## **Supporting Information**

## Screening of Electrocatalysts for Photoelectrochemical Water Oxidation on W-Doped BiVO<sub>4</sub> Photocatalysts by Scanning Electrochemical Microscopy (SECM)

Heechang Ye, Hyun S. Park and Allen J. Bard\*

Center for Electrochemistry, Department of Chemistry and Biochemistry The University of Texas at Austin, Austin, TX 78712



**Figure S1**. SECM image of  $Co_3O_4$  spots on the Bi/V/W oxide film at 0.3 V (vs. Ag/AgCl) in 0.2 M sodium phosphate buffer (pH 6.8) under visible light irradiation. Light was blocked during the scan (black arrow).



**Figure S2.** SECM images of Co/Ir array on the BiVW-O film (a) at 0.3 V (vs. Ag/AgCl) in 0.2 M sodium phosphate buffer (pH 6.8) only and (b) at 0.1 V (vs. Ag/AgCl) with 0.1 M Na<sub>2</sub>SO<sub>3</sub> as a sacrificial reagent under UV-visible light irradiation. Both images were obtained on exactly same position. Numbers under each spot represent the number of drops of dispensed Co and Ir solutions respectively.



**Figure S3.** SECM images of photoreduced Pt array on the BiVW-O film (a) at 0.3 V (vs. Ag/AgCl) in 0.2 M sodium phosphate buffer (pH 6.8) only and (b) at 0.2 V (vs. Ag/AgCl) with 0.1 M Na<sub>2</sub>SO<sub>3</sub> as a sacrificial reagent under UV-visible light irradiation.



**Figure S4.** Linear sweep voltammograms of Ir/BiVW-O films in 0.2 M sodium phosphate buffer (pH 6.8) under UV-visible irradiation. Atomic percentage of Ir is (a) 0.2 %, (b) 0.5 %, (c) 1 %, (d) 5 %, and (e) 10 % compared to total atomic amount of Bi, V, and W. Each figure shows multiple voltammograms showing decreasing current with more scans. Scan rate: 20 mV/s. Electrode area: 0.2 cm<sup>2</sup>.



**Figure S5.** Linear sweep voltammograms of Co-Pi/BiVW-O films with 30 s and 5 min Co-Pi deposition in 0.2 M sodium phosphate buffer (pH 6.8) under UV-visible light irradiation. Scan rate: 20 mV/s. The concentration of  $Co(NO_3)_2$  in the Co-Pi deposition process was 0.5 mM which is 10 times higher than that used for Figure 7 in the manuscript. Electrode area: 0.2 cm<sup>2</sup>.



**Figure S6.** UV-vis spectra of  $IrO_x$  and  $Co_3O_4$  films on FTO. 50 µL of each precursor solution (1 mM) was used to prepare the films. This is equivalent to the amount of Ir and Co in 5 mol % Ir/BiVW-O and Co/BiVW-O films.



**Figure S7.** High resolution XPS spectra of Pt electrocatalysts on BiVW-O film (a) before and (b) after PEC water oxidation experiments and  $Co_3O_4$  electrocatalyst on BiVW-O film before PEC water oxidation (c).



**Figure S8**. XRD pattern of  $Co_3O_4$  film on glass. Reference  $Co_3O_4$  pattern (JCDPS 43-1003) is shown with bar graph below.