Supplementary Information: Transient Photocurrents on Catalyst-Modified n-Si Photoelectrodes: Insight from Dual-Working Electrode Photoelectrochemistry

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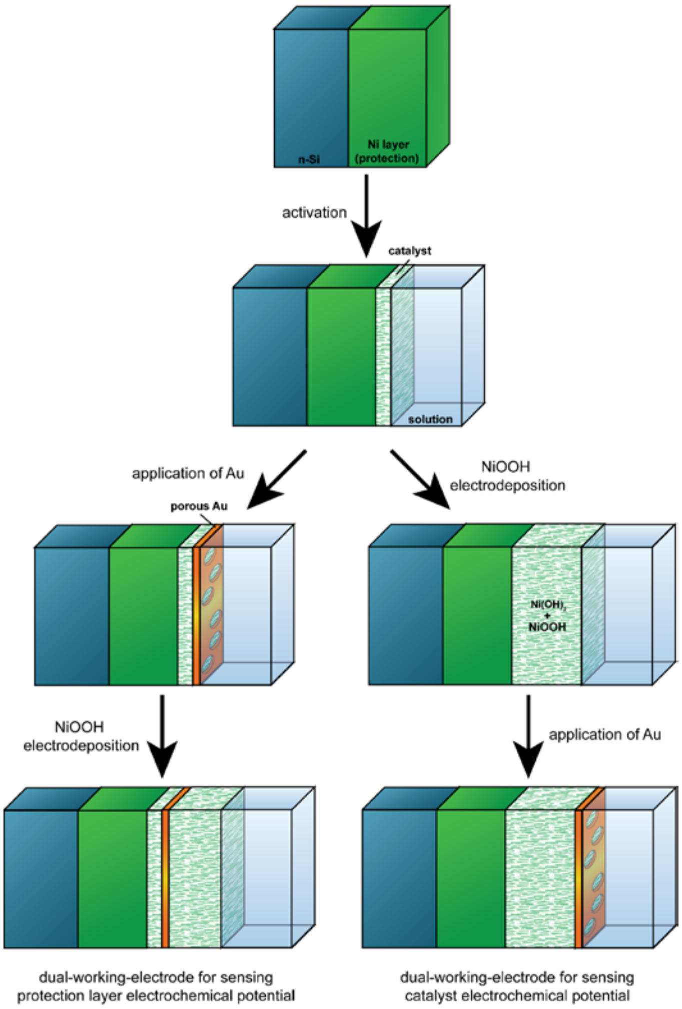

Figure S1. Two dual-working-electrode (DWE) deposition strategies. Both strategies begin by activating the metallic Ni protection layer via electrochemically cycling 50 times through potentials that span the redox wave under ~ 1 sun illumination. For a DWE that senses the protection layer electrochemical potential (depicted by the left fork), the thin porous Au contact is deposited immediately after activation. The Ni (oxy)hydroxide layer is sufficiently thin such that areas of contact form between the metallic Ni and the Au film. Additional Ni (oxy)hydroxide is then electrodeposited (photo-assisted) on top of the Au contact. For a DWE that senses the catalyst electrochemical potential (depicted by the right fork), the additional Ni (oxy)hydroxide catalyst is deposited prior to the porous Au layer. This prevents the Au film from contacting the protection layer.

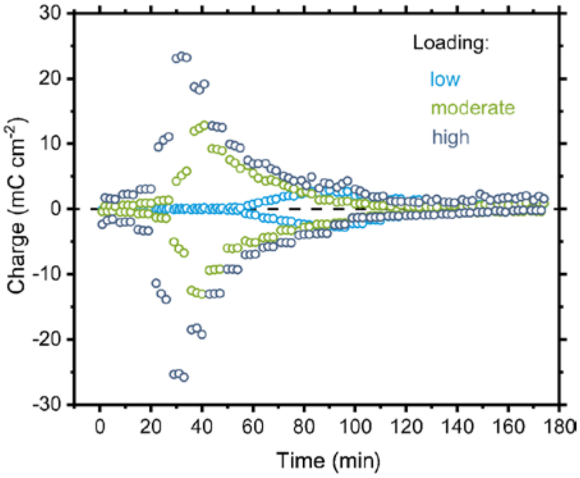

Figure S2. Transient integration comparison between the different extents of catalyst loading. All data is collected on the same electrode with Ni (oxy)hydroxide loading sequentially increased via photo-assisted electrodepositions. Increasing the amount of redox-active catalyst results in transients with larger charge integrals.

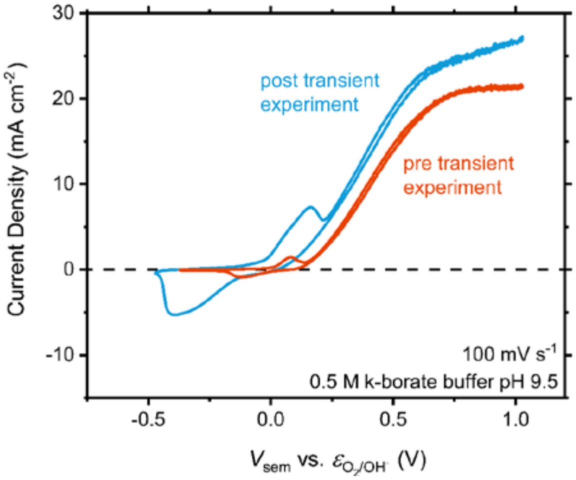

Figure S3. Comparison of electrode activity before and after the first transient experiment. Cyclic voltammograms are collected on the same electrode as in Figure 1 of the main text. The transient experiment results in a cathodic shift of oxygen evolution onset and an increase in the redox peak integrations. The data indicates that the transient experiment ages the electrode and converts some of the protection layer to redox active NiOOH/Ni(OH)$_2$. The cathodic onset shift is attributed to an increase in the photovoltage. Increased photovoltage also explains the cathodic shift in the region of large integrated transient charge for Figure 1 and Figure S2.

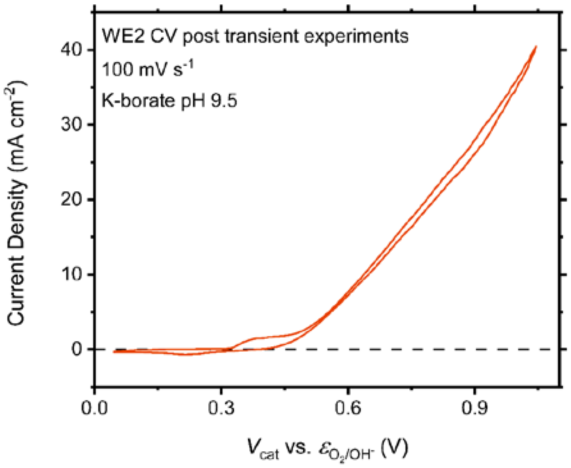

Figure S4. Cyclic voltammogram through the WE$_2$ contact after transient experiments showing the position of the oxidation and reduction waves for the catalyst. The data is from the same electrode as in Figure 3 of the main text; i.e. WE$_2$ is in direct contact with the outer catalyst layer. Note that redox integration is small here, most likely due to mechanical exfoliation of the Au contact during the experiment. The onset of catalyst oxidation occurs at ~ 0.3 vs. ε_{O_2/OH^-} while reduction occurs at ~ 0.25 vs. ε_{O_2/OH^-}.

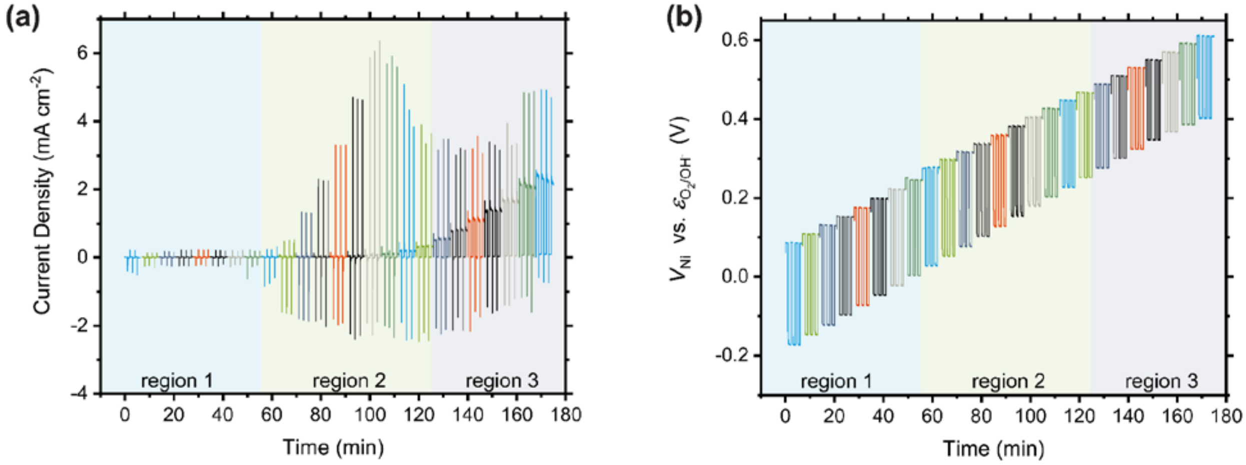

Figure S5. Full transient behavior for the electrode used to sense the protection layer electrochemical potential (from Figure 5). (a) The photocurrent transients as a function of time. The regions of transient activity are denoted as in Figure 3 of the main text. These are assigned by examining the redox integration in Figure S7. **(b)** V_{Ni} response during transient experiments. The voltage sensed by WE$_2$ always responds to changes in the applied potential or light condition. This indicates that the porous Au layer is in contact with the protection layer and is not influenced by the catalyst's conductivity transitions.

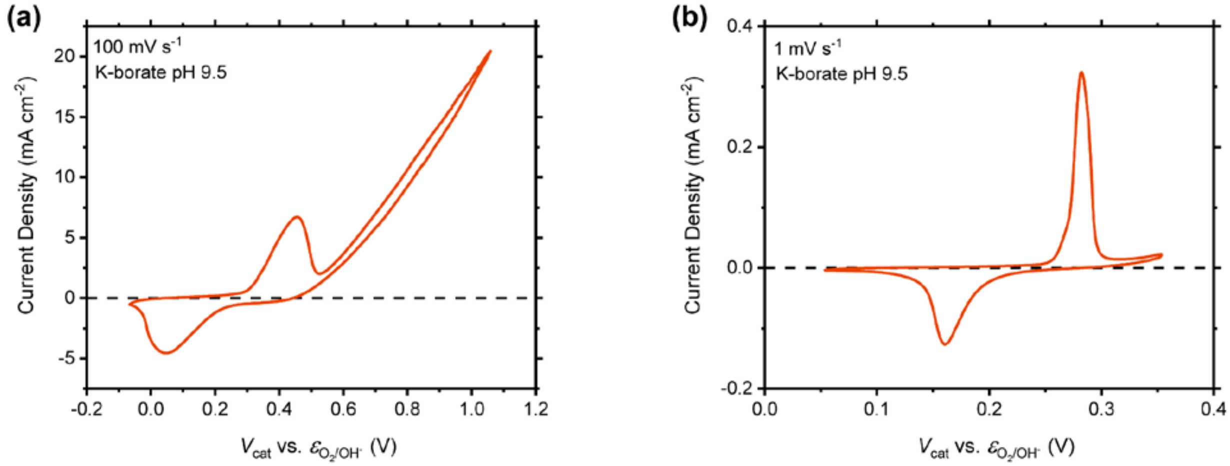

Figure S6. Cyclic voltammogram through the WE$_2$ contact after transient experiments. The data is from the same electrode as in Figure 5 of the main text; i.e. WE$_2$ is in direct contact with the Ni protection layer. **(a)** Data collected at 100 mV s^{-1} shows that onset of oxidation occurs at ~ 0.3 V vs. ε_{O_2/OH^-} while reduction occurs at ~ 0.2 V vs. ε_{O_2/OH^-}. (b) Data collected at 1 mV s^{-1} approximates steady-state behavior and shows that redox states exist over a 40-50 mV range. This range is comparable with the region of diminished decay in Figures 5b and 5c.

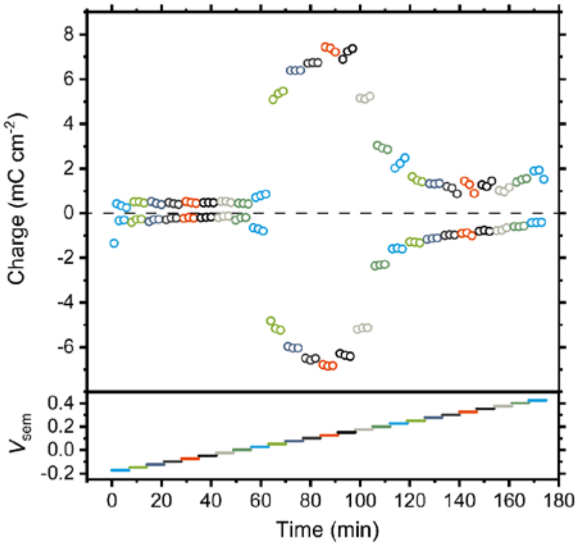

Figure S7. Integration of the photocurrent transients from Figure 5 of the main text. The behavior is similar to the transients from Figure 2, where a region of increased integrated transient charge occurs. The region with increased integration is defined as “region 2”. The bottom pane shows V_{sem} vs. ε_{O_2/OH^-} as a function of time.