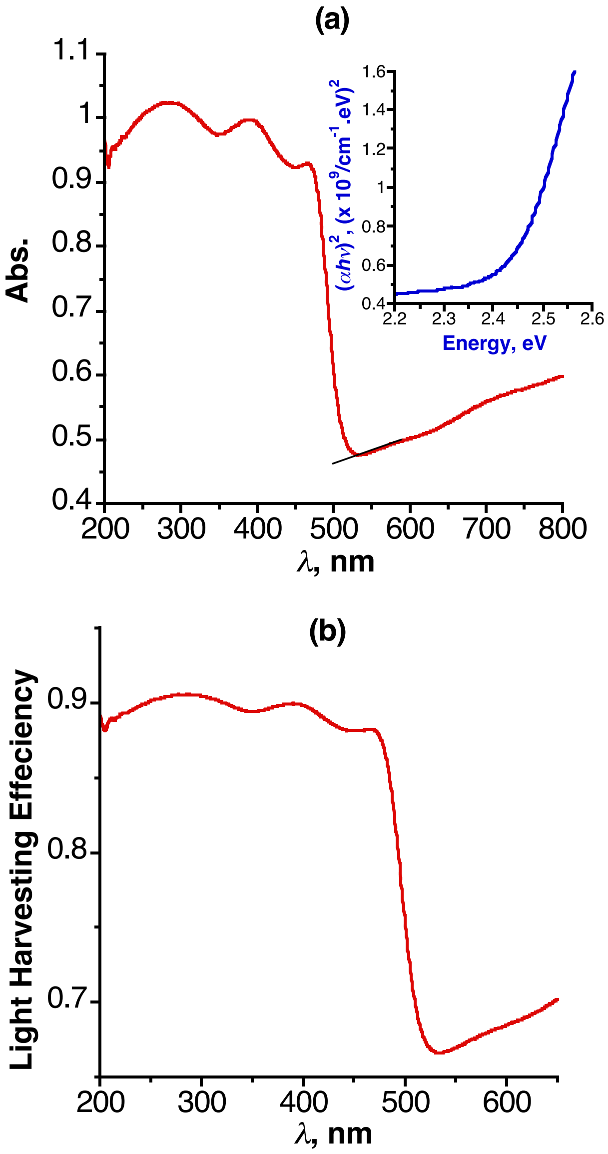


Figure S3. **(a)** UV-vis of the FTO/EMI s-m $BiVO_4$ photoanode; Inset Tauc plot derived from the UV-vis spectrum **(b)** its LHE-λ relationship.

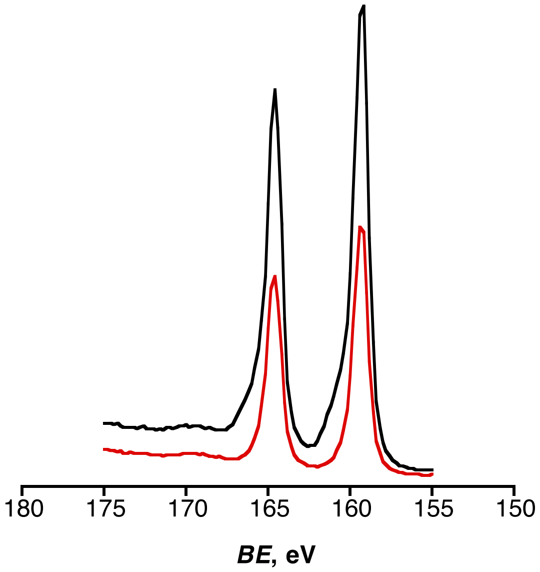


Figure S4. XP spectral region of S 2p that hampered by the strong Bi 4f peaks of FTO/$BiVO_4$ (black line) and FTO/EMI s-m $BiVO_4$ (red line).

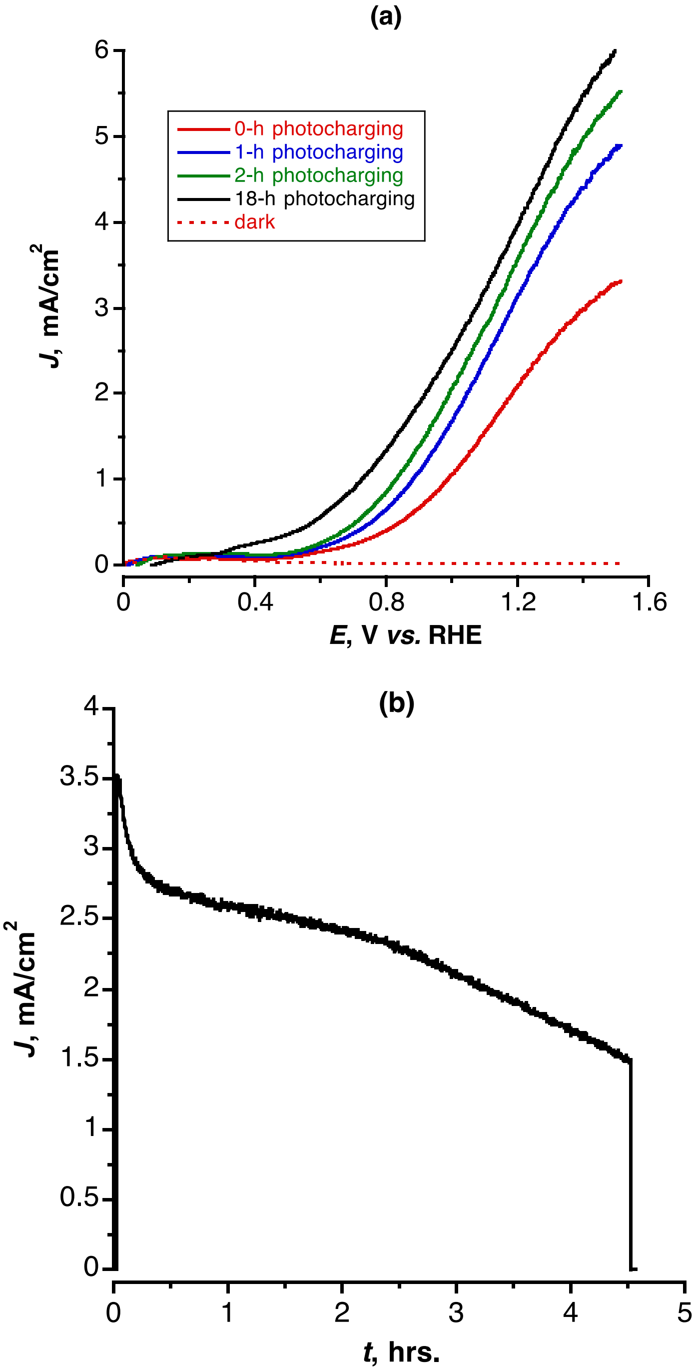


Figure S5. **(a)** *J*-*E* curves at 10 mV/s scan rate under backside AM 1.5, 100 mA/cm^2 illuminations in a 0.1 M K-Pi buffer solution (pH 7.0) of the untreated FTO/EMI s-m $BiVO_4$ photoanode (red line) and that photocharged at 0.65 V for 1-h (blue line), 2-h (green line) and 18-h (black line). The *J*-*E* curve under dark is shown as red dotted line. (b) *J*-*t* profile recorder at 1.23 V of FTO/EMI s-m $BiVO_4$ photoanode photocharged for 18-h in 0.1M K-Pi (pH 7.0) under backside AM 1.5, 100 mW/cm^2 illumination.

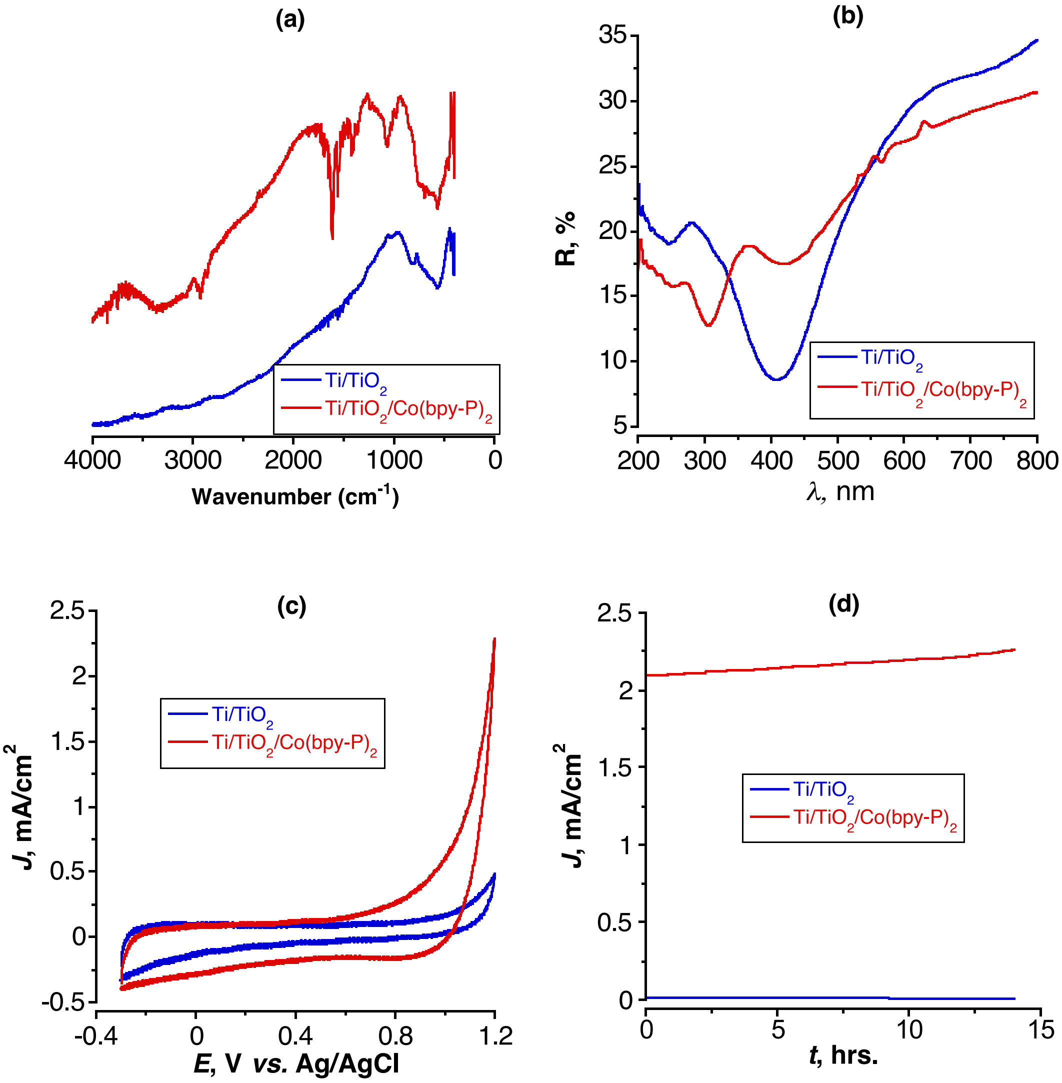


Figure S6. (a) Surface FT-IR spectra of Ti/TiO$_2$ electrode (blue line) and that modified with Co(bpy-P)$_2$ (red line). **(b)** Reflectance UV-vis spectra of Ti/TiO$_2$ electrode (blue line) and that modified with Co(bpy-P)$_2$ (red line). **(c)** CV of Ti/TiO$_2$ electrode (blue line) and that modified with Co(bpy-P)$_2$ (red line) in 0.1 M K-Pi buffer solution (pH 7) at 50 mV/s scan rate. **(d)** *J-t* profile of Ti/TiO$_2$ blank (blue line) and that modified with Co(bpy-P)$_2$ (red line) in 0.1 M K-Pi buffer solution (pH 7) at 1.2 V vs. Ag/AgCl applied potential.

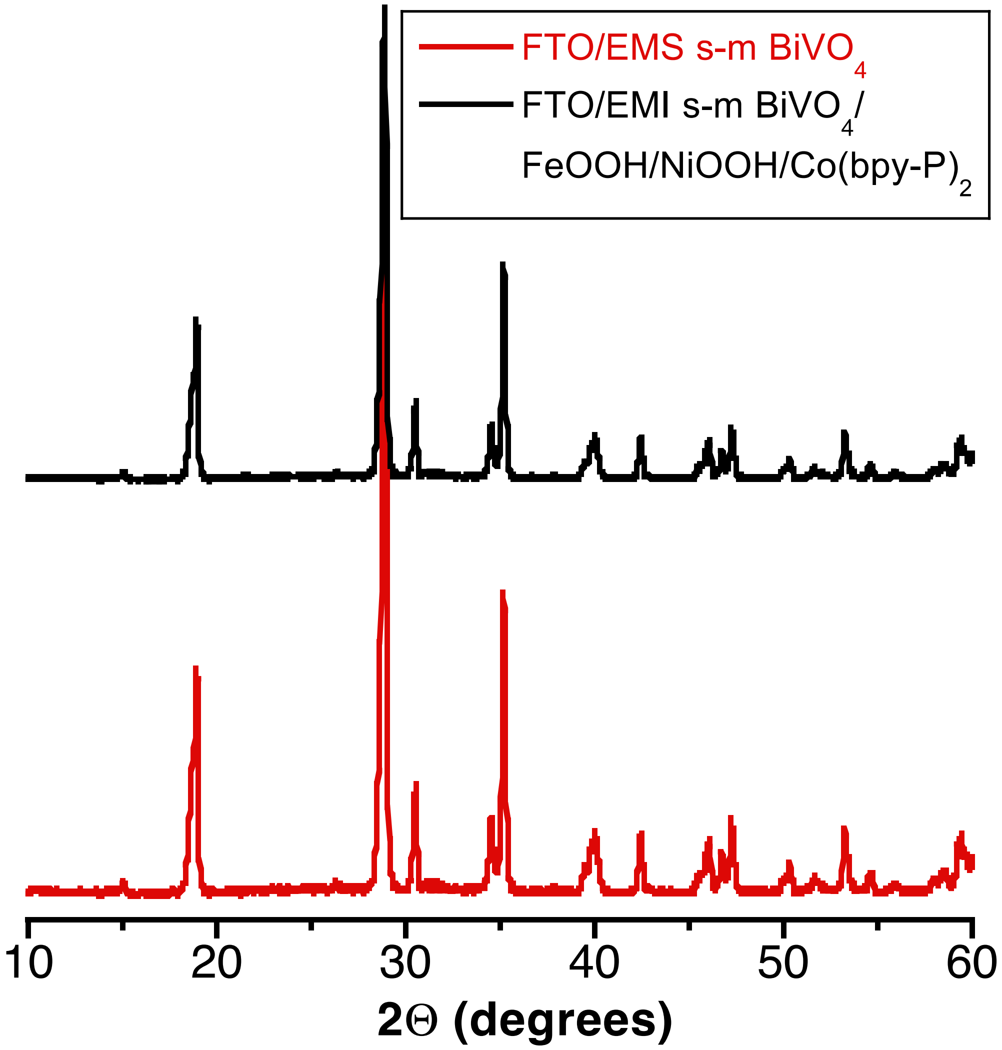


Figure S7. XRD patterns of FTO/EMI s-m $BiVO_4$ photoanode (red line) and that modified with tri-layers WOCs (black line).

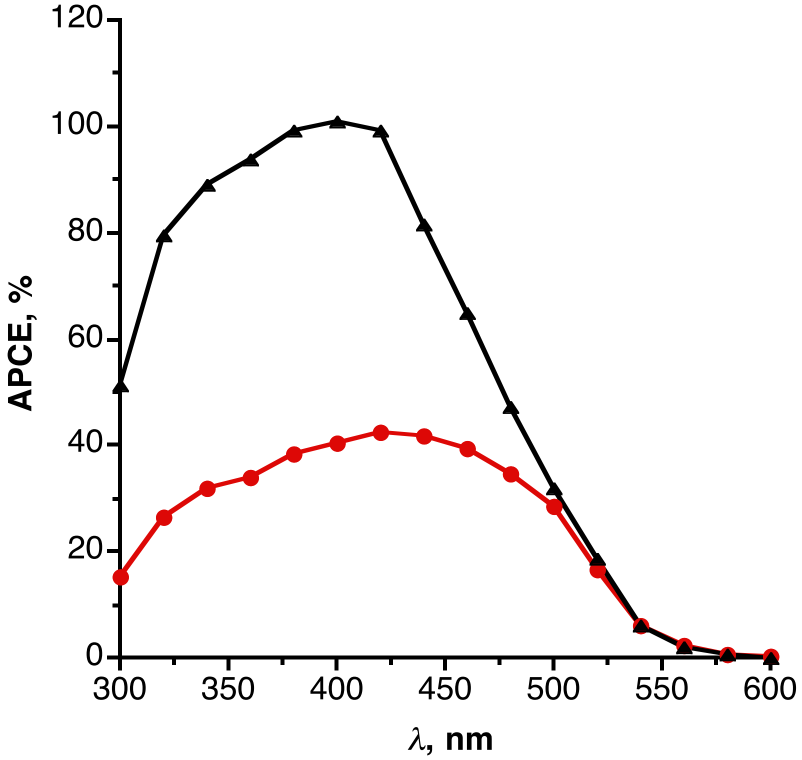


Figure S8. APCE of FTO/EMI s-m $BiVO_4$ photoanode (red line) and that modified with ternary WOCs (black line).

1 I. Gillaizeau-Gauthier, F. Odobel, M. Alebbi, R. Argazzi, E. Costa, C. A. Bignozzi, P. Qu and G. J. Meyer, *Inorg. Chem.*, 2001, **40**, 6073–6079.
2 X. Zhou, T. Zhang, C. W. Abney, Z. Li and W. Lin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 18475–18479.
3 S. Yamaguchi, R. Khanna, T. Matsushita, A. Wang, T. Ohta, Y. Naruta and H. Takadama, *RSC Adv.*, 2015, **5**, 47876–47883.
4 T. W. Kim and K.-S. K.-S. Choi, *Science*, 2014, **343**, 990–994.