Supporting Information: A Scanning Probe Investigation of the Role of Surface Motifs in the Behavior of p-WSe₂ Photocathodes

Jesus M. Velazquez,^{‡1,2}Jimmy John,^{‡1} Daniel V. Esposito,^{3,4} Adam Pieterick,^{2,5} Ragip Pala,^{2,5} Guofeng Sun,² Xinghao Zhou,^{2,5} Zhuangqun Huang,⁹ Shane Ardo,⁶ Manuel P. Soriaga,² Bruce S. Brunschwig^{2,7} and Nathan S. Lewis^{*1,2,7,8}

[1] Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, USA

[2] Joint Center for Artificial Photosynthesis, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, USA

[3] Columbia University in the City of New York, 500 W. 120th St., New York, NY 10027, USA

[4] National Institute of Standards and Technology, Materials Measurement Laboratory, 100 Bureau Drive, Gaithersburg, MD 20899-1070 USA

[5] Division of Engineering and Applied Science, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, USA

[6] Department of Chemistry and Department of Chemical Engineering and Materials Science, University of California at Irvine, Irvine, CA 92697, USA

[7] Molecular Materials Research Center, Beckman Institute, California Institute of Technology, Pasadena, CA 91125, USA

[8] Kavli Nanoscience Institute, California Institute of Technology, Pasadena, CA 91125, USA

[9] Bruker Nano Surfaces, 122 Robin Hill Road, Goleta, CA 93101, USA

[‡] These authors contributed equally to this work

E-mail: nslewis@caltech.edu



Figure S1 (a) Soldering of In metal contacts and a Cu wire onto a Si substrate before (b) mounting the p-WSe₂ single crystal onto the substrate. (c) A mounted p-WSe₂ electrode fully encapsulated with two-part epoxy and cured for 24 hours. (d) The fully assembled Teflon cell with two layers of electroplaters tape placed over the p-WSe₂ photoelectrode.



Figure S2: (a) Atomic force microscope (AFM) image of a p-WSe₂ sample showing micrometer sized terraces in macroscopically smooth regions of terraces. (b) 3D view of small terraces depicted in (a).



Figure S3: Photocurrent line scan obtained on a bare p-WSe₂ electrode in contact with 10 mmol L⁻¹ Ru(NH₃)₆³⁺ / 0.5 mol L⁻¹ KH₂PO₄(aq) at pH = 4.2. Applied potential: -0.05 V vs Ag/AgCl. Incident laser power: 12.65 μ W. Scan speed: 0.38 μ m s⁻¹. Beam wavelength: 532 nm.



Figure S4: (a) Optical image of an area of a bare p-WSe₂ electrode. (b) The external quantum yield (Φ_{ext}) map of the area in (a). (c) Reflectance map of the same area. Both (b) and (c) were performed with the electrode in contact with 10 mmol L⁻¹ Ru(NH₃)₆³⁺ / 0.5 mol L⁻¹ KH₂PO₄(aq). Applied potential: (b) -0.05 V vs sat. Ag/AgCl and (c) at open circuit. Incident laser wavelength: 533 nm.



Figure S5: Scanning photocurrent microscopy (SPCM) measurements of the platinized p-WSe₂ electrode from Figure 3 in contact with 10 mmol L⁻¹ Ru(NH₃)₆³⁺ / 0.5 mol L⁻¹ KH₂PO₄(aq). (a) Scanning electron microscope (SEM) images of the area of the photoelectrode shown in Figure 3a of the main text after platinization. The granularity seen on the crystal surface is from the deposited Pt nanoparticles. (b) Higher resolution SEM image showing the distribution of Pt at the electrode surface. (c) Energy-dispersive X-ray spectra (EDS) obtained for the point indicated by the yellow star in (a) and located within the triangular terrace confirming the presence of Pt. (d) Two-dimensional external quantum yield (Φ_{ext}) map of the area denoted by the dotted rectangle in Figure 3a of the main text after platinization. Applied potential: -0.05 V vs Ag/AgCl. Scan speed: 14 µm s⁻¹. Beam spot size: ~ 10 µm. Beam wavelength: 532 nm. Incident laser power: 4.2 µW.



Figure S6: *Effect of Pt on the photoreduction of Ru(NH₃)*₆³⁺(*aq*): Difference external quantum yield ($\Delta \Phi_{ext}$) map constructed from the Φ_{ext} maps in Figure 4b and 4c of the main text by subtracting $\Phi_{ext}^{Bare}(X,Y)$ (the Φ_{ext} value at a given position (X,Y) on a bare p-WSe₂ in contact with 10 mmol L⁻¹ Ru(NH₃)₆³⁺ / 0.5 mol L⁻¹ KH₂PO₄(aq) from Figure 4b of the main text) from $\Phi_{ext}^{Pt}(X,Y)$ (the Φ_{ext} value after platinization of the photoelectrode at the same position from Figure 4c of the main text) i.e. $\Delta \Phi_{ext}(X,Y) = \Phi_{ext}^{Pt}(X,Y) - \Phi_{ext}^{Bare}(X,Y)$. All the experimental parameters are the same as specified in Figure 4 of the main text.



Figure S7: (a) Local linear sweep voltammograms (LSVs) under illumination at the same location on bare and Pt/p-WSe₂ in 0.5 M H₂SO₄(aq). External quantum yield (Φ_{ext}) maps of the same region on a (b) bare, and (d) platinized p-WSe₂ electrode, each in 0.5 mol L⁻¹ H₂SO₄(aq). Applied potential: -0.13 V vs sat. Ag/AgCl. Beam spot size: ~ 10 µm. Beam wavelength: 532 nm. (c) Scanning electron microscopy (SEM) image of the same region as in (b) and (d) the corresponding conductive AFM scan showing non-uniform Pt decoration on the edge.



Figure S8: (a) SEM image of the area of the photoelectrode shown in **Figure 4** of the main text after platinization. The granularity seen on the crystal surface is from the deposited Pt nanoparticles. (b) External quantum yield (Φ_{ext}) map of bare WSe₂ in contact with 0.5 mol L⁻¹ H₂SO₄(aq). Applied potential: -0.13 V vs sat. Ag/AgCl.



Figure S9: *Local spectral response measurements*: (a) Optical image of an area of a bare p-WSe₂ electrode where local spectral measurements were carried out. The locations are denoted by the dots with the numbers identifying them. (b)-(c) Local spectral response curves obtained at various locations shown in (a) on the surface of the bare p-WSe₂ electrode in contact with 10 mmol L⁻¹ Ru(NH₃)₆³⁺ / 0.5 mol L⁻¹ KH₂PO₄(aq). The number identifying the location – with the value of external quantum yield (Φ_{ext}) at 533 nm ($\Phi_{ext,533}$) in brackets – is shown beside each curve in (b) and (c). For the sake of presentation, the local spectral responses are categorized based on the value of $\Phi^{\lambda = 533 \text{ nm}}_{ext} \Phi_{ext,533} > 0.15$ and (c) locations that had $\Phi^{\lambda = 533 \text{ nm}}_{ext} \Phi_{ext,533} < 0.15$. Applied potential: - 0.05 V vs sat. Ag/AgCl. The area highlighted in grey represent the wavelength region below

the direct bandgap of WSe₂ ($E_{g,direct} = 1.57$ eV or 790 nm). The spectra shown here are the unnormalized data for the corresponding normalized spectra in Figure 5 of the main text.



Figure S10: Representative cyclic voltammogram of n-WSe₂ in 1 mol L⁻¹ H₂SO₄(aq) in the dark. Solution stirred and purged with H₂. Scan rate: 50 mV s⁻¹.