

Supporting Information

Metal Doping of BiVO_4 by Composite Electrodeposition with Improved Photoelectrochemical Water Oxidation

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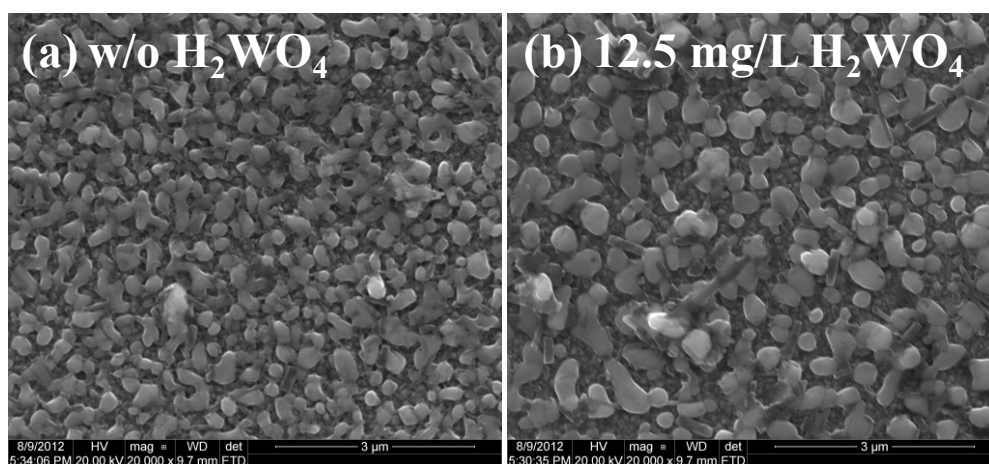


Figure S1. SEM images of BiVO_4 electrodeposited (a) without and (b) with 12.5 mg/L H_2WO_4 .

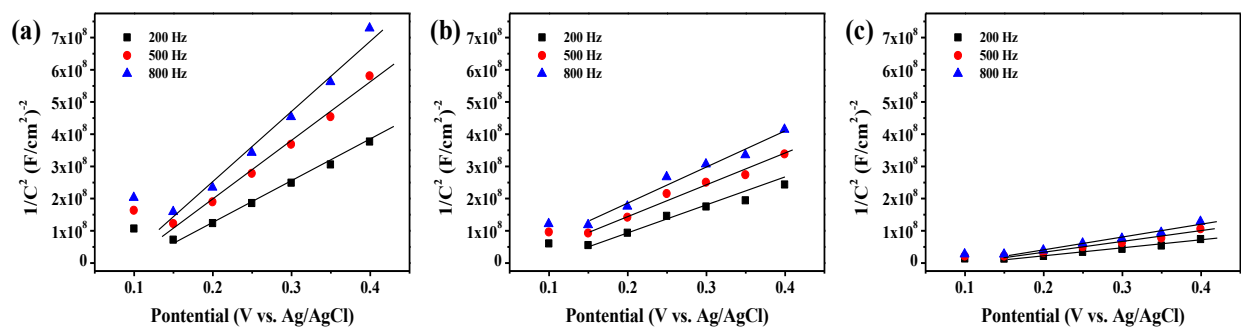


Figure S2. Mott-Schottky plots of BiVO_4 electrodeposited with (a) 0 mg/L, (b) 6.25 mg/L, and (c) 12.5 mg/L of H_2WO_4 , measured in pH 7 0.2 M phosphate solution. AC amplitude of 5 mV was applied for each potential, and three different AC frequencies (200, 500, and 800 Hz) were used for the measurements. The slope of the linear fits is inversely proportional to the carrier density and the results indicate that the carrier density increases with the addition of H_2WO_4 in the plating solution.

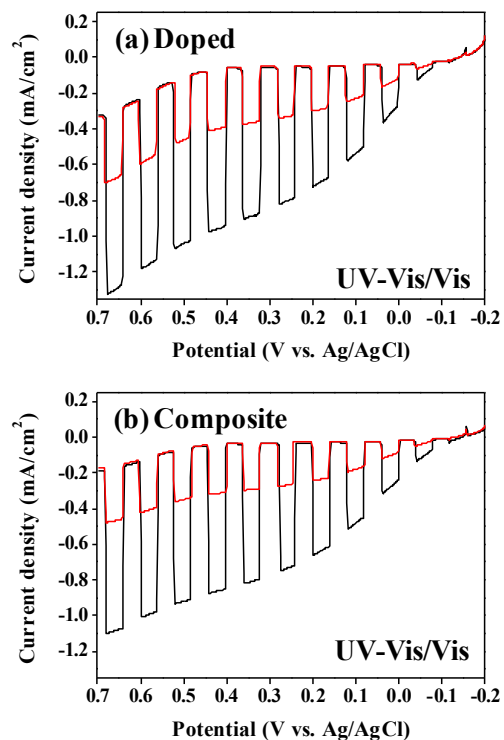


Figure S3. Linear sweep voltammograms of BiVO₄ electrodeposited with (a) 25 mg/L and (b) 300 mg/l H₂WO₄ in 0.1 M Na₂SO₃/0.1 M Na₂SO₄ aqueous solution with chopped light under UV-visible (black line) or visible (red) irradiation. Intensity of light from a full xenon lamp was about 100 mW/cm², and the scan rate was 20 mV/s.

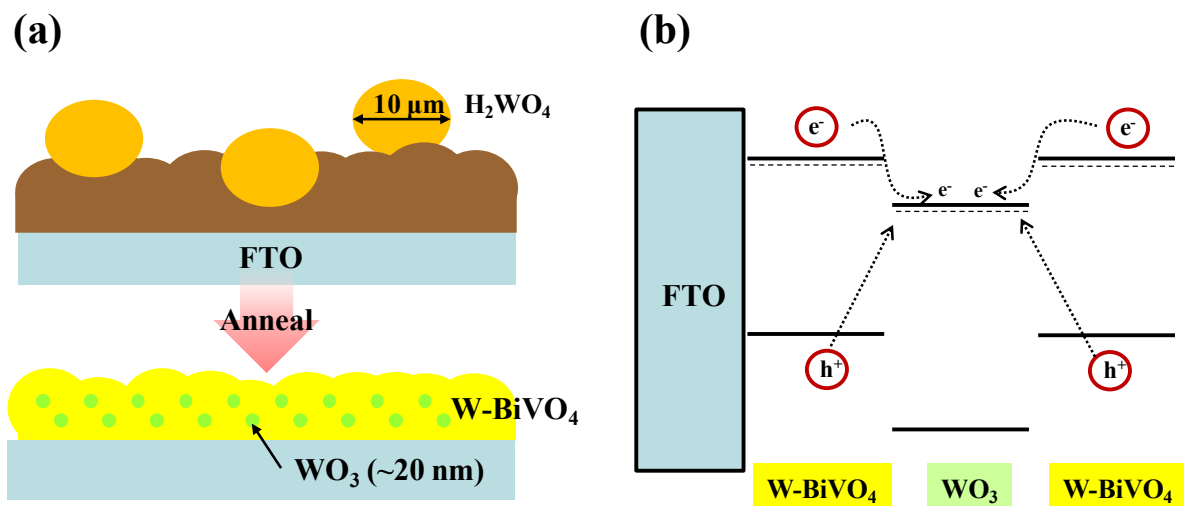


Figure S4. (a) Schematic diagrams of BiVO₄ film electrodeposited with H₂WO₄ before and after annealing (550°C), and (b) the band diagram of W-BiVO₄ and WO₃ composite film.

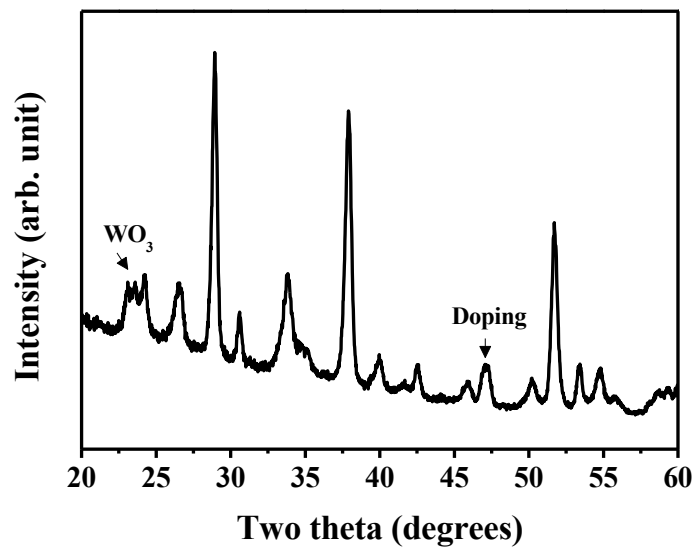


Figure S5. X-ray diffraction spectrum of BiVO_4 film electrodeposited with 250 mg/L H_2WO_4 in the plating solution. FTO glass was vertically mounted on the plating cell to prevent the settled particle from being incorporated in the deposit film during electrodeposition.

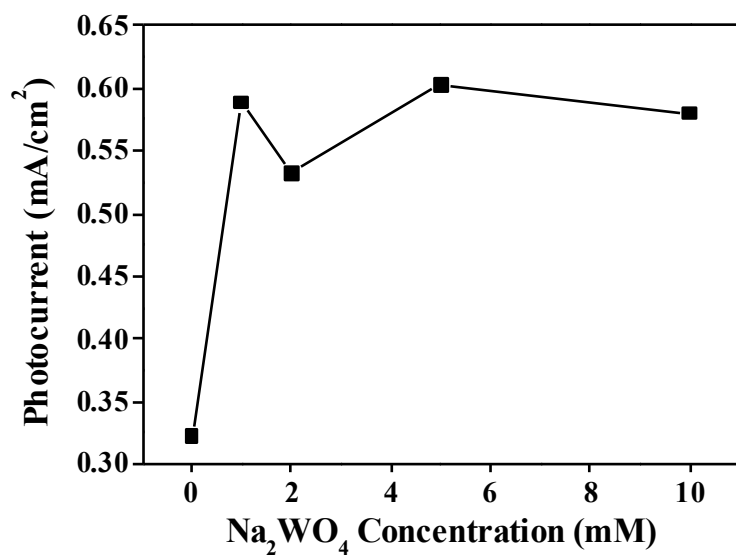


Figure S6. Photocurrents of BiVO₄ films electrodeposited with various amounts of Na₂WO₄, which were measured at 0.4 V (vs. Ag/AgCl) in 0.1 M Na₂SO₃/0.1 M Na₂SO₄ aqueous solution with 100 mW/cm² UV-visible light irradiation.

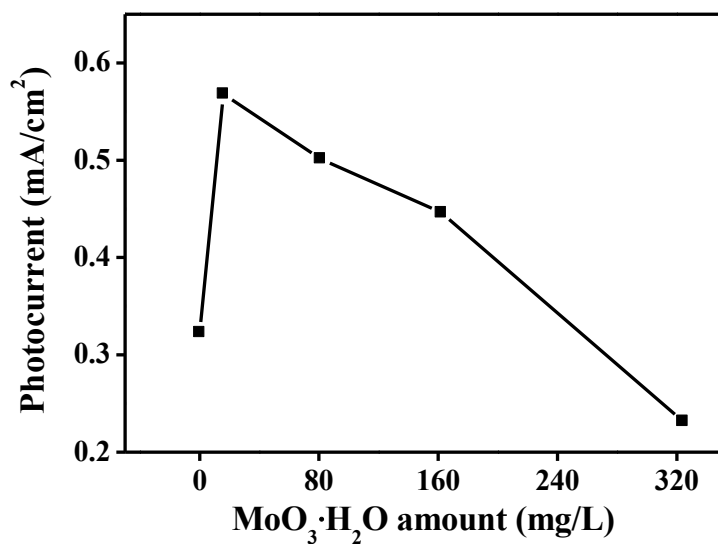


Figure S7. Photocurrents of BiVO₄ films electrodeposited with various amounts of MoO₃·H₂O, which were measured at 0.4 V (vs. Ag/AgCl) in 0.1 M Na₂SO₃/0.1 M Na₂SO₄ aqueous solution with 100 mW/cm² UV-visible light irradiation.

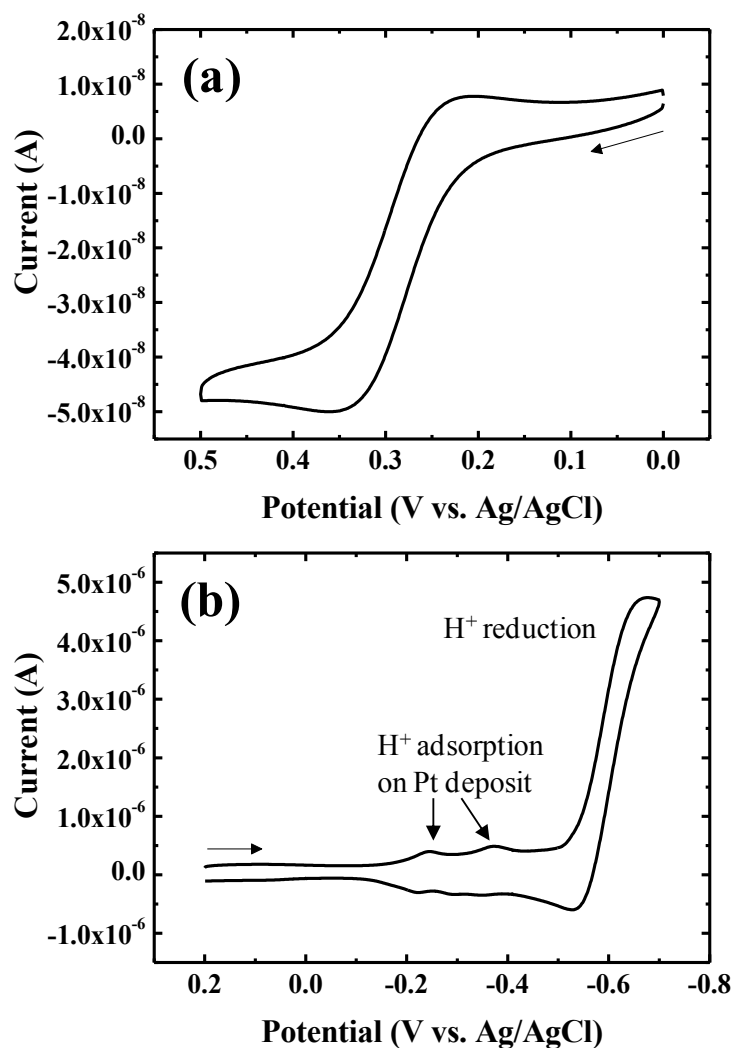


Figure S8. Cyclic voltammograms of optical fiber-mounted Au ring electrode in (a) 1 mM ferrocene methanol and 0.1 M Na₂SO₄ aqueous solution and in (b) 0.2 M sodium phosphate buffered aqueous solution (pH 7) after Pt electrodeposition that was carried out in 10 mM H₂PtCl₆ and 0.1 M Na₂SO₄ with potential multi-cycle from 0.2 V to -0.7 V (vs. Ag/AgCl). Scan rate was 20 mV/s.

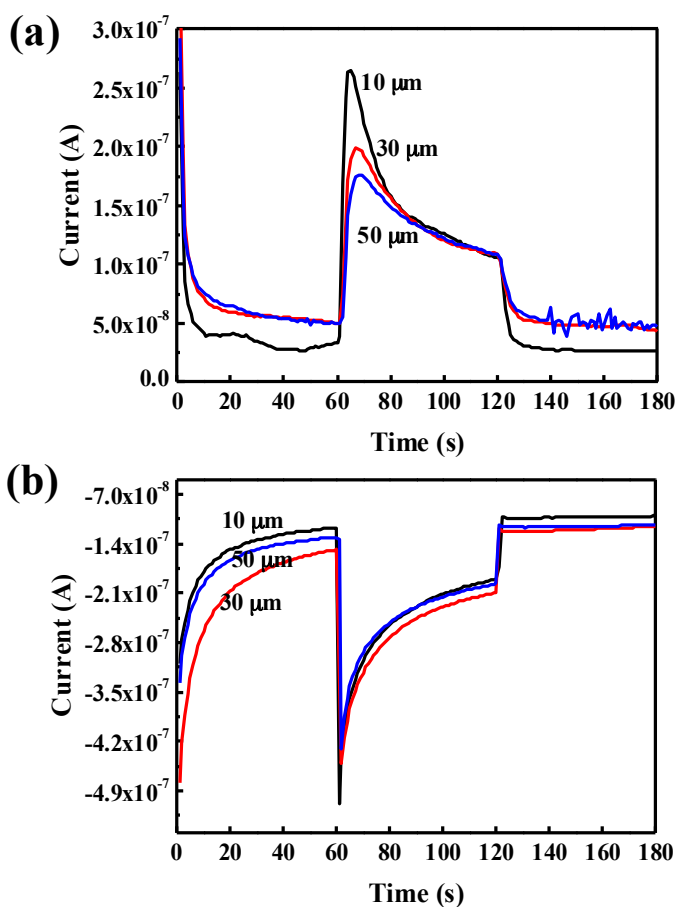


Figure S9. Chronoamperograms of (a) Au ring electrode tip collection and (b) substrate generation for water oxidation on W-doped BiVO_4 electrodes with change in the distance between tip and substrate in 0.2 M sodium phosphate buffered aqueous solution (pH 7). The measurements started in the dark and UV-vis light began to be irradiated at 60 s and finished at 120 s.

Melting Point Depression

The reduction of melting point of nanoparticle can be expressed by Gibbs-Thomson equation¹;

$$\frac{\Delta T}{T_m} = \frac{4V}{\Delta H_f d} \sigma$$

Where

T_m : melting point (for bulk WO_3 : 1470°C)

V : molar volume (WO_3 : 32.38 cm^3/mol)

ΔH_f : heat of fusion (WO_3 : 13940 cal/mol)

σ : solid-liquid interface energy (WO_3 : 0.241 J/m^2 , ref [2])

The particle size and the calculated melting point are listed as follows.

Particle size (d in nm)	T_m
20	779
18	701
15	548

This equation was derived for metal nanoparticles under constant pressure conditions. If particles are bonded covalently (e.g. semiconductor), the melting point depression is less pronounced. The calculated temperature, therefore, would be considered as a minimum melting temperature.

¹ Jackson, C. L.; McKenna, G. B. *J. Chem. Phys.* **1990**, *93*, 9002–9011.

² Boulova M.; Lucazeau G. *J. Solid State Chem.* **2002**, *167*, 425-434.