Supporting Information

Photoelectrochemical Oxidation of Water Using Nanostructured $BiVO_4$ Films

Sean P. Berglund,[†] David W. Flaherty,[†] Nathan T. Hahn,[†] Allen J. Bard,[‡] C. Buddie Mullins[†‡*]

Department of Chemical Engineering,[†] *Department of 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

[*]address correspondence to mullins@che.utexas.edu

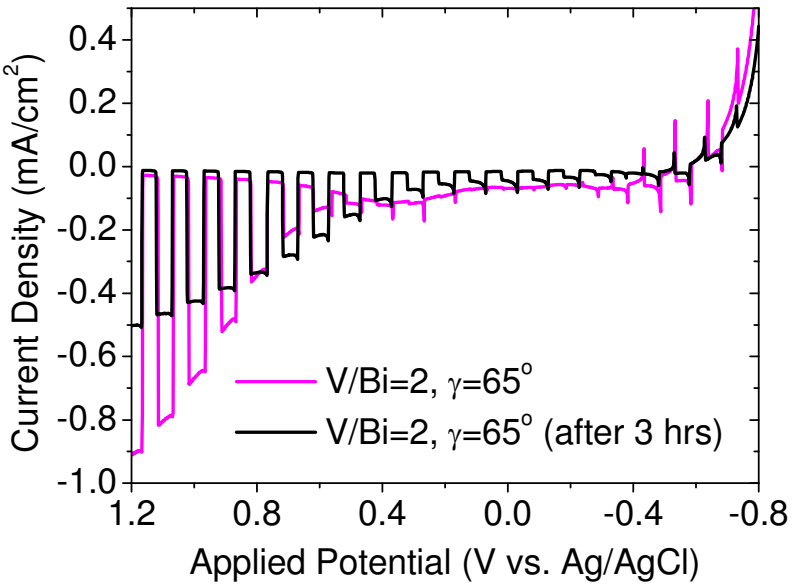

Figure S1. Chopped (dark and white light) LSV scans for a $BiVO_4$ film synthesized by RBD (V/Bi=2, γ=65°, thickness=0.5 μm) in 0.5 M Na_2SO_4. The film was measured initially (magenta) and after illumination for 3 hours at a constant potential of 1.0 V vs. Ag/AgCl (black). The scan rate was 0.025 V/s.

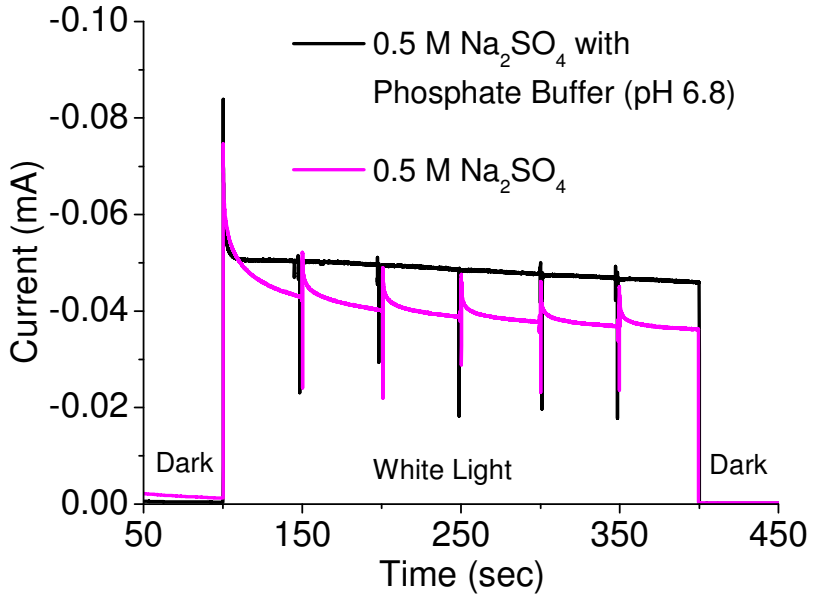

Figure S2. Amperometric i-t curve for a $BiVO_4$ film synthesized by RBD (V/Bi=2, γ=65°, thickness=0.5 μm) in 0.5 M Na_2SO_4 (magenta) and 0.5 M Na_2SO_4 with 0.5 M phosphate buffer solution (pH 6.8) (black) at a constant applied potential of 1.0 V vs. Ag/AgCl. During white light illumination the film was flushed with fresh electrolyte every 50 seconds causing the spikes in photocurrent. For non-buffered 0.5 M Na_2SO_4 local pH changes near the film surface caused by the water oxidation reaction resulted in gradual photocurrent decay after each flush.

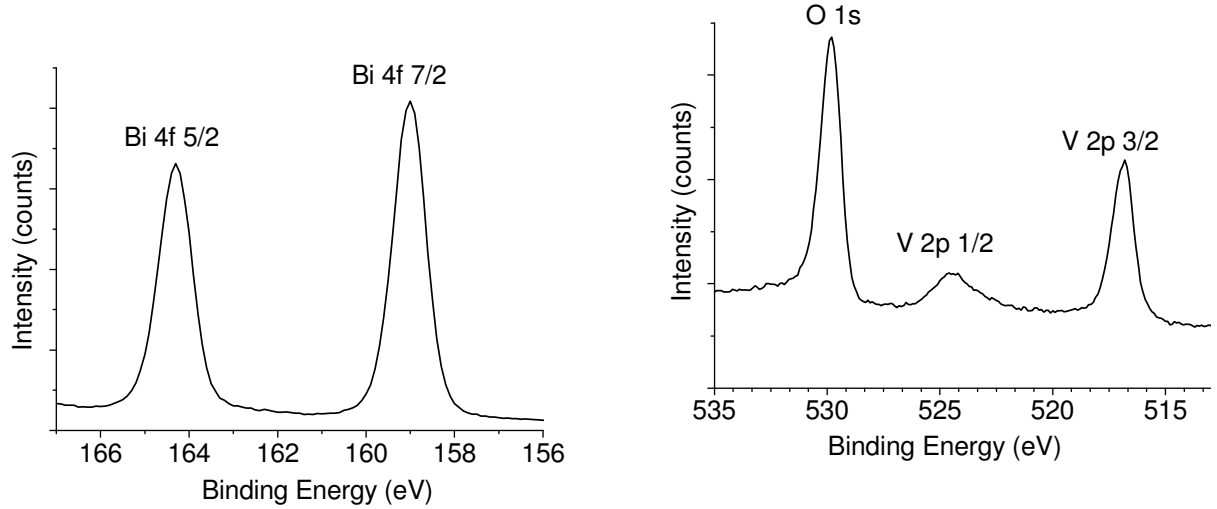

Figure S3. XPS spectra for $BiVO_4$ film synthesized by RBD (V/Bi=2, γ=65°, thickness=0.5 μm) obtained before PEC testing. Binding energies of 159.0 eV for Bi 4f 7/2, 516.8 eV for V 2p 3/2, and 529.8 eV for O 1s imply oxidation states of Bi^{3+}, V^{5+}, and O^{2-}.

Film Deposition Parameters and Surface Treatments	Ion Concentrations (ppb) in Unused Electrolyte		Ion Concentrations (ppb) in Used Electrolyte (3 hrs of illumination at 1.0V vs. Ag/AgCl)	
	Bi	V	Bi	V
V/Bi=2, $\gamma=65^{o}$	0.1	1.2	0.3	247
V/Bi=1, $\gamma=65^{o}$ (Co surface)	0.4	0.9	0.4	0.9

Table S1. ICP-MS results for electrolyte solutions used with two different $BiVO_4$ films synthesized by RBD. A batch of 0.1 M Na_2SO_4 was prepared for each film and measured to obtain the ion concentrations in unused electrolyte. About 25 mL of each 0.1 M Na_2SO_4 solution was used for PEC testing (over 3 hours of illumination at constant applied bias of 1.0 V vs. Ag/AgCl) and measured to obtain the ion concentrations in used electrolyte. All values were below the detection limits of the ICP-MS system except for the V concentration in used electrolyte from the V/Bi=2 film.