Supporting Information

Incorporation of Mo and W into Nanostructured BiVO₄ Films to Improve Photoelectrochemical Water Oxidation Performance

Sean P. Berglund, Alexander J.E. Rettie, Son Hoang, and C. Buddie Mullins*

Departments of Chemical Engineering and Chemistry and Biochemistry, Center for Electrochemistry, Texas Materials Institute, and Center for Nano- and Molecular Science
University of Texas at Austin
1 University Station C0400
Austin, TX 78712 (U.S.)

*address correspondence to: mullins@che.utexas.edu

Figure S1. Typical power density spectrum for light that was incident on the film during IPCE measurements. The power was measured using a UV enhanced silicon photo-detector.
Figure S2. Chopped (dark and white light) LSV scans for BiVO$_4$ films deposited in vacuum with no background gas and with 5x10$^{-6}$ Torr of O$_2$. After deposition both films were annealed in air at 500°C in for 2 hours. Measurements were conducted in mixture of 0.1 M Na$_2$SO$_4$ and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of 0.025 V s$^{-1}$.

Figure S3. SEM images of films with a Bi:V:Mo:W atomic ratio of 50:50:0:0 deposited at $\gamma=55^\circ$ (a) in vacuum with no background gas and (b) with 5x10$^{-6}$ Torr of O$_2$. The films have not been annealed.
Figure S4. SEM images of films with Bi:V:Mo:W atomic ratios of 46:46:6:2 deposited in vacuum at different deposition angles (γ) taken before and after annealing in air at 500 °C for 2 hours: (a) γ=0°, before annealing (b) γ=0°, after annealing (c) γ=55°, before annealing (d) γ=55°, after annealing (e) γ=75°, before annealing (f) γ=75°, after annealing.
Figure S5. Trends showing improvement in photocurrent density with age since annealing for BiVO₄ films with varying atomic percentages of Mo and W (relative to the total Bi, V, Mo, and W). The photocurrent density values were taken from LSV scans (value at 1.6 V vs. RHE) in 0.1 M Na₂SO₄ and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of 0.025 V s⁻¹. Between measurements the films were simply left in plastic container in the laboratory at normal atmospheric conditions.
Figure S6. Mott-Schottky plot for (a) pure BiVO₄ and (b) 6% Mo, 2% W BiVO₄ films conducted in 0.1 M Na₂SO₄ and 0.1 M
phosphate buffer solution (pH 6.8).

Figure S7. XPS spectra for a single 6% Mo, 2% W BiVO₄ film taken 1 day and 41 days after annealing.
**Figure S8.** Chopped (dark and white light) LSV scans for a 6% Mo, 2% W BiVO₄ film before brushing the film surface (frontside and backside illumination) and after brushing the film surface and rinsing it with de-mineralized water to remove irregular surface structures (frontside and backside illumination). Measurements were conducted in mixture of 0.1 M Na₂SO₄ and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of 0.025 V s⁻¹.

**Figure S9.** Top view SEM images of a 6% Mo, 2% W BiVO₄ film (a) before brushing the film surface and (b) after brushing the film surface and rinsing it with de-mineralized water.
Figure S10. UV-Vis absorbance spectrum for a 6% Mo, 2% W BiVO₄ film taken before and after brushing the film surface and rinsing it with de-mineralized water. The measurements were taken using a Cary 5000 spectrophotometer in transmission mode so any diffusely scattered light contributed to the measured absorbance.