

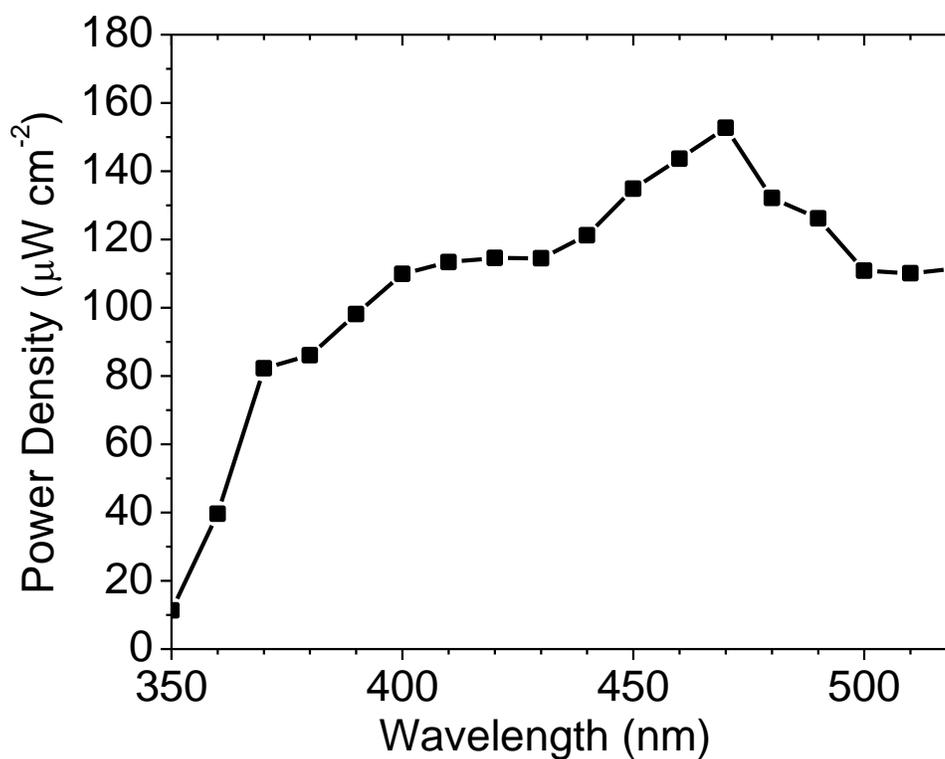
Supporting Information

## Incorporation of Mo and W into Nanostructured BiVO<sub>4</sub> Films to Improve Photoelectrochemical Water Oxidation Performance

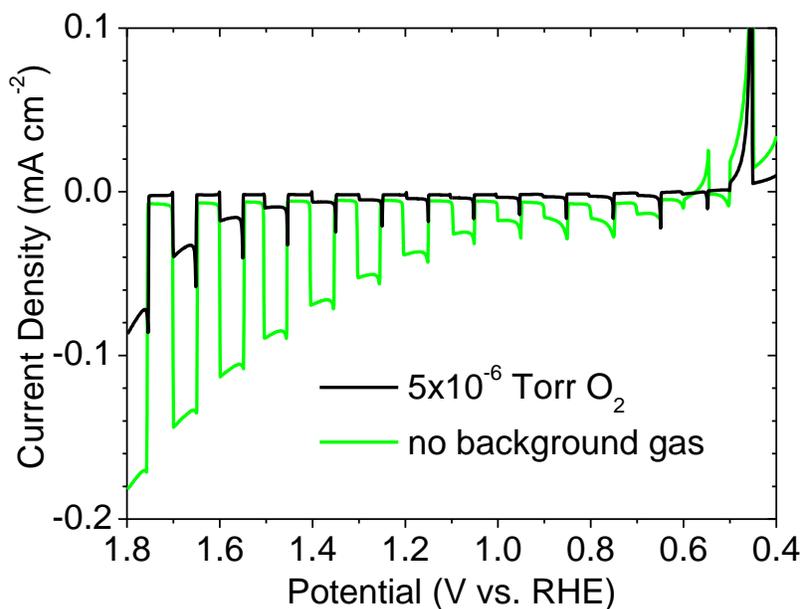
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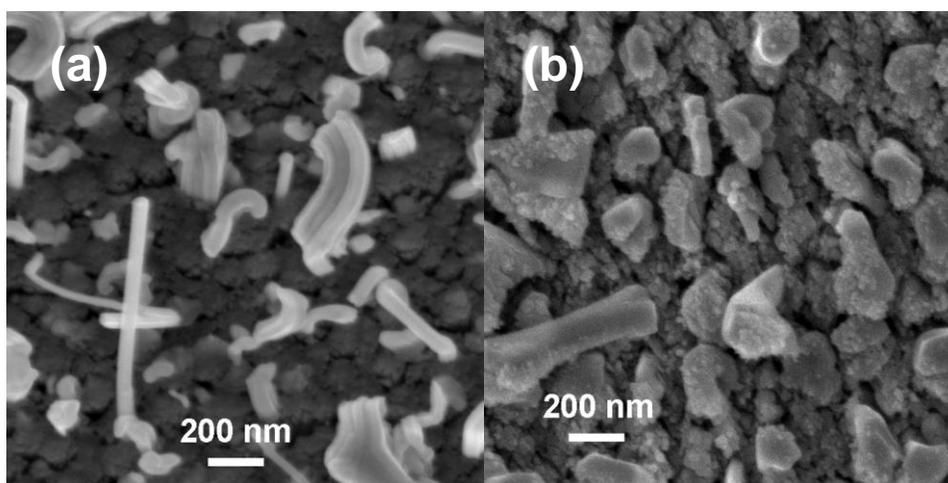
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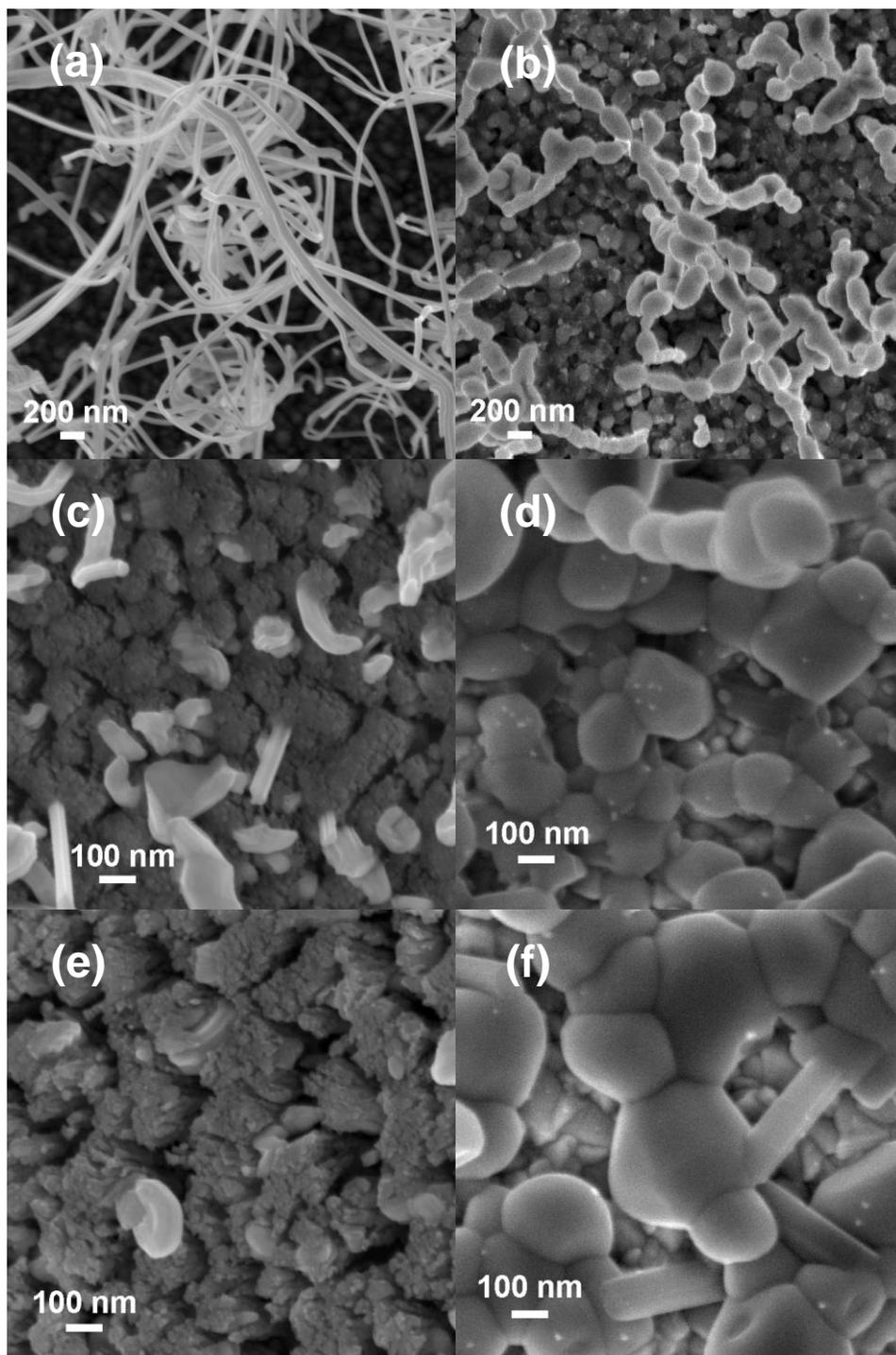
**Figure S1.** Typical power density spectrum for light that was incident on the film during IPCE measurements. The power was measured using a UV enhanced silicon photo-detector.



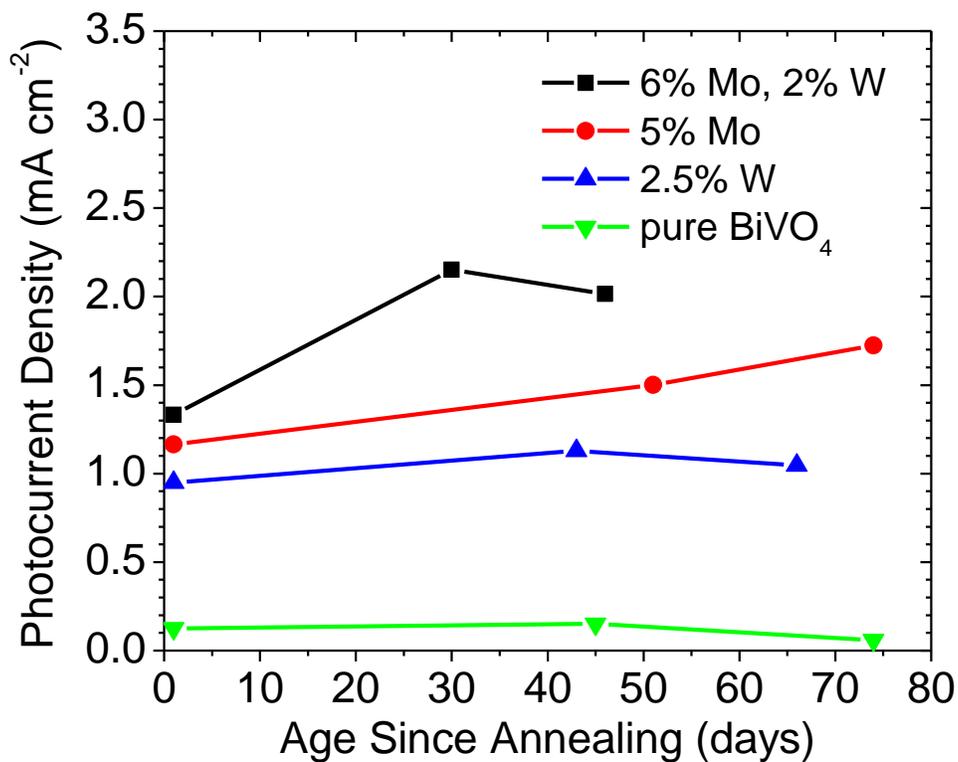
**Figure S2.** Chopped (dark and white light) LSV scans for BiVO<sub>4</sub> films deposited in vacuum with no background gas and with 5x10<sup>-6</sup> Torr of O<sub>2</sub>. After deposition both films were annealed in air at 500°C in for 2 hours. Measurements were conducted in mixture of 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of 0.025 V s<sup>-1</sup>.



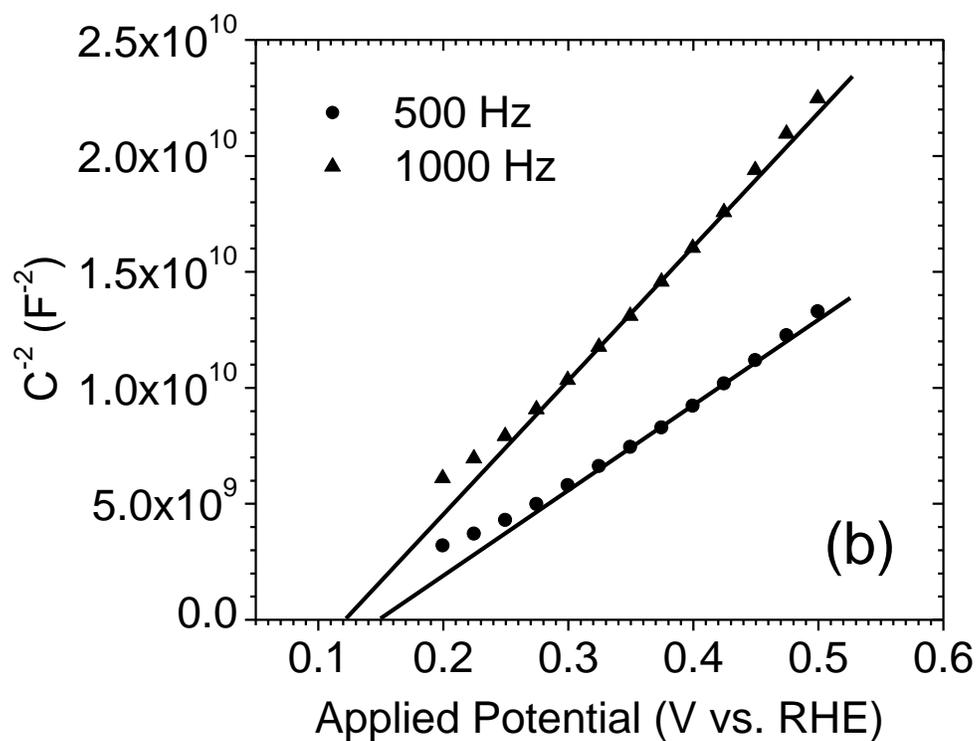
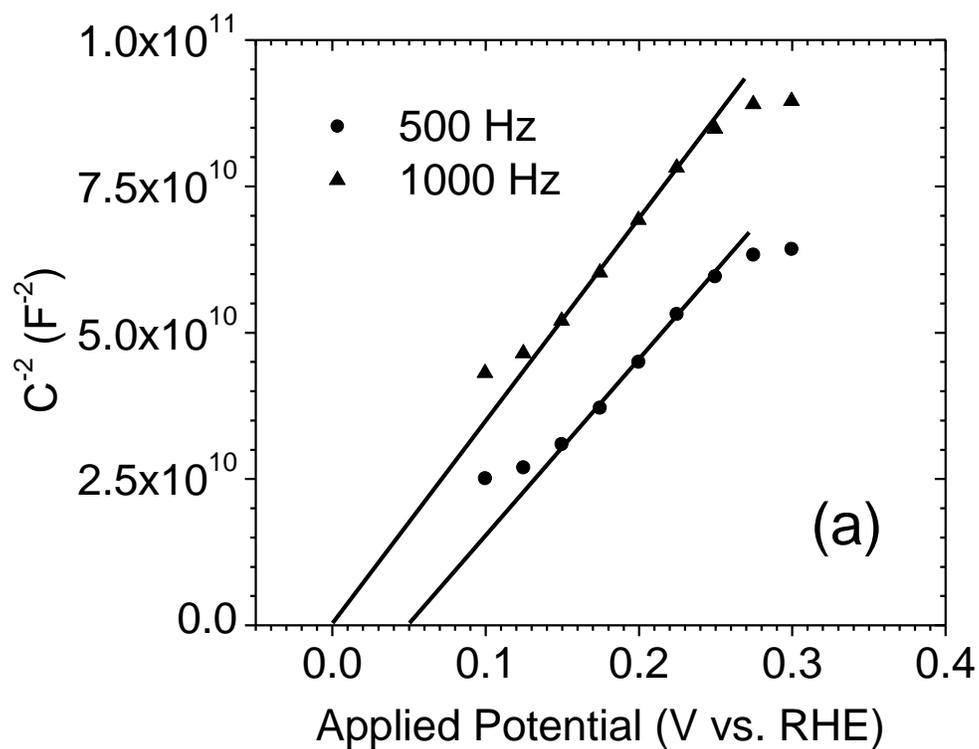
**Figure S3.** SEM images of films with a Bi:V:Mo:W atomic ratio of 50:50:0:0 deposited at  $\gamma=55^\circ$  (a) in vacuum with no background gas and (b) with 5x10<sup>-6</sup> Torr of O<sub>2</sub>. The films have not been annealed.



**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 ( $\gamma$ ) taken before and after annealing in air at 500 °C for 2 hours: (a)  $\gamma=0^\circ$ , before annealing (b)  $\gamma=0^\circ$ , after annealing (c)  $\gamma=55^\circ$ , before annealing (d)  $\gamma=55^\circ$ , after annealing (e)  $\gamma=75^\circ$ , before annealing (f)  $\gamma=75^\circ$ , after annealing.

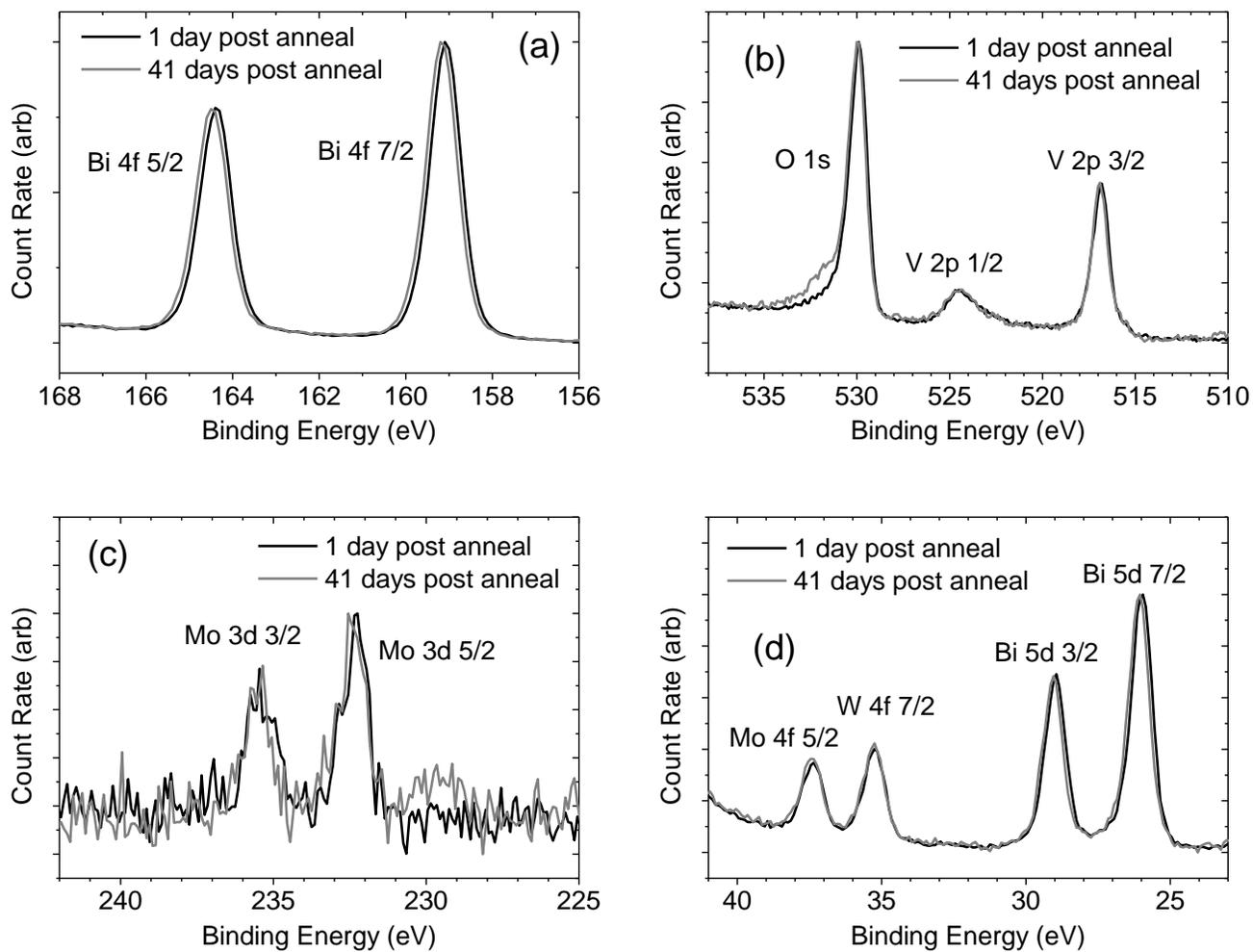


**Figure S5.** Trends showing improvement in photocurrent density with age since annealing for BiVO<sub>4</sub> films with varying atomic percentages of Mo and W (relative to the total Bi, V, Mo, and W). The photocurrent density values were taken from LSV scans (value at 1.6 V vs. RHE) in 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of 0.025 V s<sup>-1</sup>. Between measurements the films were simply left in plastic container in the laboratory at normal atmospheric conditions.

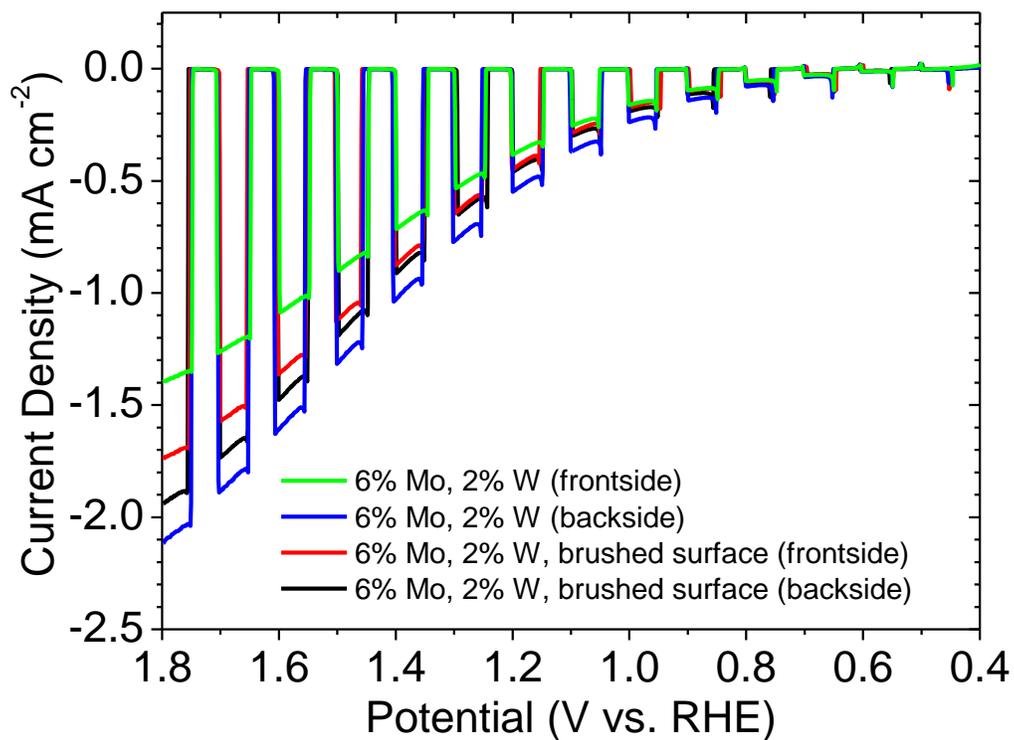


**Figure S6.** Mott-Schottky plot for (a) pure  $\text{BiVO}_4$  and (b) 6% Mo, 2% W  $\text{BiVO}_4$  films conducted in 0.1 M  $\text{Na}_2\text{SO}_4$  and 0.1 M

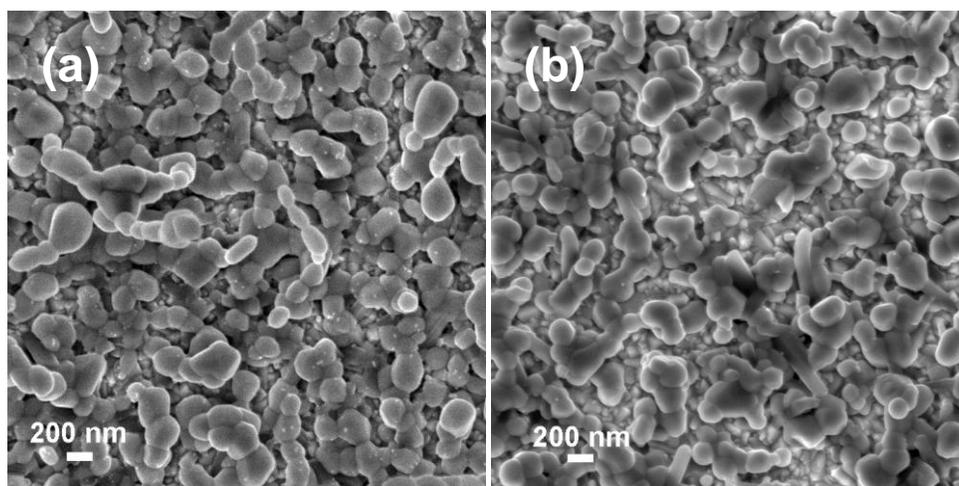
phosphate buffer solution (pH 6.8).



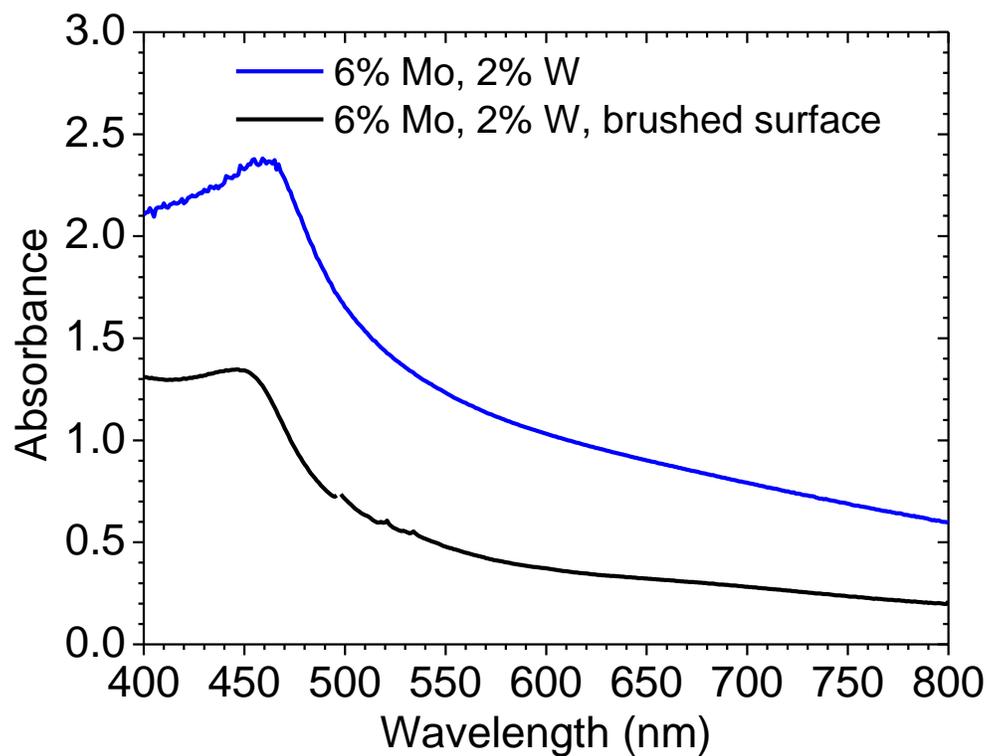
**Figure S7.** XPS spectra for a single 6% Mo, 2% W BiVO<sub>4</sub> film taken 1 day and 41 days after annealing.



**Figure S8.** Chopped (dark and white light) LSV scans for a 6% Mo, 2% W  $\text{BiVO}_4$  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  $\text{Na}_2\text{SO}_4$  and 0.1 M phosphate buffer solution (pH 6.8) with a scan rate of  $0.025 \text{ V s}^{-1}$ .



**Figure S9.** Top view SEM images of a 6% Mo, 2% W  $\text{BiVO}_4$  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 BiVO<sub>4</sub> 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.