

Supplementary Information

Spontaneous Phase Transition of Hexagonal Wurtzite CoO: Application to Electrochemical and Photoelectrochemical Water Splitting

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Experimental section

Materials. Fluorine-doped tin oxide (FTO, TEC 15, WY-GMS) coated glass, and indium tin oxide (ITO coated flexible plastic, WY-GMS) coated flexible plastic were used as the substrate for the electrodes. $\text{Co}(\text{acac})_3$ (99.99+%, Sigma-Aldrich), benzylamine (99%, Sigma-Aldrich), $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.99 %, Sigma-Aldrich), Co_3O_4 (99.5 %, Sigma-Aldrich), VCl_3 (97 %, Sigma-Aldrich), were used as received. In addition, Na_2SO_4 , Na_2HPO_4 , NaH_2PO_4 , ethylene glycol (99.0 %), acetone (99.0 %), and ethanol (99.5 %) were purchased from Daejung Chemicals (Korea). Deionized (DI) water was used as the solvent in the electrochemical experiments.

Preparation of hexagonal wurtzite CoO nanocrystals. Synthesis of the CoO nanocrystals was carried out using standard Schlenk techniques under an argon atmosphere. A slurry of $\text{Co}(\text{acac})_3$ (0.20 g, 0.56 mmol) and benzylamine (12.0 g, 112.0 mmol, 200 equiv.) in a 100 mL flask connected to a bubbler was submerged in a preheated oil bath at 190 °C along with vigorous stirring. The reaction mixture was maintained at this temperature for 2 h, and the resulting green reaction mixture was cooled to room temperature. Ethanol (10 mL) was added to the green suspension, the suspension was centrifuged, and the supernatant was removed. The residue was washed with ethanol (10 mL, 3 times) to provide green h-CoO nanocrystals. The resulting nanocrystals were hexagonal pyramids with an average side edge length of 40 ± 6.4 nm and a basal edge length of 20 ± 5.0 nm.

Preparation of cubic rock-salt CoO nanocrystals. A slurry of $\text{Co}(\text{acac})_3$ (0.40 g, 1.12 mmol) in benzylamine (6.02 g, 56.1 mmol, 50 equiv.) was submerged in a preheated oil bath at 130 °C along with vigorous stirring and the reaction mixture was maintained at this temperature for 3 h. After that, the reaction mixture was heated to 190 °C with a ramping rate of 10 °C/min and was maintained at this temperature for 2 h. Separation and purification procedures similar to those above yielded 38 ± 4.6 nm quasi-cube-shaped c-CoO nanocrystals.

Phase Transition of h-CoO to β -Co(OH)₂. The h-CoO nanocrystals in ethanol (10 mM, 2 ml) were mixed with 8 ml of DI water at 30 °C for 1h under an argon condition, and a phase transition involving conversion from h-CoO to the hexagonal phase of cobalt hydroxide (β -Co(OH)₂) took place

spontaneously. Ethanol (10 mL) were added to the brown suspension, the suspension was centrifuged, and the supernatant was removed. The residue was washed with ethanol (10 mL, 3 times) to provide brown β -Co(OH)₂ nanocrystals. The resulting nanocrystals were hexagonal plate shape with an average side edge length of 72 ± 11 nm. Note that the further phase transformation of the β -Co(OH)₂ to spinel Co₃O₄ nanocrystals can be progressed in a thermal process (above 100 °C in air) due to the spontaneous oxidation reaction by O₂ in air.

Spontaneous formation of β -Co(OH)₂ nanoplates on various substrates. When the h-CoO nanocrystals (1 mM, 200 μ L) were dropped on substrates (BiVO₄, Pt, FTO, Ni foam, and ITO) and then DI water was added, the conversion from h-CoO to β -Co(OH)₂ took place spontaneously at the room temperature for 3 h.

Preparation of BiVO₄ electrode. BiVO₄ electrode was grown on FTO substrates using a seed-mediated sonochemical method. FTO substrates were first cleaned in deionized water and ethanol and then sonicated in ethanol for at least 1h. For the BiVO₄ seed, 200 μ L of BiVO₄ precursor (5 mM, the atomic ratio of Bi to V was 1 : 1) in ethylene glycol was dropped onto the FTO substrate (~ 1.5 cm \times 2 cm) followed by a drying step at 120 °C in air. The prepared films were annealed at 500 °C for 3h (with a 3 h ramp time) in air to form the BiVO₄ seed layer.

A sonochemical technique was used to create the BiVO₄ electrode. The seeded BiVO₄ substrate (5 mM of BiVO₄ seed layer on FTO substrate) was horizontally placed into a 100 mL beaker. The 10 mM BiVO₄ precursor in ethylene glycol/water (1 : 1) solution was prepared (10 mM), and the sonochemical reaction was performed by directly immersing an ultrasound apparatus with a titanium horn having a 0.5 inch tip diameter (VCX-750, Sonics & Materials Inc.). The frequency of the ultrasonic wave was 20 kHz under ambient conditions. An ultrasonic wave was introduced at 50 % amplitude for 60 min. The prepared films were annealed at 500 °C for 3h (with a 3 h ramp time) in air to form the BiVO₄ electrode.

Characterization. The cobalt oxide nanocrystals were characterized by XRD (Rigaku D/MAX-RB diffractometer, using graphite-monochromatized Cu K α radiation at 40 kV and 100 mA), SEM (Philips XL30SFEG), and by TEM (FEI Tecnai G2 F30) with selected area electron diffraction (SAED) patterns,

energy-dispersive analyses of X-ray emission (EDX) at KRISS. The X-ray photoelectron spectrum (XPS) analysis was carried out with a Sigma Probe (Thermo VG Scientific) spectrometer.

Electrochemical measurements. Electrochemical characterization was performed in a specially designed cell using a three-electrode configuration with the thin film as the working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The working electrode with an actual geometric area of 0.28 cm^2 was exposed to electrolyte solution. The electrochemical measurements were performed in aqueous solutions of $0.1 \text{ M Na}_2\text{SO}_4$ with a phosphate buffer (0.1 M , pH 7) for water oxidation, using a DY2321 potentiostat (Digi-Ivy). The electrode was first cycled 5 times by cyclic voltammetry until a stable cyclic voltammetry curve was developed before measuring linear sweep voltammetry. Scan rate was 20 mV/s . Photoelectrochemical (PEC) characterizations were performed in a specially designed U-type cell in a 3 electrode configuration, with the FTO/ BiVO_4 as the working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. A 150 W xenon lamp (ABET technologies) was used as the light source in the PEC characterization step, and the light illumination area was 0.28 cm^2 . Chopped light linear sweep voltammetry (LSV) was utilized to obtain the photocurrent responses using a DY2321 potentiostat (Digi-Ivy) and a CH Instruments Model 630 potentiostat (Austin, TX). The PEC measurements were taken in aqueous solutions of Na_2SO_4 (0.1 M) with a phosphate buffer (pH 7) for water oxidation. In all tests, the intensity of the lamp on the sample was measured and found to be 100 mW/cm^2 using a Si solar cell (AIST). A 425 nm long-pass filter was used to cut the UV portion of the spectrum and to provide only visible light illumination. A monochromator (ORIEL) was used to obtain the action spectra of photo-response as a function of the wavelength.

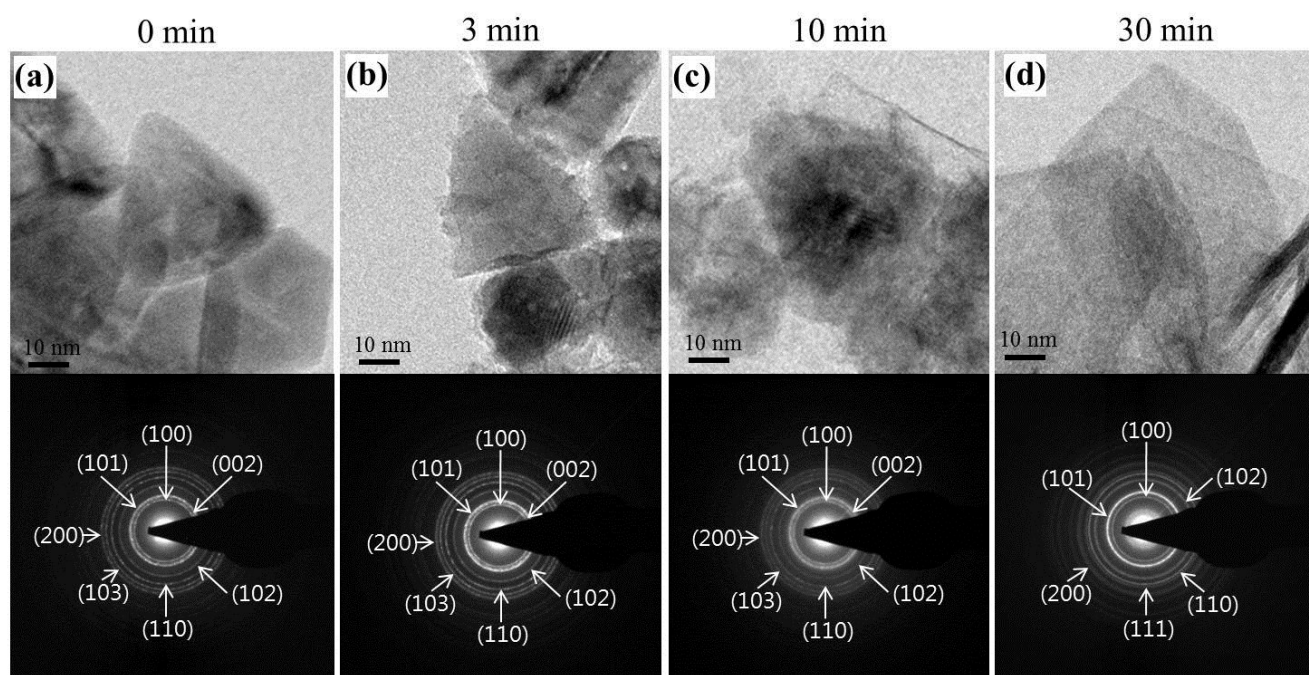


Figure S1. (a) TEM image and SAED pattern of h-CoO nanocrystal. TEM image and SAED pattern of h-CoO nanocrystals after water treatment for (b) 3 min, (c) 10 min, and (d) 30 min in inert condition.

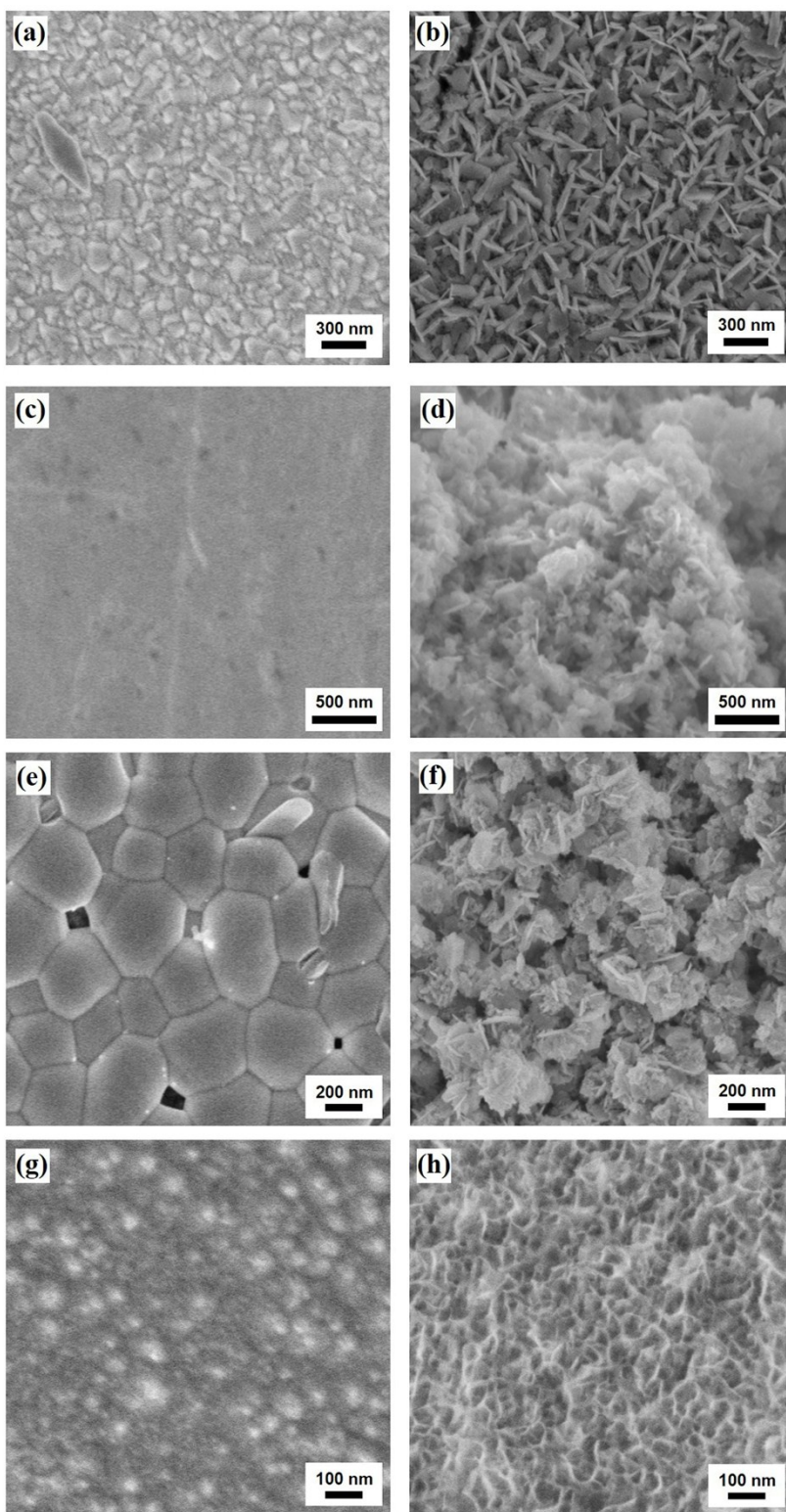


Figure S2. SEM images of (a) bare FTO, (b) $\beta\text{-Co(OH)}_2$ on the FTO, (c) bare Pt, (d) $\beta\text{-Co(OH)}_2$ on the Pt, (e) bare BiVO_4 , and (f) $\beta\text{-Co(OH)}_2$ on the BiVO_4 , (g) bare Ni foam, (h) $\beta\text{-Co(OH)}_2$ on the Ni foam.

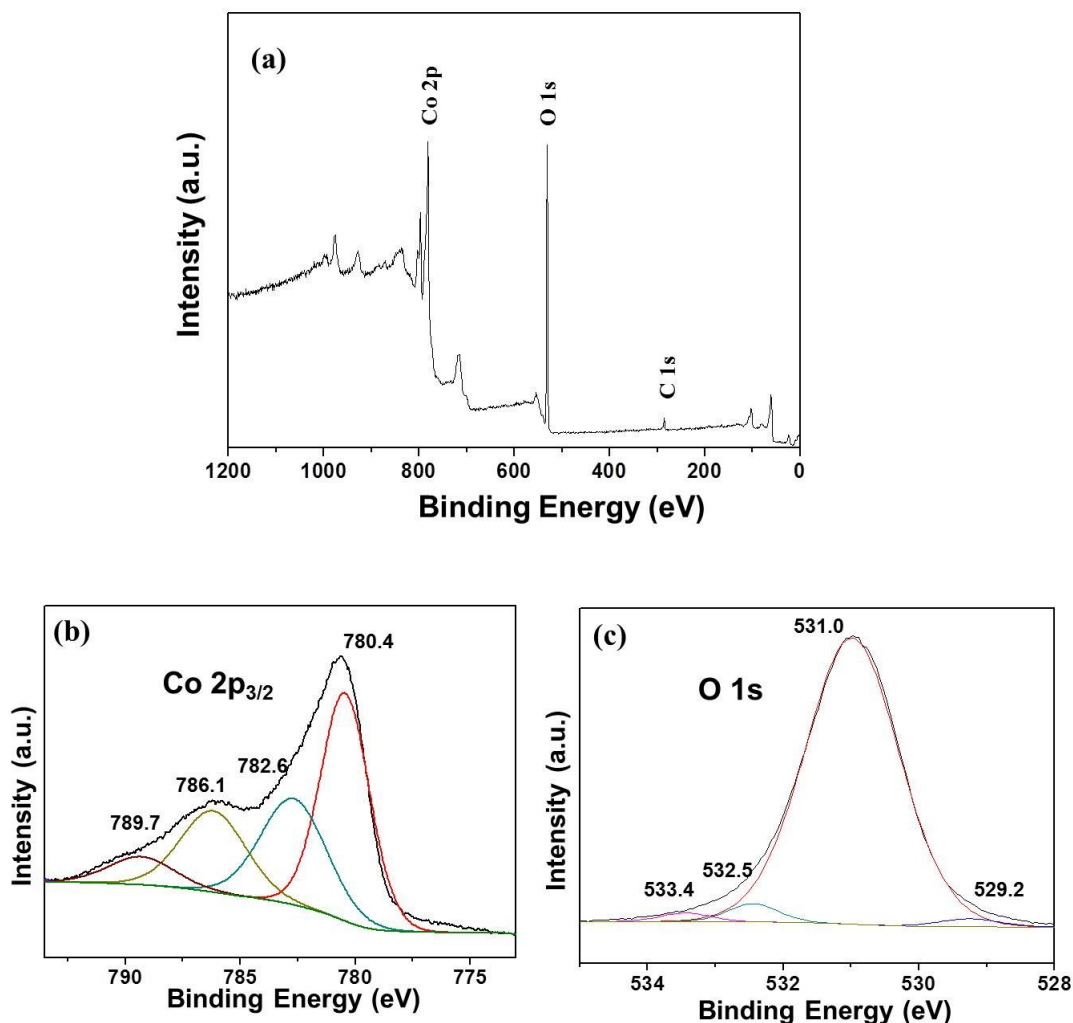


Figure S3. (a) XPS survey spectra of β -Co(OH)₂ on the FTO substrate. High resolution XPS spectra of the β -Co(OH)₂ nanoplates in the (b) Co 2p, and (c) O 1s regions. The Co 2p spectrum shows spin-orbit splitting into 2p_{1/2} and 2p_{3/2} components, and both components qualitatively contain the same chemical information. In the Co 2p_{3/2} region, the spectra have four major peaks assigned at 780.4, 782.6, 786.1, and 789.7 eV for Co²⁺. In the O 1s region, the major binding energy peak at 531.0 eV can be assigned to oxygen atoms in the hydroxyl group, which match well with the Co(OH)₂ spectra.

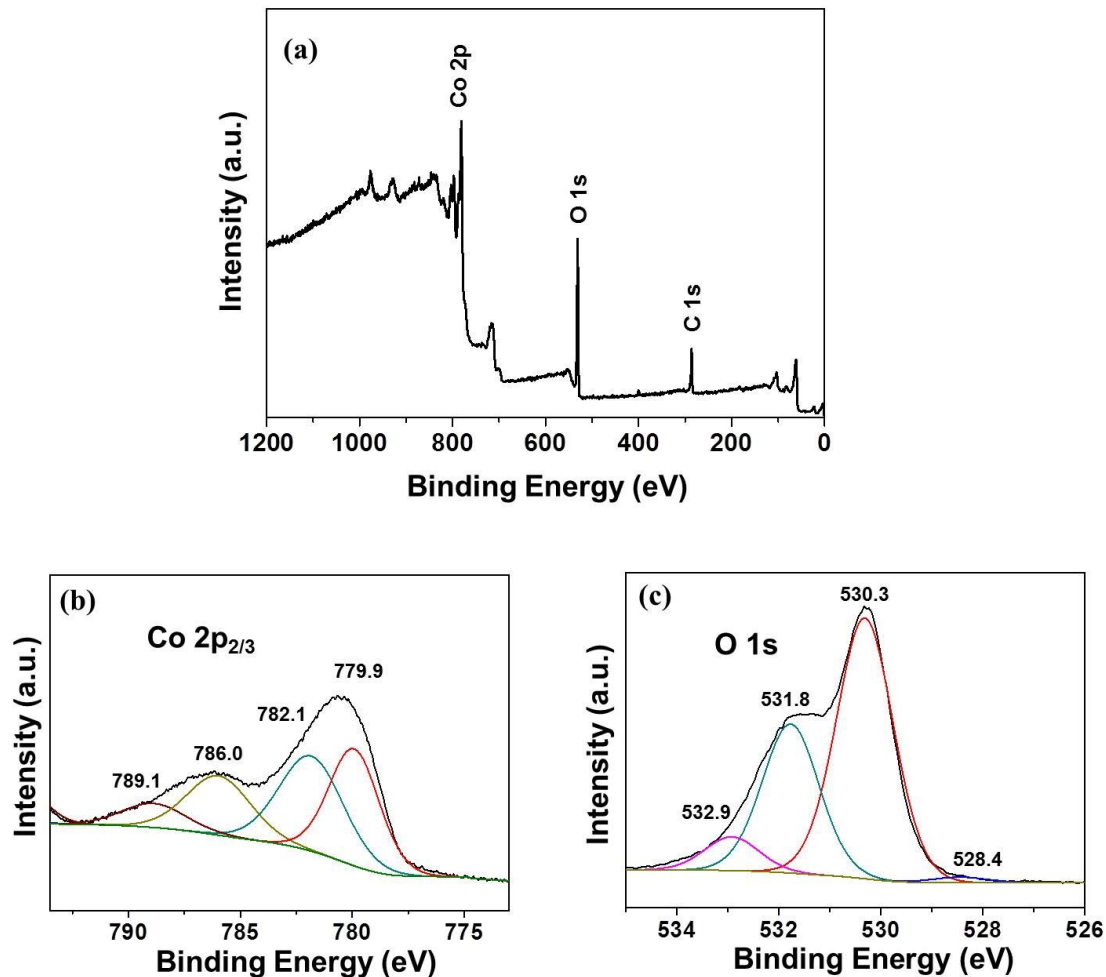


Figure S4. (a) XPS survey spectra of h-CoO on the FTO substrate. High resolution XPS spectra of the h-CoO nanocrystals in the (b) Co 2p, and (c) O 1s regions. The Co 2p spectrum shows spin-orbit splitting into $2p_{1/2}$ and $2p_{3/2}$ components, and both components qualitatively contain the same chemical information. In the O 1s region, the major binding energy peak at 530.2 can be assigned to the lattice hydroxyl group, O 1s (Co-OH), and the peak at 531.3 eV is assigned to oxygen atoms in the cobalt oxide lattice, O 1s (Co-O), that is well matched with the CoO spectra.

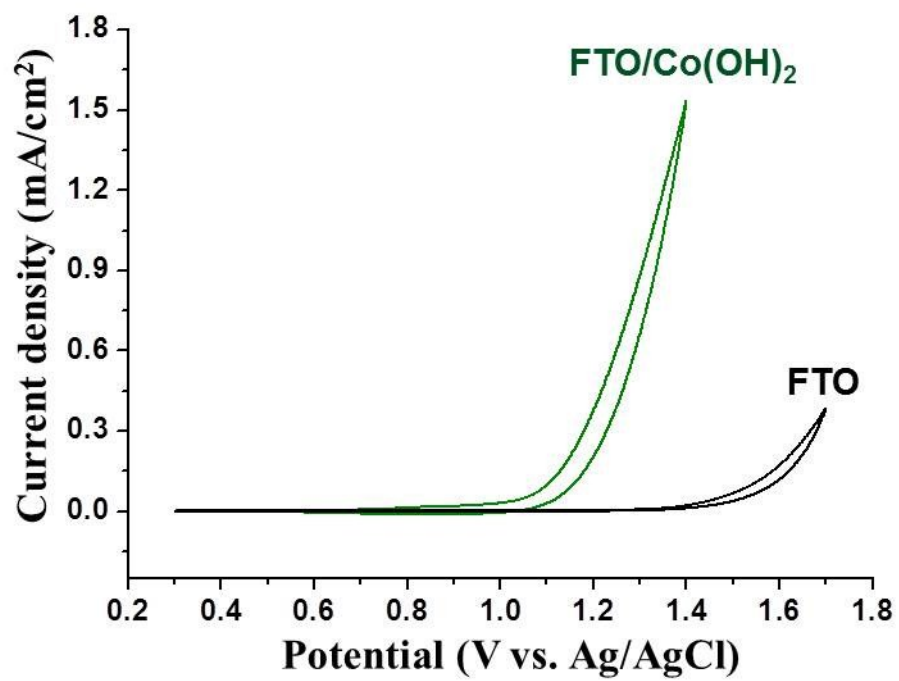


Figure S5. CV curves of the FTO, and FTO/ β -Co(OH)₂ in 0.1 M phosphate buffer (pH 7). Scan rate: 20 mV/s.

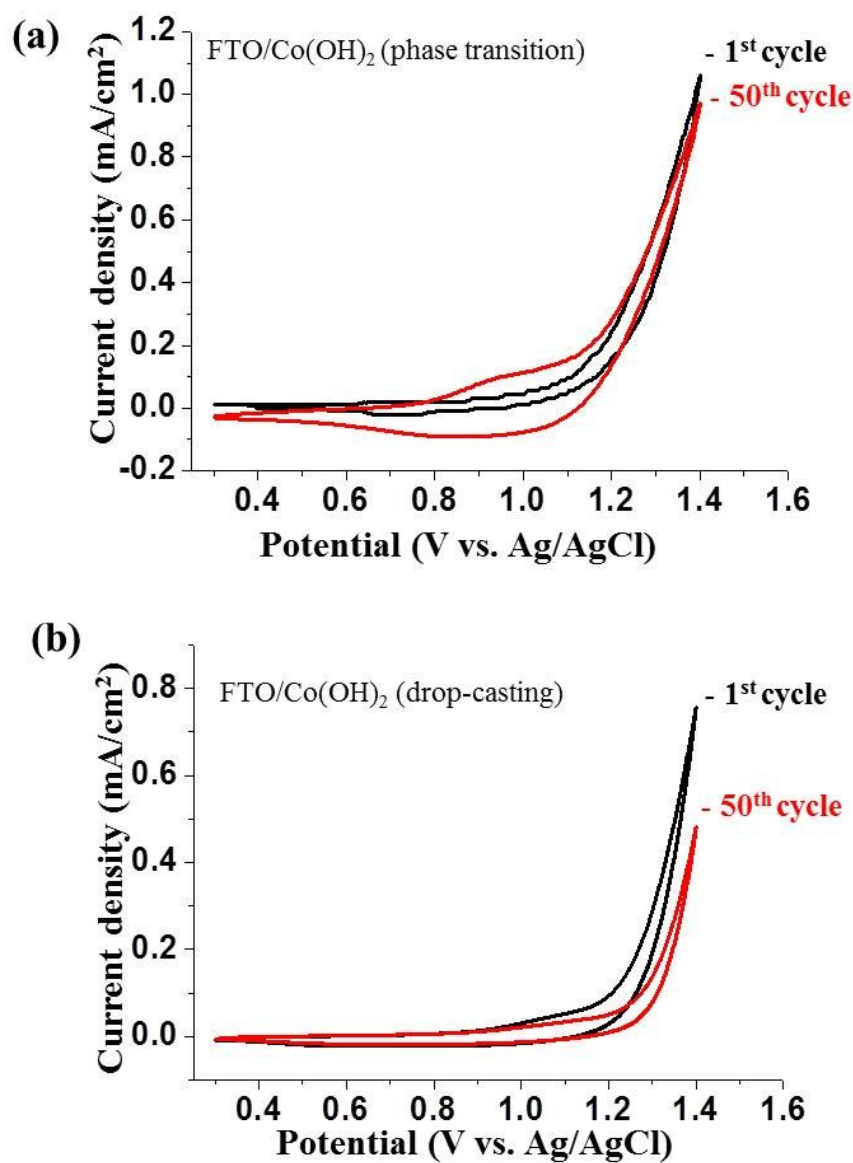


Figure S6. (a) LSVs recorded at 1st and 50th scans for FTO/ β -Co(OH)₂ (phase transition) electrode, and (b) 1st and 50th scans for drop-casted Co(OH)₂ on FTO electrode in pH 7 phosphate buffer after given number of CV cycles at a scan rate of 20 mV/s.

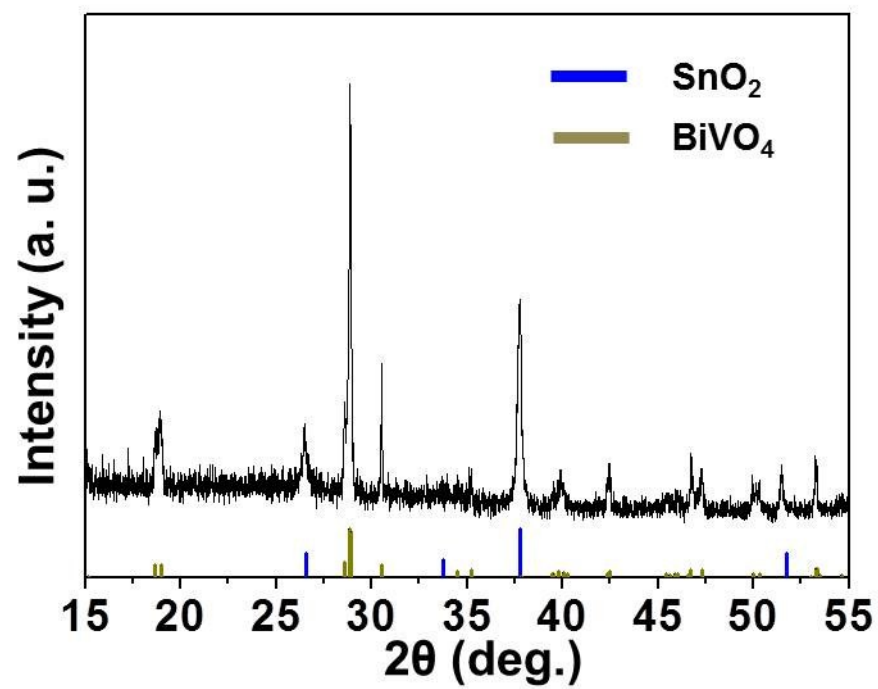


Figure S7. XRD pattern of BiVO₄ on FTO (F-doped SnO₂) substrate.

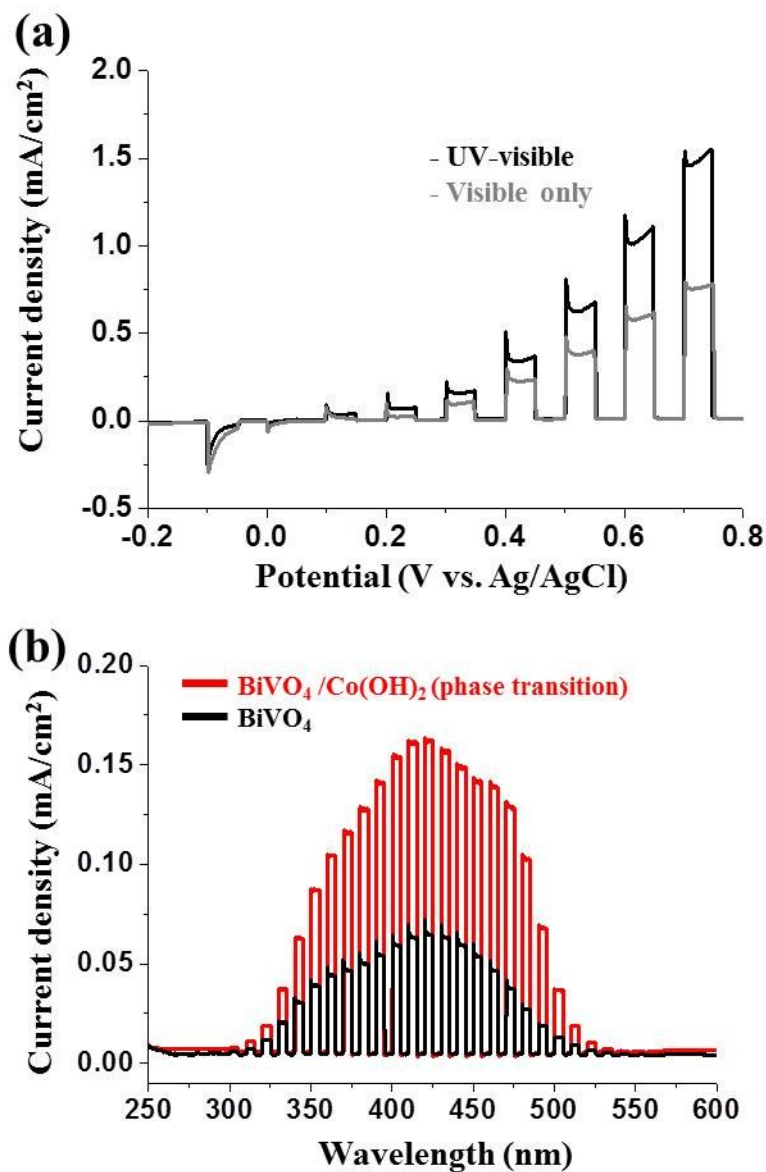


Figure S8. (a) LSVs of FTO/BiVO₄ electrode in phosphate buffer (pH 7) under UV-visible, and visible illuminations. Scan rate: 20 mV/s. Light intensity: 100 mW/cm². (b) Action spectrum of the FTO/BiVO₄, and FTO/BiVO₄/Co(OH)₂ electrodes at an applied potential of 0.5 V versus Ag/AgCl in a phosphate buffer (pH 7).