

Supplementary Information

Ultrasonic-assisted Preparation of a Pinhole-free BiVO₄ Photoanode for Enhanced Photoelectrochemical Water Oxidation

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Experimental section

Materials. Fluorine-doped tin oxide (FTO, TEC 15, WY-GMS) coated glass was used as the substrate for the thin film electrode. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.999 %, Sigma-Aldrich), VCl_3 (97 %, Sigma-Aldrich) and NH_4VO_3 (99 %, Deajung Chemicals) were used as the metal precursor salts and used as received. In addition, Na_2HPO_4 , NaH_2PO_4 , Na_2SO_4 (99.0 %), Na_2SO_3 (96.0 %), ethylene glycol (99.0 %), acetone (99.0 %), nitric acid (60 %) and ethanol (99.5 %) were purchased from Daejung Chemicals (Korea). Deionized (DI) water was used as the solvent in electrochemical experiments.

Preparation of BiVO_4 seed layer. FTO substrates were first cleaned in ethanol. A drop-casting technique was used to formation of thin film electrode. Here 200 μL of a 5 mM $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 5 mM VCl_3 precursor solutions in ethylene glycol was dropped onto the FTO substrate (1.5 cm \times 2 cm) with a drying step at 130 $^\circ\text{C}$ in air. The prepared film was annealed at 500 $^\circ\text{C}$ for 3h (with a 3h ramp time) in air to form the BiVO_4 seed layer.

Preparation of pinhole-free BiVO_4 sono-crystals. BiVO_4 sono-crystals were grown on FTO substrate using a seed-mediated sonochemical synthetic method. The BiVO_4 seeded FTO substrate was horizontally placed into a glass flask with the volume of 50 mL. A mixture of 0.2 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and VCl_3 precursor solution in ethylene glycol (a mixture of ethylene glycol 30 ml and DI water 20 ml) was prepared, 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 1 h. The prepared film was annealed at 500 $^\circ\text{C}$ for 3h (with a 3h ramp time) in air to form the BiVO_4 seed layer.

Preparation of BiVO_4 solid-crystals. BiVO_4 solid-crystals were grown on FTO substrate using a drop

casting technique. Here 200 μL of a 5 mM $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 5 mM VCl_3 precursor solutions in ethylene glycol was dropped onto the FTO substrate ($1.5 \text{ cm} \times 2 \text{ cm}$) with a drying step at $130 \text{ }^\circ\text{C}$ in air.

The prepared film was annealed at $500 \text{ }^\circ\text{C}$ for 3h (with a 3h ramp time) in air to form the BiVO_4 seed layer.

Preparation of BiVO_4 hydro-crystals. BiVO_4 hydro-crystals were grown on FTO substrate using a seed-mediated hydrothermal synthetic method. The BiVO_4 seeded FTO substrate was horizontally placed into a Teflon-lined stainless steel autoclave with the volume of 50 mL. A mixture of 0.2 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 precursor in ethylene glycol solution (a mixture of citric acid and DI water 50 ml) was prepared, and then transferred into an autoclave. The sealed autoclave was heated in an electric oven at $180 \text{ }^\circ\text{C}$ for 6 h and then cooled to room temperature. The prepared film was annealed at $500 \text{ }^\circ\text{C}$ for 3h (with a 3h ramp time) in air to form the BiVO_4 hydro-crystals.

Preparation of powdered BiVO_4 crystals. BiVO_4 hydro-crystals were prepared using a hydrothermal synthetic method. A mixture of 0.2 M $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and NH_4VO_3 precursor in ethylene glycol solution (a mixture of citric acid and DI water 50 ml) was prepared, and then transferred into an autoclave. The sealed autoclave was heated in an electric oven at $180 \text{ }^\circ\text{C}$ for 6 h and then cooled to room temperature. The prepared powdered BiVO_4 crystals (20 mM in ethylene glycol) were annealed on the FTO at $500 \text{ }^\circ\text{C}$ for 3h (with a 3h ramp time) in air to form the powdered BiVO_4 electrode. The powdered BiVO_4 is difficult to deposit, and have limited interactions on the conductive FTO substrate, even after the annealing process. The powdered BiVO_4 electrode showed negligible photocurrent under UV-visible irradiation compared to BiVO_4 sono-crystals, BiVO_4 hydro-crystals, and BiVO_4 solid-

crystals.

Preparation of BiVO₄ sc-amorphous. BiVO₄ solid-crystals were grown on FTO substrate using a drop casting technique. Here 200 μ L of a 5 mM Bi(NO₃)₃·5H₂O and 5 mM VCl₃ precursor solutions in ethylene glycol was dropped onto the FTO substrate (1.5 cm \times 2 cm) with a drying step at 130 °C in air.

The prepared film was annealed at 500 °C for 3h (with a 3h ramp time) in air to form the BiVO₄ seed layer. And then amorphous BiVO₄ was deposited to cover the exposed FTO using above sonochemical method, but without the subsequent annealing process.

Electrochemical characterization of electrodes. Electrochemical characterization was performed in a specially designed cell in a three-electrode configuration with the BiVO₄ materials as the working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The working electrode with the actual geometric area of 0.28 cm² was exposed to electrolyte solution. A 150 W xenon lamp (ABET technologies) was used as the light source in the PEC characterization step, and light illumination area was 0.28 cm². 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 Na₂SO₄ (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/cm² 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.

Characterization. The BiVO₄ crystals were characterized by scanning electron microscopy (SEM, Magellan 400 operated at 2 kV). The X-ray diffraction (XRD) spectra were measured using Cu K α .

radiation at 40 kV and 300 mA (Rigaku, D/MAX-2500). The UV-Vis absorption spectra were acquired from the photoelectrode film with a UV-3600 UV-VIS-NIR spectrophotometer using a solid sample holder in the wavelengths ranging from 300 to 800 nm.

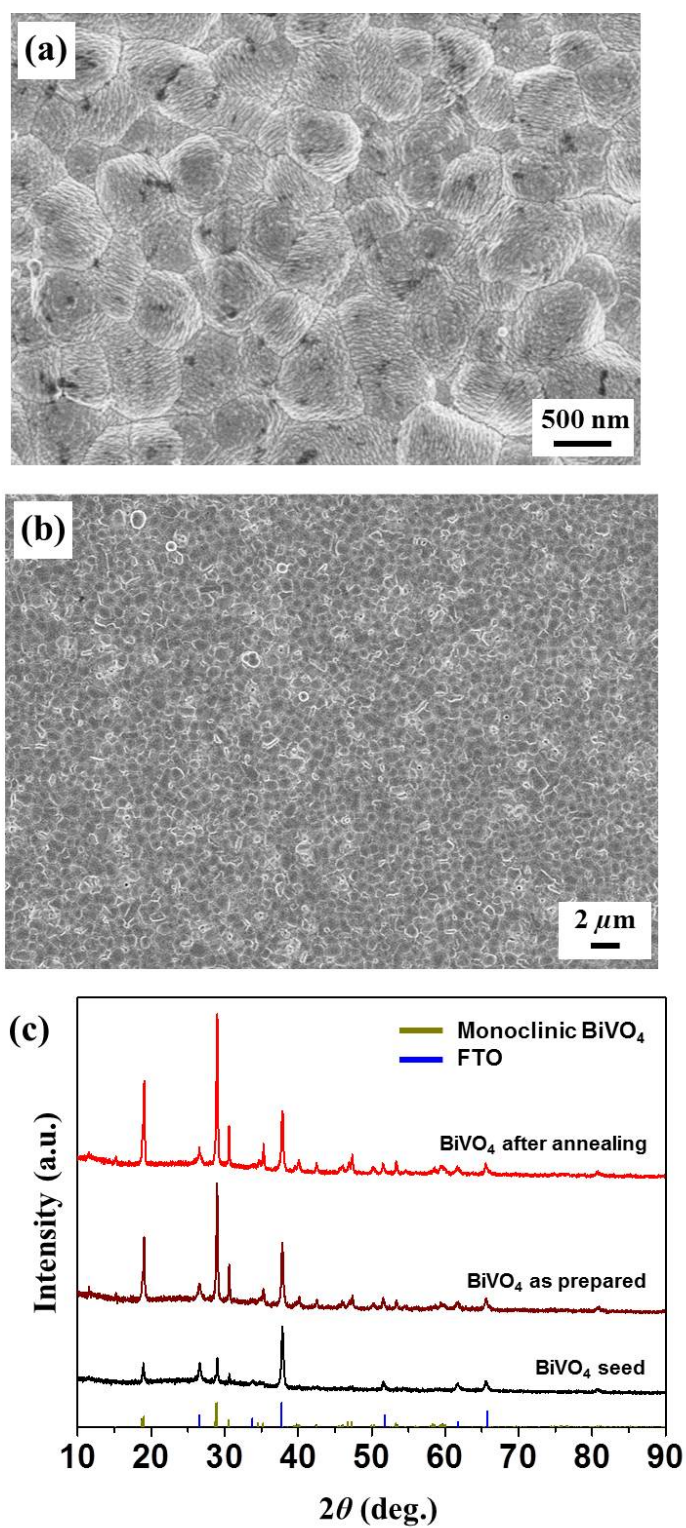


Figure S1. SEM images of the (a) as prepared BiVO₄ crystals and (b) BiVO₄ sono-crystals on the FTO. (c) XRD patterns of BiVO₄ films depending on the reaction conditions.

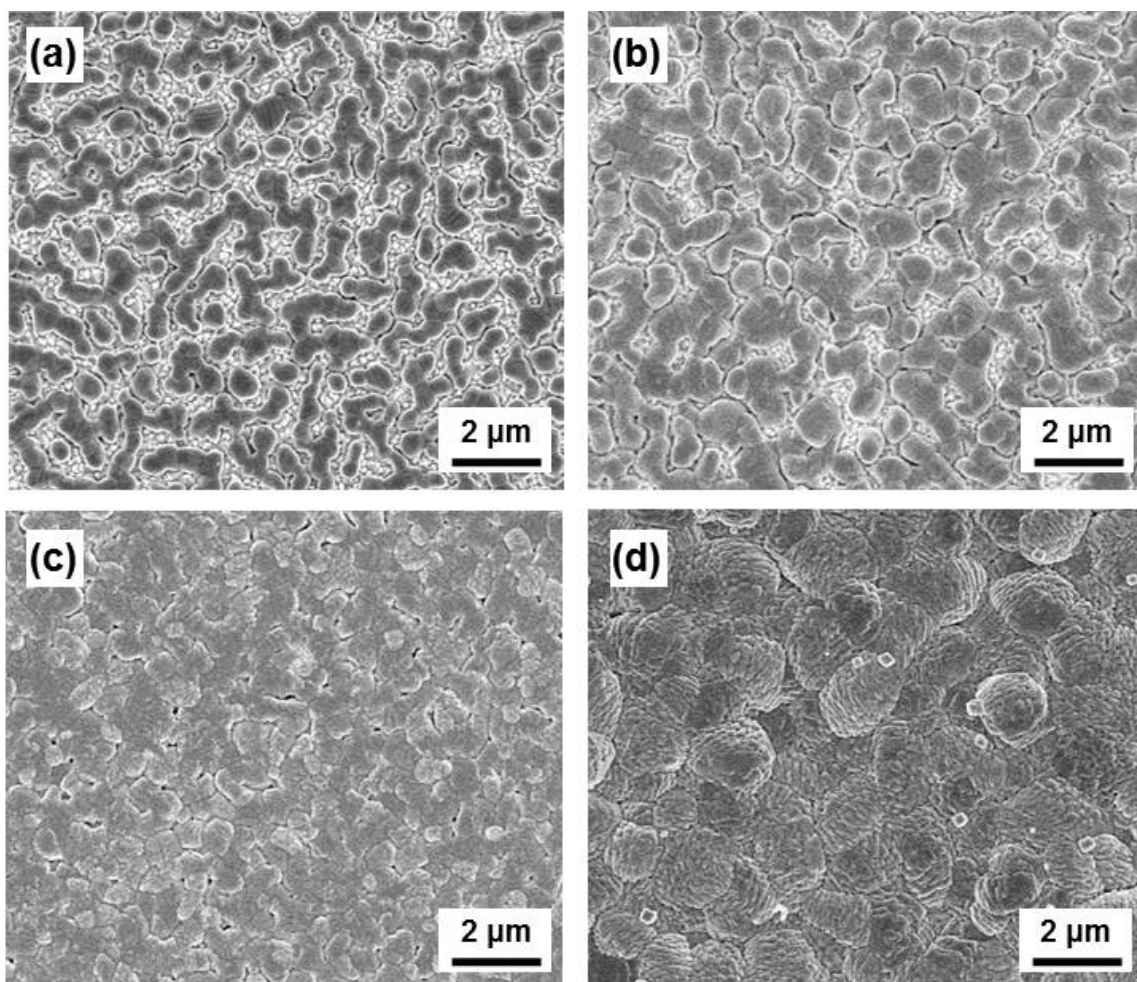


Figure S2. SEM images of BiVO₄ film on the FTO after ultrasonication for (a) 0 min (seed), (b) 10 min, (c) 20 min, and (d) 45 min under ambient conditions.

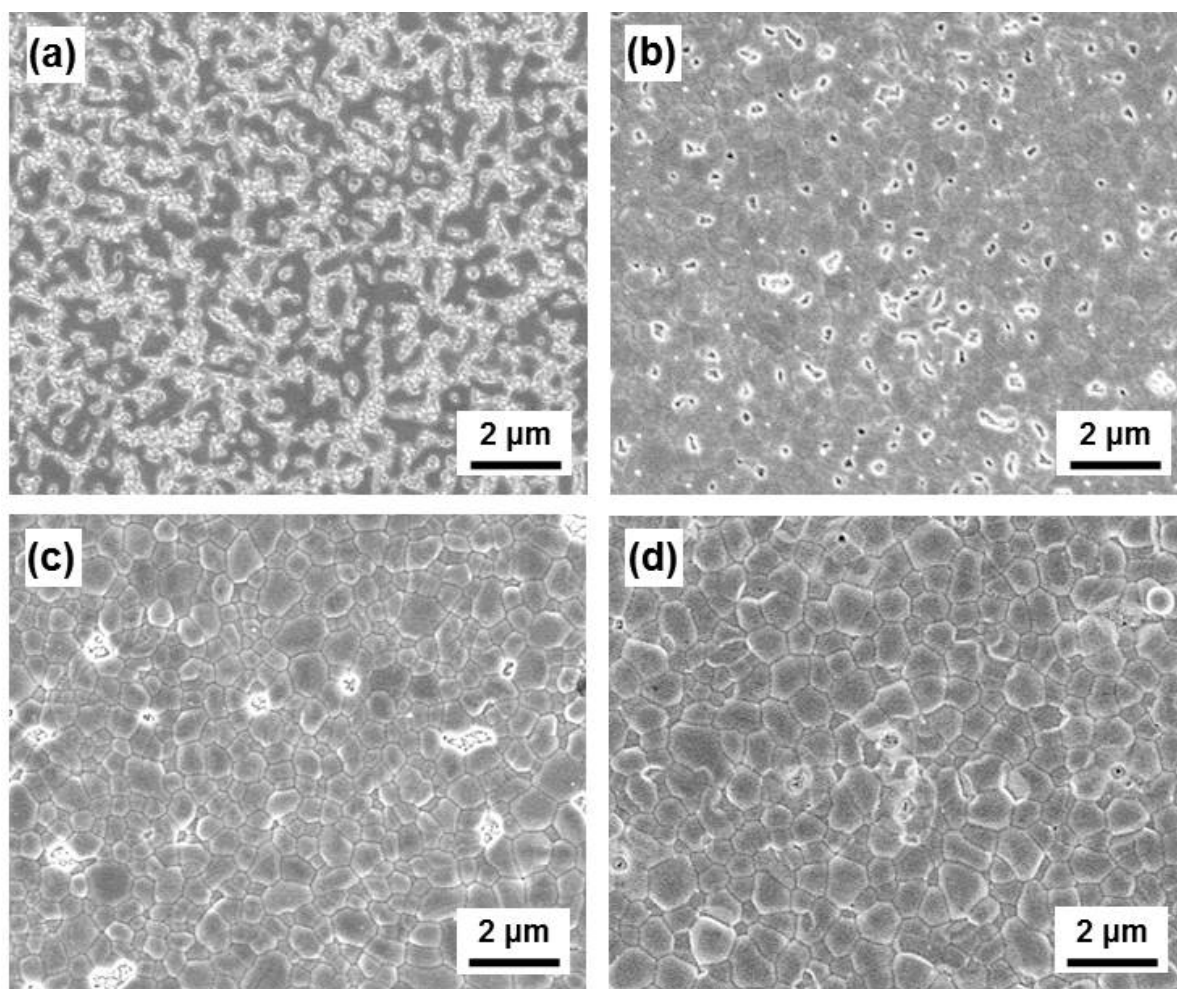


Figure S3. SEM images of BiVO₄ film on the FTO after ultrasonication for (a) 0 min, (b) 10 min, (c) 20 min, and (d) 45 min after annealed at 500 °C for 3 h in air.

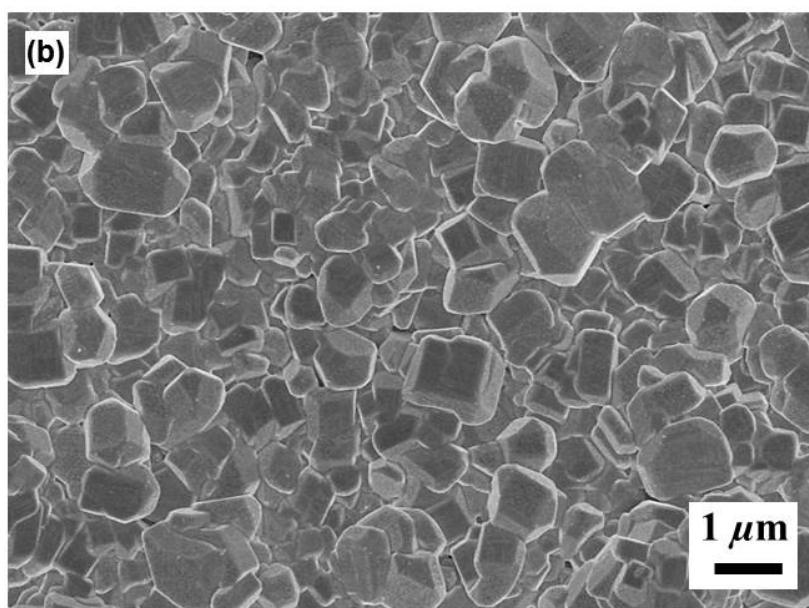
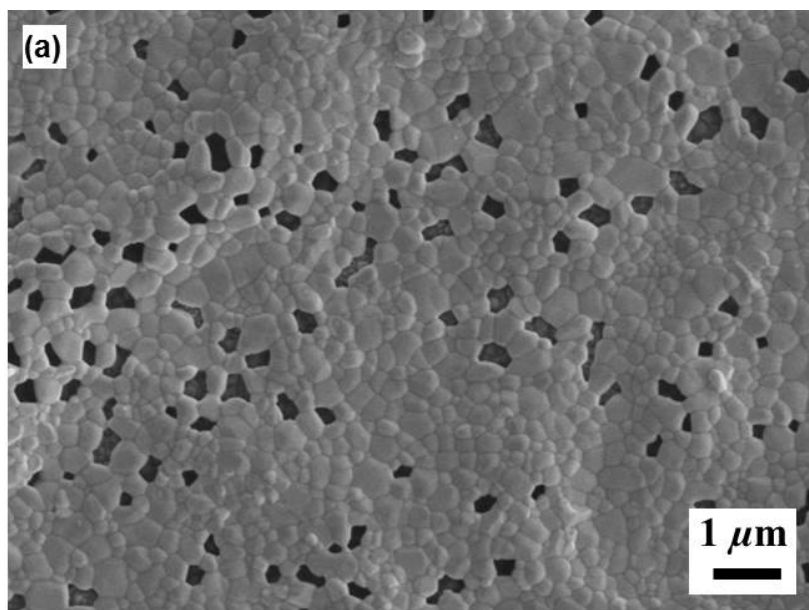


Figure S4. SEM images of (a) BiVO_4 solid-crystals, and (b) BiVO_4 hydro-crystals on the FTO substrate.

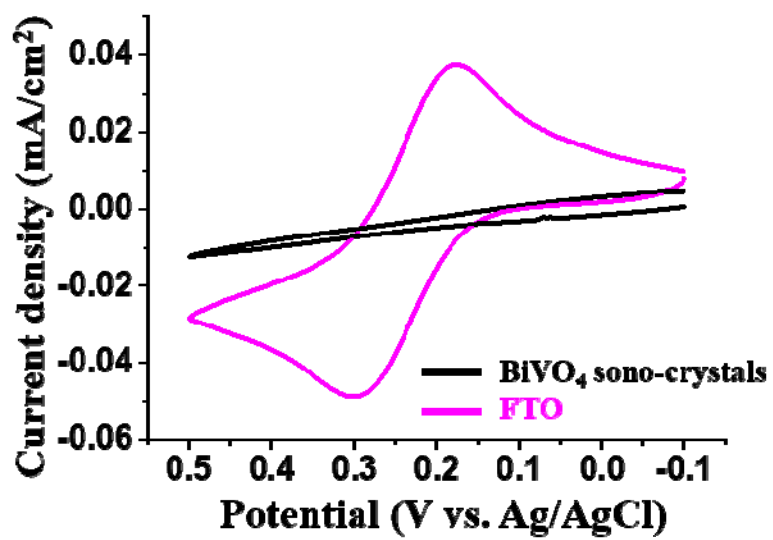


Figure S5. CV curves of the FTO, and BiVO₄ sono-crystals in 1 mM FcMeOH (0.1 M phosphate buffer, pH 7) solution. Scan rate: 10 mV/s.

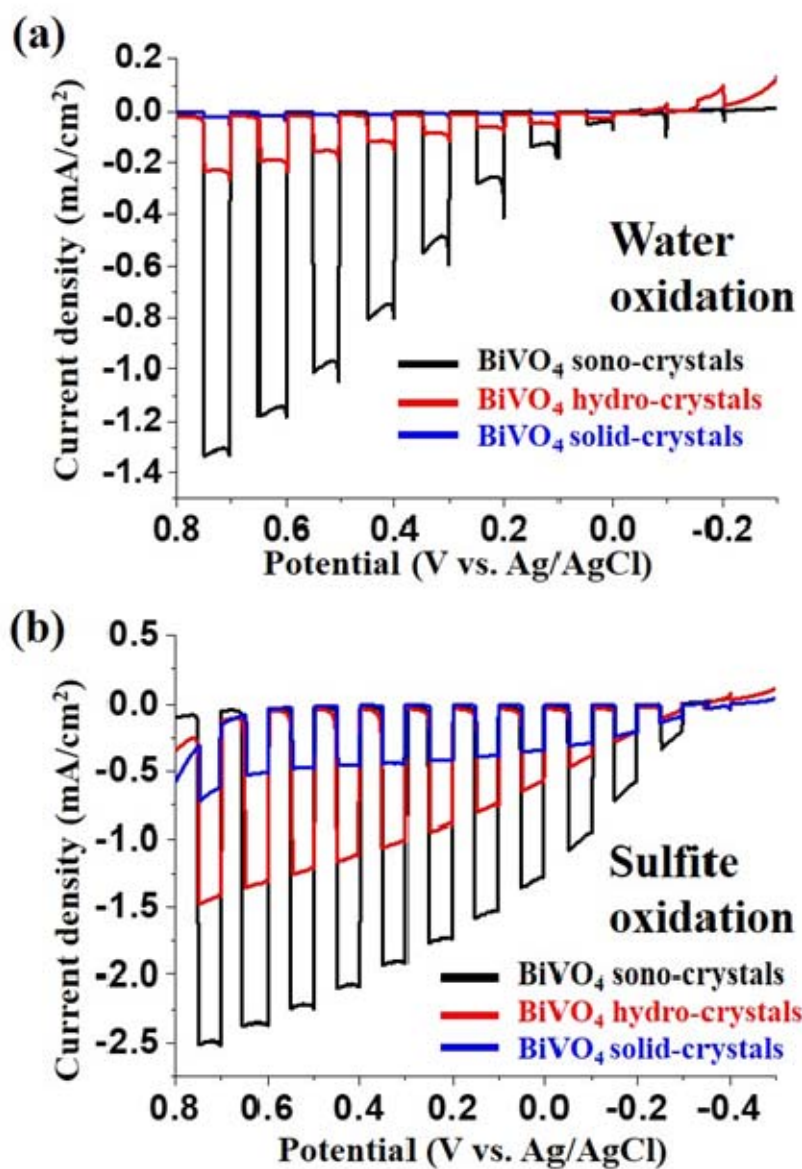


Figure S6. LSVs of BiVO₄ solid-crystals (blue-line), BiVO₄ hydro-crystals (red-line), and BiVO₄ sono-crystals (black-line) (a) for water oxidation in a phosphate buffer (pH 7), and (b) Sulfite oxidation (0.1 M Na₂SO₄ + 0.1 M Na₂SO₃) under visible illumination (>425 nm). Scan rate: 20 mV/s. Light intensity: 100 mW/cm².

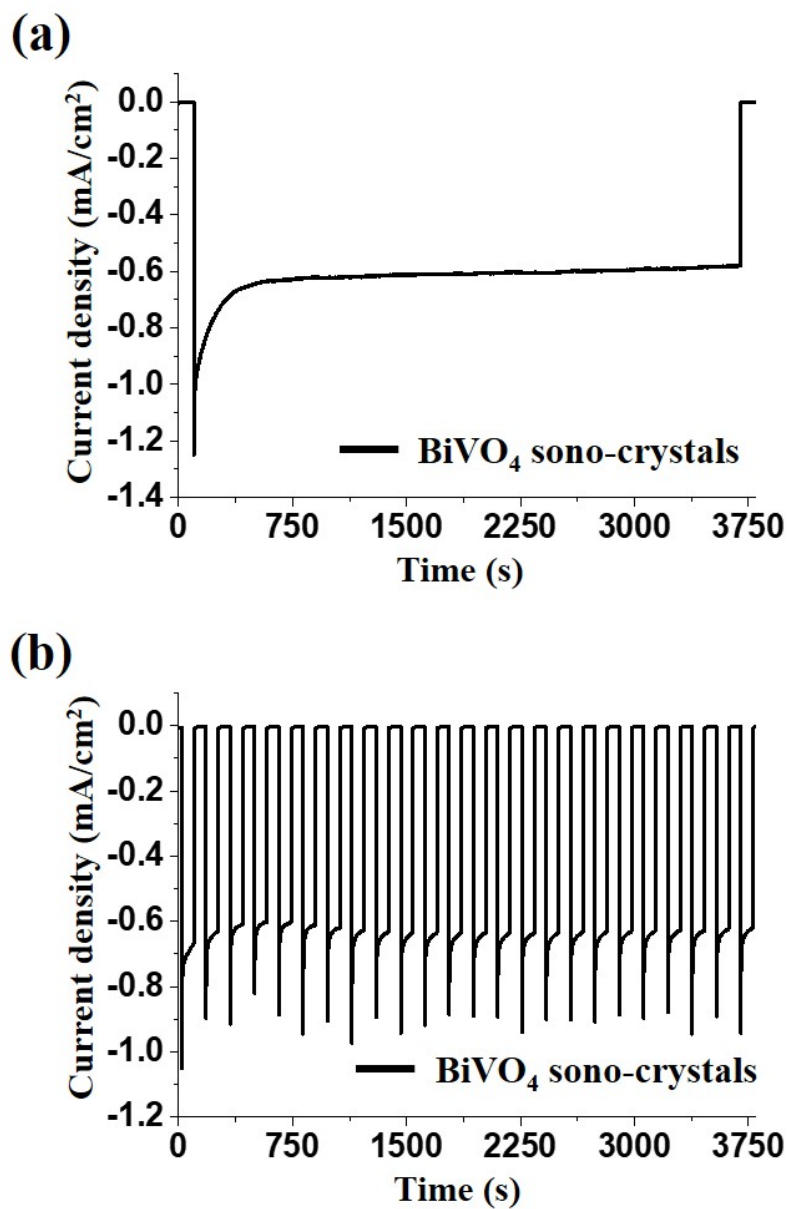


Figure S7. Current-time response curves (0.3 V vs. Ag/AgCl) of the BiVO₄ sono-crystals under (a) continuous UV-visible illumination, and (b) under chopping light in a 1.0 M borate buffer (pH 9). Light intensity: 100 mW/cm².

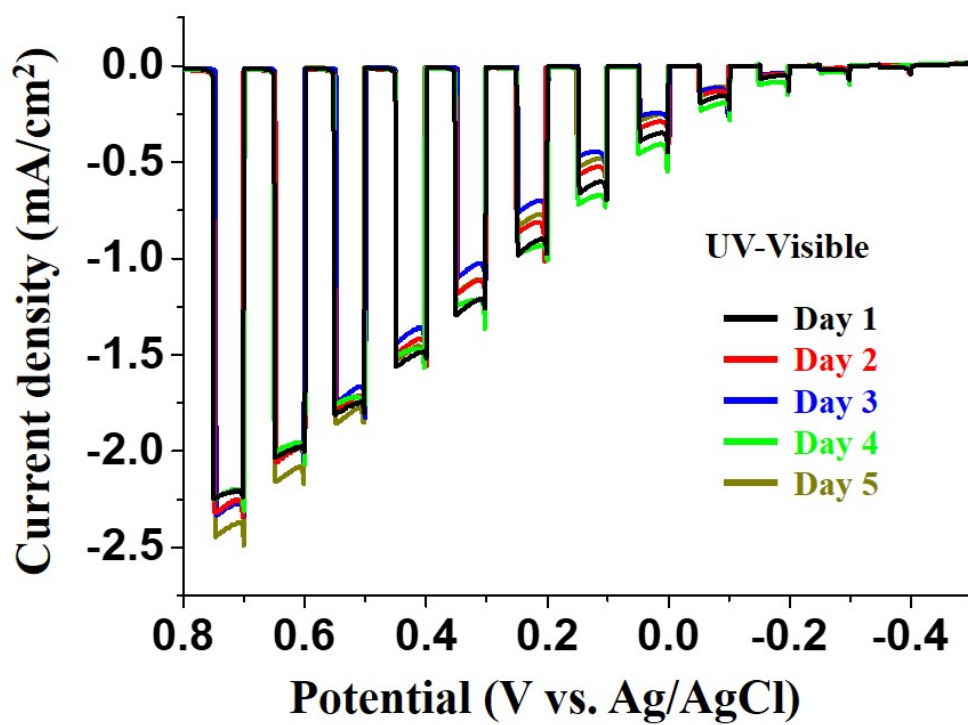


Figure S8. LSVs of the BiVO₄ sono-crystals after the stability tests in a 1.0 M borate buffer (pH 9). Light intensity: 100 mW/cm².

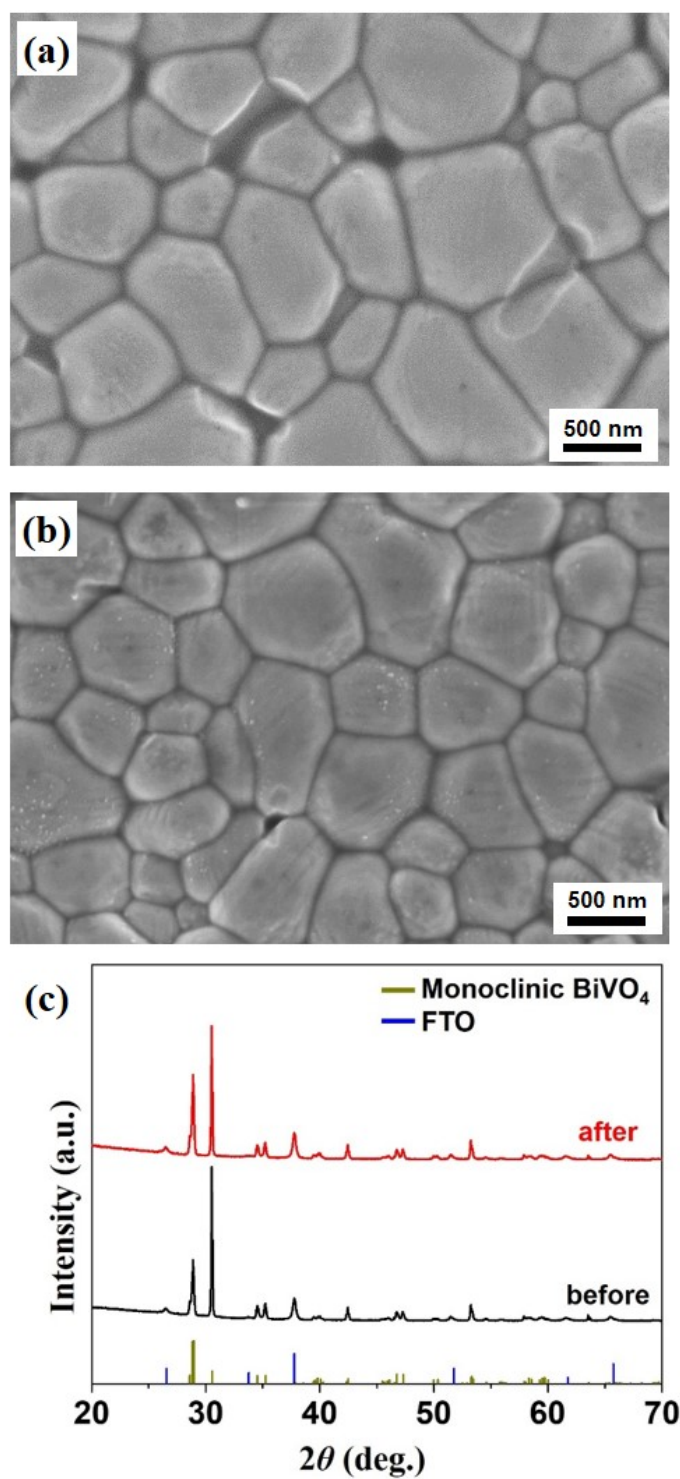


Figure S9. SEM images of BiVO₄ sono-crystals, (a) before and (b) after the stability test. (c) XRD patterns of BiVO₄ sono-crystals before (black) and after (red) after the stability test.

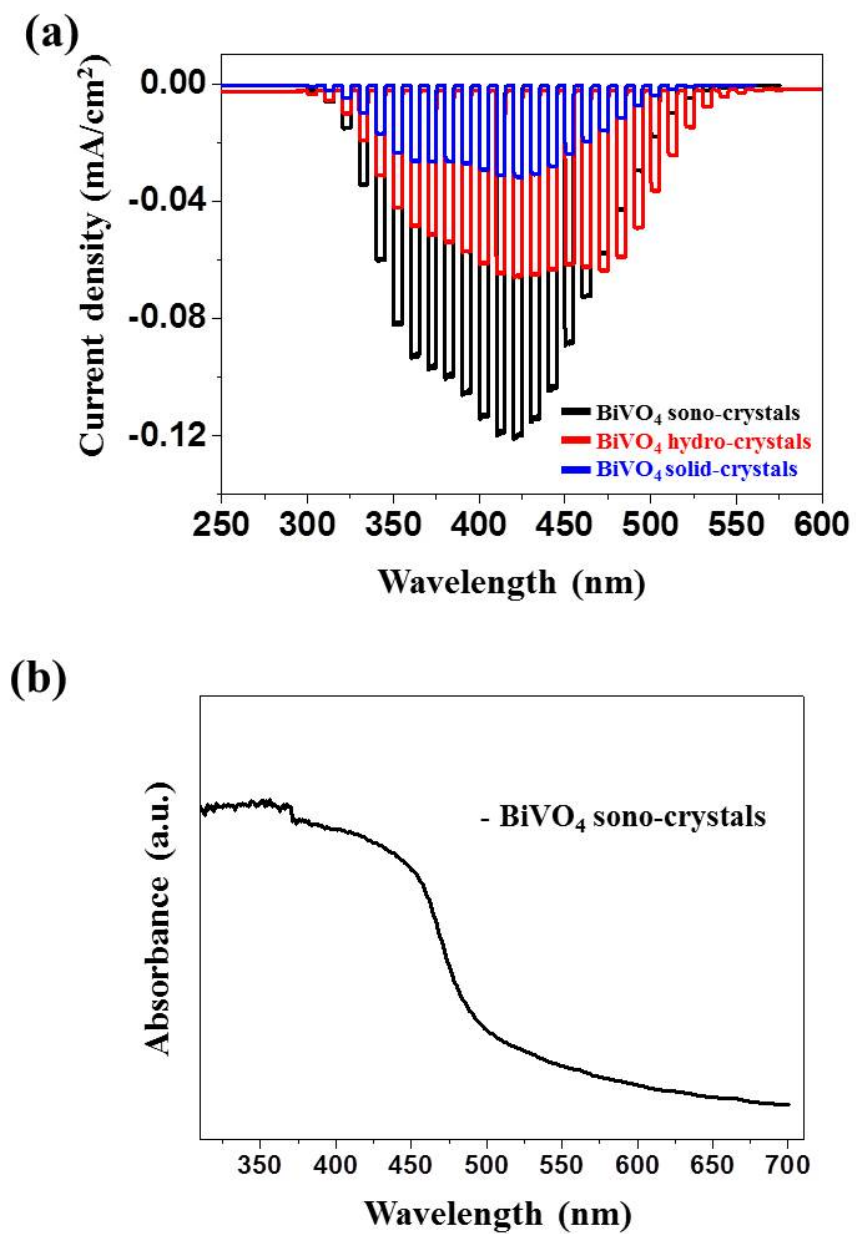


Figure S10. (a) Action spectrum of BiVO₄ electrodes at an applied potential of 0.3 V versus Ag/AgCl in 0.1 M Na₂SO₄ + 0.1 M Na₂SO₃. (b) UV-vis absorption spectrum of BiVO₄ solid-crystals.

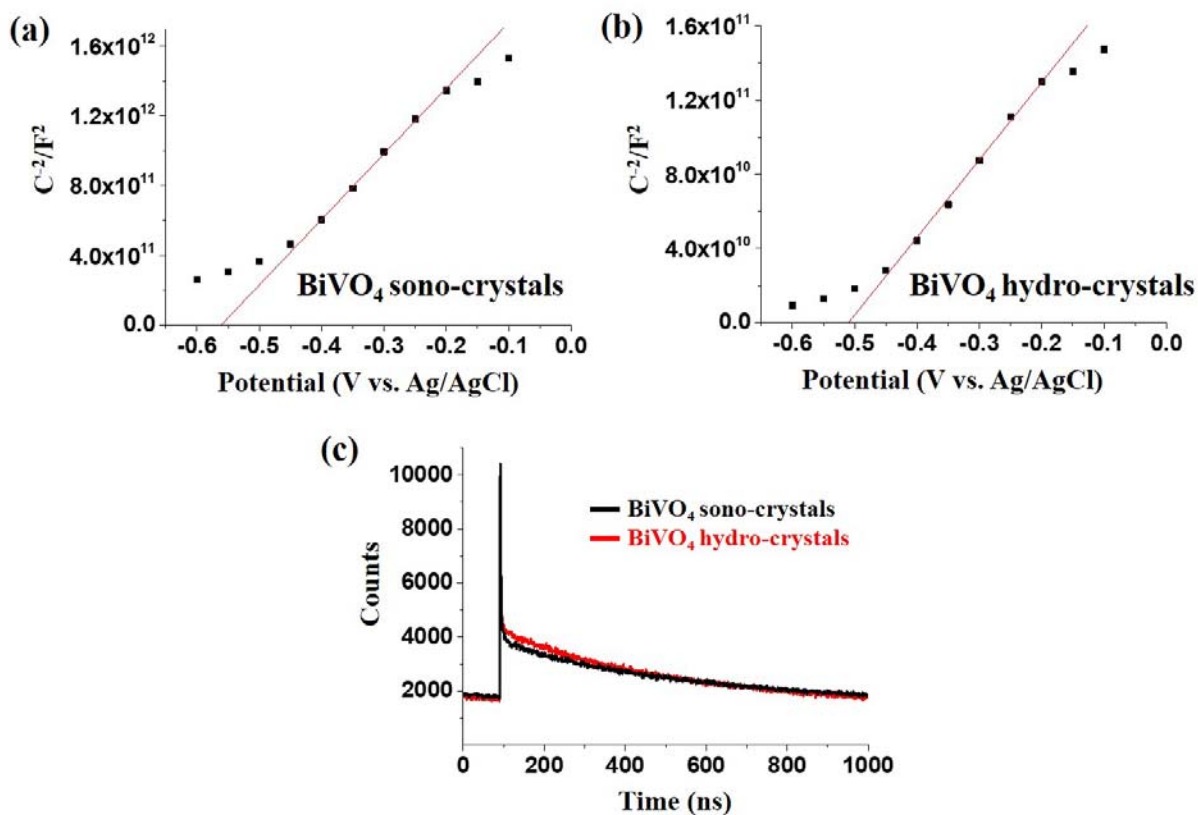


Figure S11. Mott-Schottky plots of (a) BiVO₄ sono-crystals and (b) BiVO₄ hydro-crystals obtained from the AC impedance capacitance measurements in 0.1 M phosphate buffer (pH 7). Carrier concentrations of $6.57 \times 10^{16} \text{ cm}^{-3}$ and $2.79 \times 10^{17} \text{ cm}^{-3}$ are calculated using Mott-Schottky equation for sono-crystals and hydro-crystals, respectively. (c) Transient absorption spectra at 500 nm on BiVO₄ sono-crystals (black), and BiVO₄ hydro-crystals (red) by the irradiation of laser light (375 nm). The calculated lifetime (τ_1) of BiVO₄ sono-crystals is 1.85 ns, which is slightly shorter than that of BiVO₄ hydro-crystals (2.47 ns).

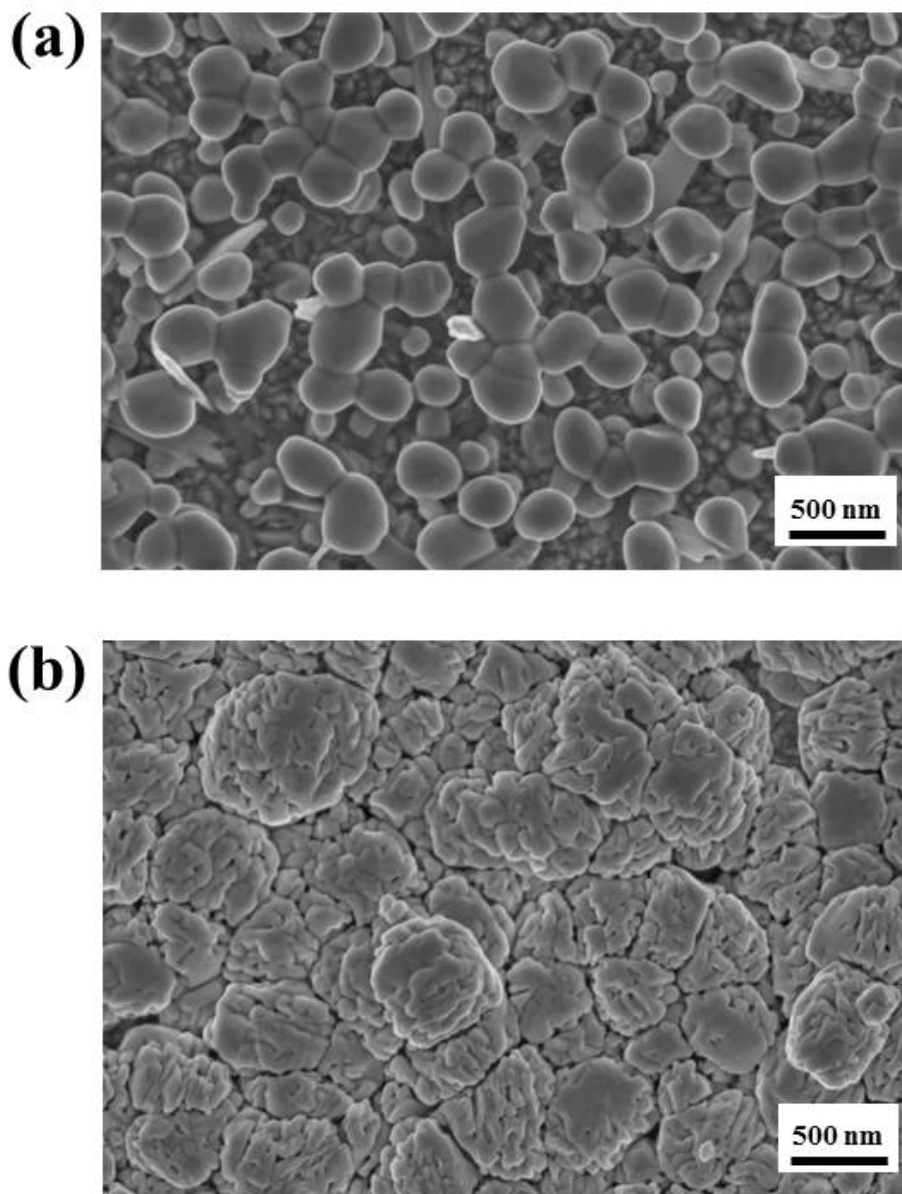


Figure S12. SEM images of BiVO₄ solid-crystals on the FTO (a) before and (b) after ultrasonication for 1 h under ambient conditions.

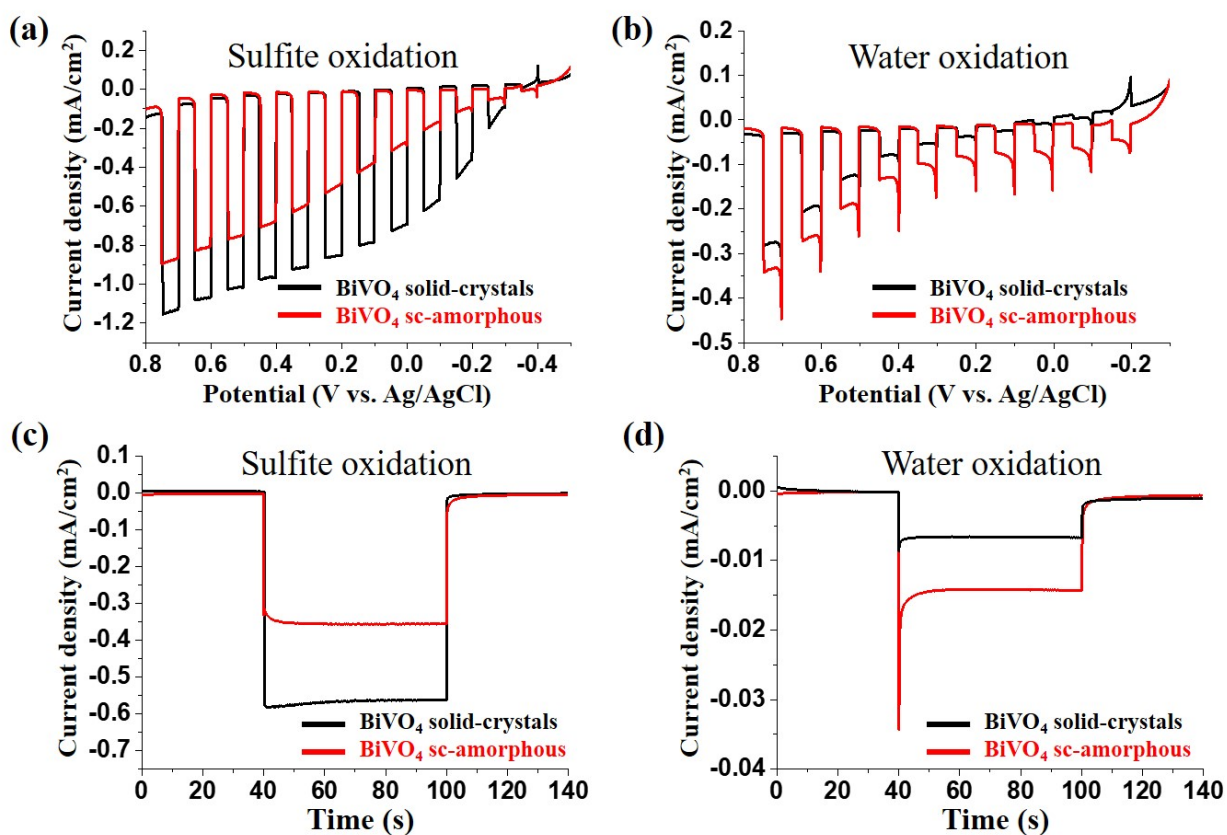


Figure S13. LSVs of BiVO₄ solid-crystals (black-line), and BiVO₄ sc-amorphous (red-line) for for (a) sulfite oxidation (0.1 M Na₂SO₄ + 0.1 M Na₂SO₃), and (b) water oxidation in a phosphate buffer (pH 7) under UV-visible illumination. Scan rate: 20 mV/s. Current-time response curve of the BiVO₄ solid-crystals (black line) and BiVO₄ sc-amorphous (red line) for (c) sulfite oxidation (0.1 M Na₂SO₄ + 0.1 M Na₂SO₃), and (d) water oxidation in a phosphate buffer (pH 7) at an applied potential of 0.2 V vs Ag/AgCl under UV-visible illumination. Light intensity: 100 mW/cm².

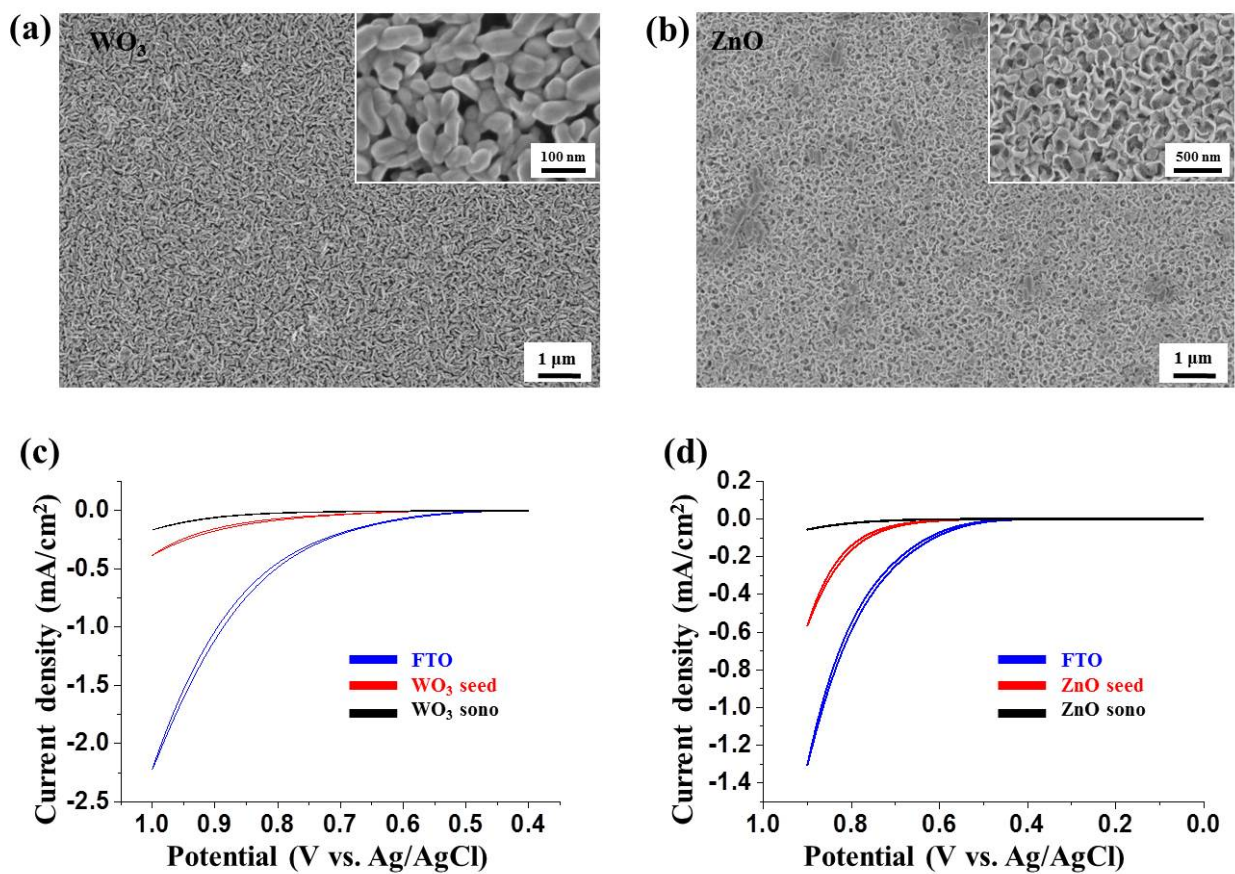


Figure S14. SEM images of (a) WO_3 sono-crystals, and (b) ZnO sono-crystals on the FTO substrate. CV curves of the (c) WO_3 sono-crystals, and (d) ZnO sono-crystals in 0.1 M Na_2SO_3 + 0.1 M Na_2SO_4 solution. Scan rate: 20 mV/s.