Supporting Information

Factors in the Metal Doping of $BiVO_4$ for Improved Photoelectrocatalytic Activity as Studied by Scanning Electrochemical Microscopy (SECM) and First-Principles Density-Functional Calculation

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Instruments: X-ray diffraction (XRD) measurement was performed using a Bruker-Nonius D8 Advanced powder diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (λ=1.54 Å). Grazing incidence XRD (GIXRD) with incidence angle of 1° on detector scan mode was conducted to obtain the diffractogram from the thin film electrodes. The scan rate was 12° per minute in 0.02° increments of 2θ from 10° to 90°. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD instrument (Manchester, UK) with a monochromatic Al X-ray source with 180° hemispherical electron energy analyzer. For XPS, thin metal oxide films were prepared on FTO substrate. Scanning electron microscopy (SEM) images were obtained with a LEO1530 SEM at a working voltage of 10 kV with working distance of 5 mm.

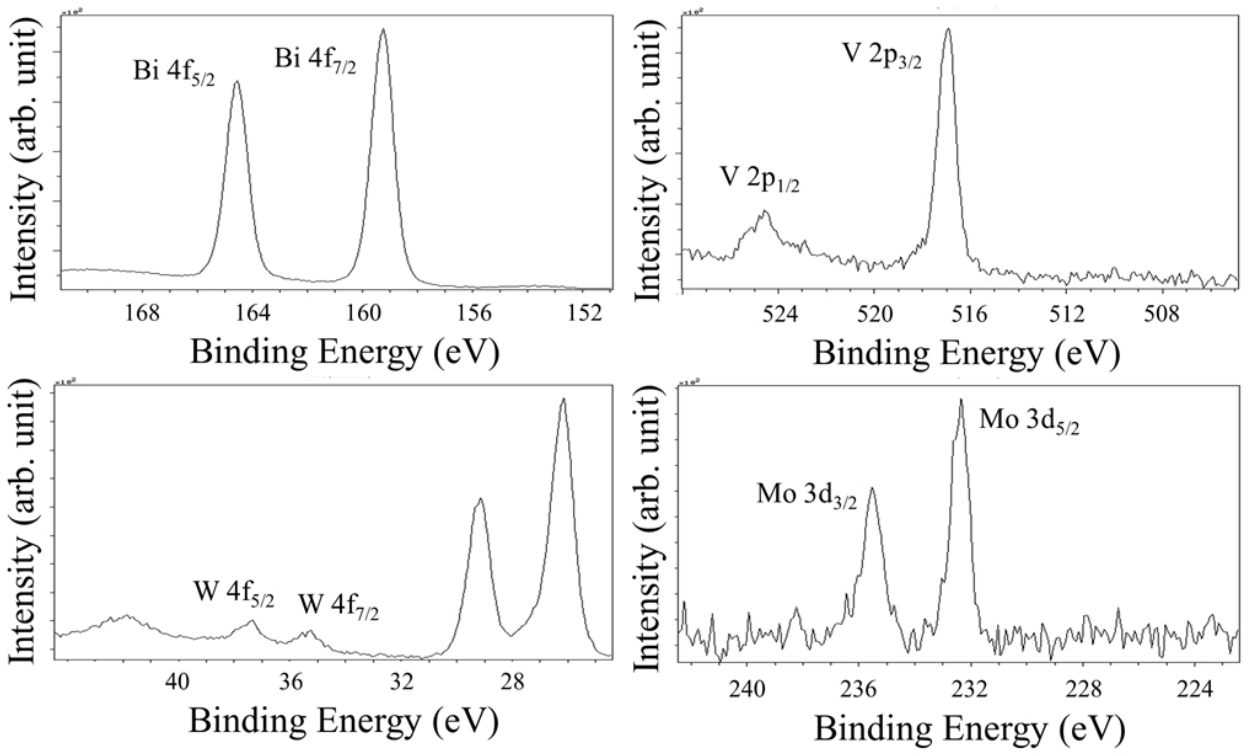

Figure S1. XPS of W/Mo-doped $BiVO_4$. The $BiVO_4$ film doped with 2 at% of W and 6 at% of Mo was prepared on the FTO substrate. The spectra were obtained from the film after about an hour of electrochemical experiment in 0.1 M Na_2SO_4 (pH 7, 0.2 M sodium phosphate buffered) and vigorously rinsed with D.I. water before XPS measurement.

Peak	Position BE (eV)	FWHM (eV)	Raw area (cps)	RSF	Atomic mass	Atomic conc.%	Mass conc.%
Bi 4f	159	0.932	37369	9.14	209	58	82
V 2p	517	0.875	5544	2.12	51	33	11
W 4f	37	0.863	493	3.52	184	2	3
Mo 3d	232	0.765	1548	3.32	96	6	4

Table S1. Atomic composition of W/Mo-doped $BiVO_4$ calculated based on XPS data shown in Figure S2.

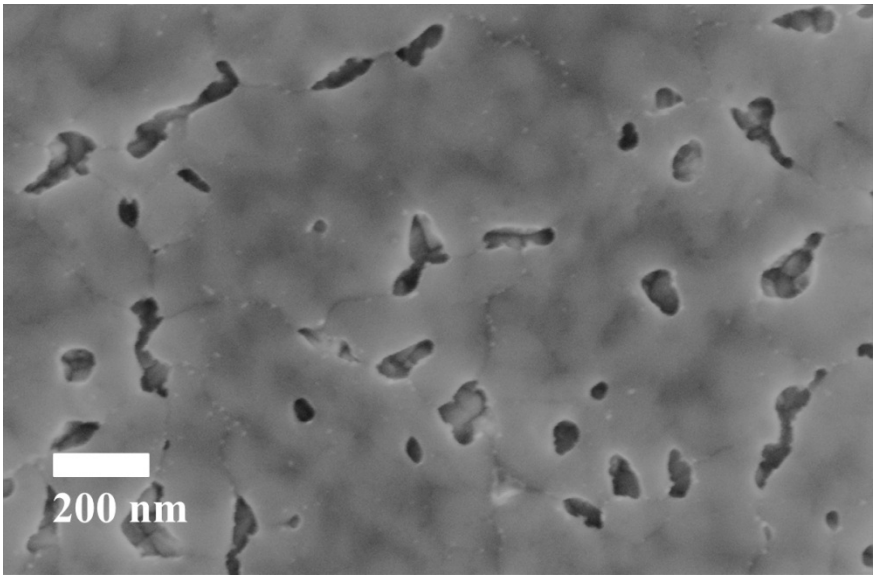

Figure S2. SEM image of W/Mo-doped $BiVO_4$ films which was drop casted on the FTO substrate.

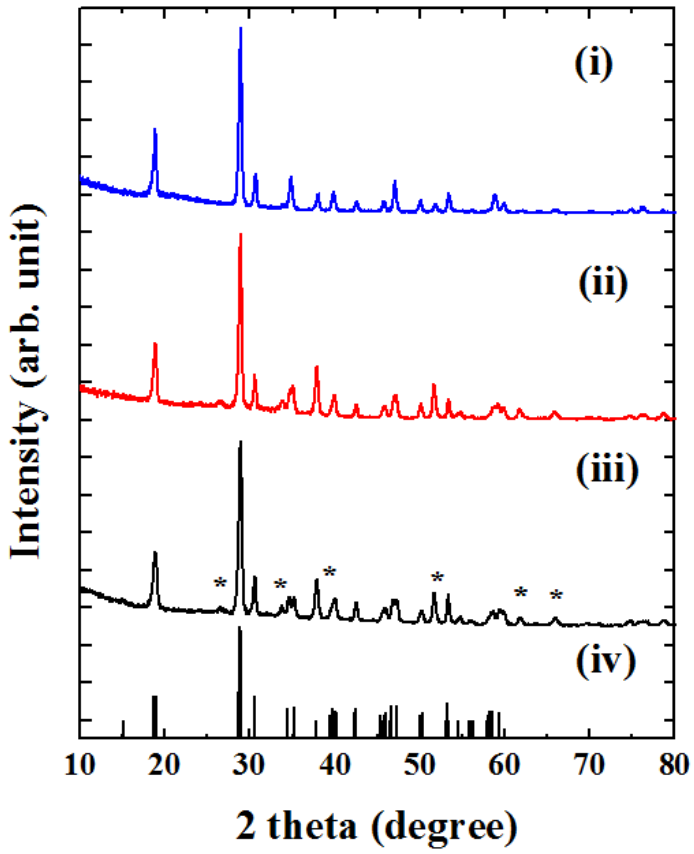

Figure S3. XRD patterns obtained from (i) W/Mo-doped $BiVO_4$, (ii) W-doped $BiVO_4$, and (iii) $BiVO_4$ without doping. The patterns shown here were obtained from more wide range of 2θ than that shown in Figure 7 to show the overall diffractograms of the bulk semiconductor films. The reference pattern of the monoclinic scheelite-like $BiVO_4$ (iv, PDF# 14-0688) and the peaks from FTO substrate (*) are also indicated in the diffractograms.

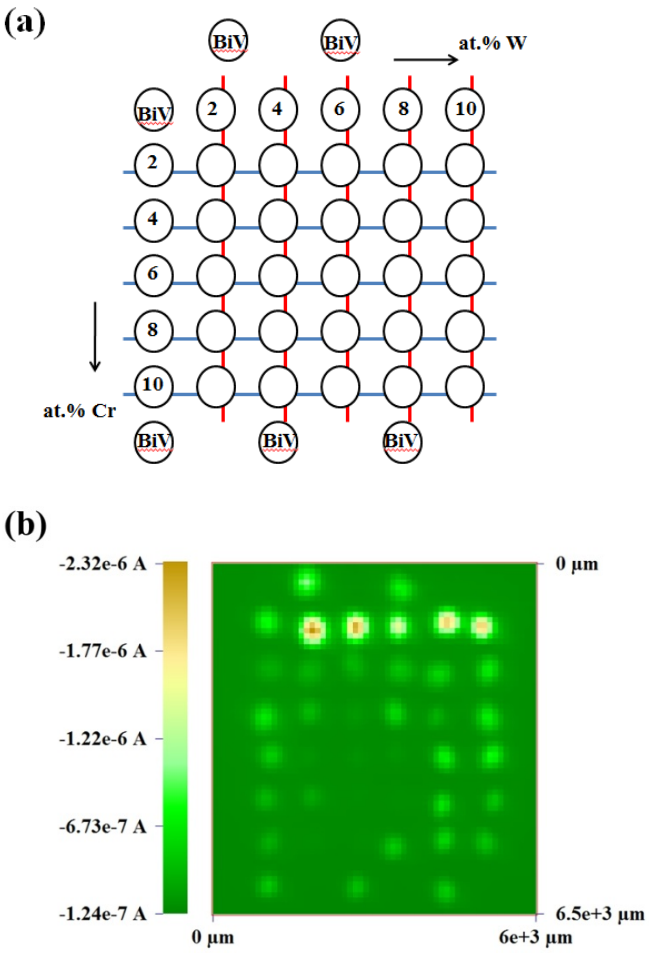

Figure S4. Schematic diagram of the atomic composition of dispensed photoelectrocatalysts on FTO substrate (a) and the SECM image measuring photooxidation current in 0.1 M Na_2SO_3 aqueous solution (b). The physical dimensions and preparation method are described in Figure 1. However, the precursor solution of Cr (0.02 M) in ethylene glycol was used instead of the Mo precursor solution. The photooxidation current was measured at the applied potential of 0.4 V. Scan rate of fiber optic was 100 µm per 0.1 second. The fiber optic was placed 150 µm away from the sample substrate.