Supporting Information

Efficient Photoelectrochemical Hydrogen Evolution Using Pseudocapacitive NiO_x/Si Junction with Misaligned Energy Levels

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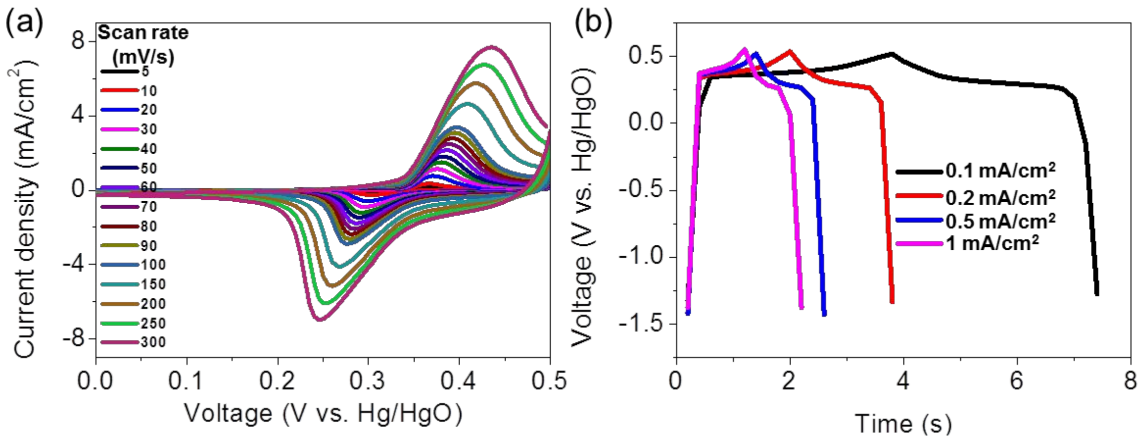

Figure S1. Scan rate-dependent CV and current density-dependent GCD for the porous NiO_x thin film-coated Ni foil. CV curves show a pair of redox peaks because of the Faradic redox reactions, and GCD curves exhibit gradually decreased charge and discharge times with an increase in current density. These results indicate the pseudocapacitive characteristics of the NiO_x thin film.

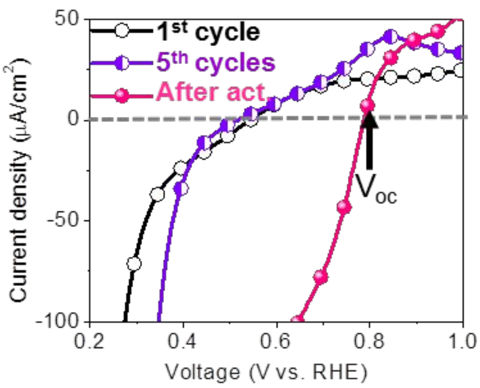

Figure S2. The V_{oc} characterization from the low-current-density level range (<−8 μA/cm^2) of the LSV curves in Figure 2b.

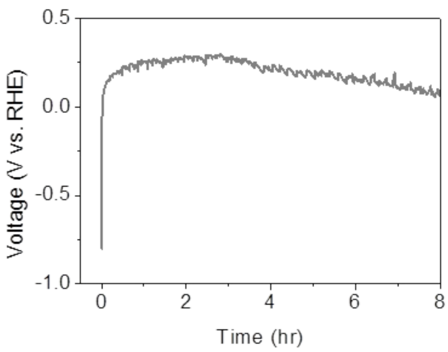

Figure S3. Chronopotentiometry (potential change) measurement of the $NiO_x/SiO_2/Si$ photocathode for stability and activation tests.

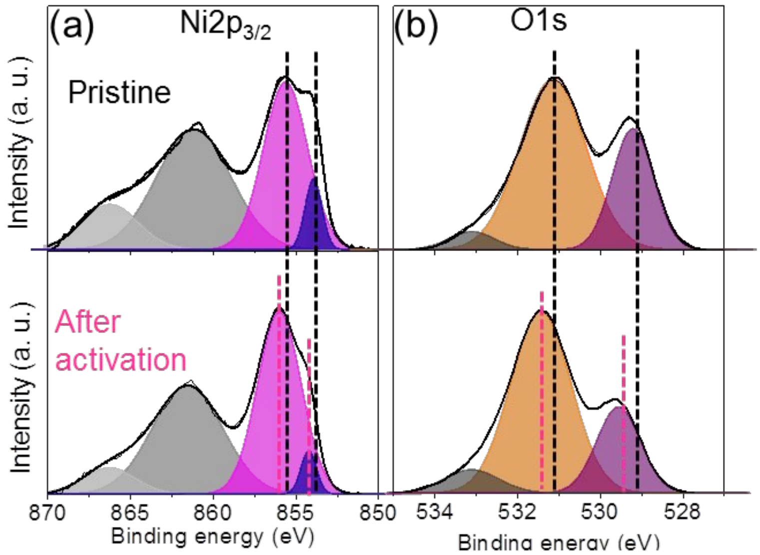

Figure S4. (a) Ni 2*p* and (b) O 1*s* XPS spectra of the NiO_x thin film in pristine (top) and test samples after activation for 1 h (bottom). The magenta and navy peaks in the Ni 2*p* spectra are associated with Ni–OH and Ni–O, respectively. The gray peaks represent satellite features. The yellow, purple, and gray peaks in the O 1*s* spectra are associated with Ni–O, Ni–OH, and adsorbed H_2O, respectively. The vertical dotted lines indicate the peak positions for the samples in pristine (black) and post-activation (pink) conditions.

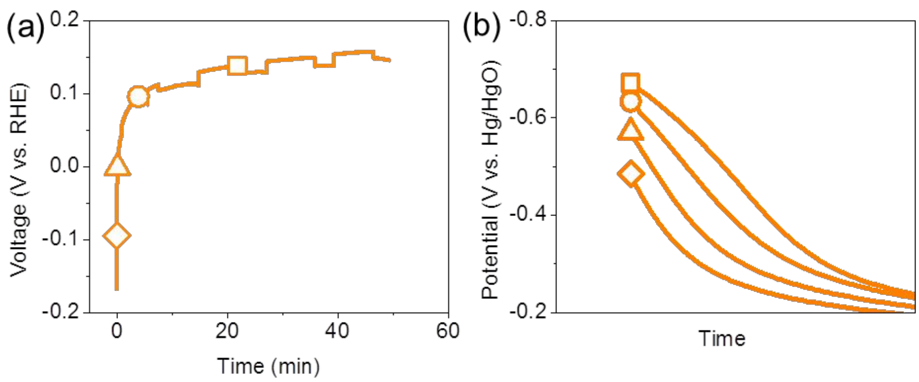

Figure S5. Plots of (a) PEC-HER potential and (b) the charged electrochemical potential according to the activation. The activation causes an anodic shift of the PEC-HER potential as well as a negative shift of the electrochemical potential.

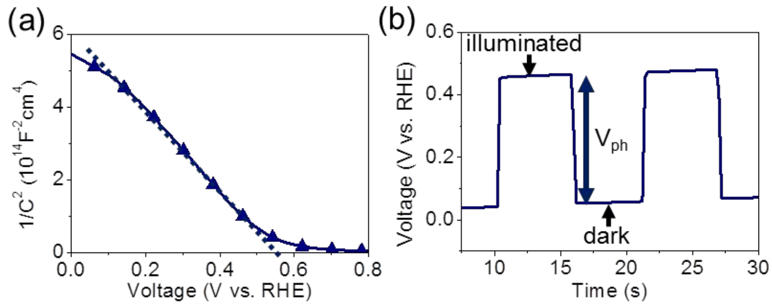

Figure S6. (a) M-S plots and (b) photovoltage measurement for the $NiO_x/Ti/SiO_2/Si$ photocathode.

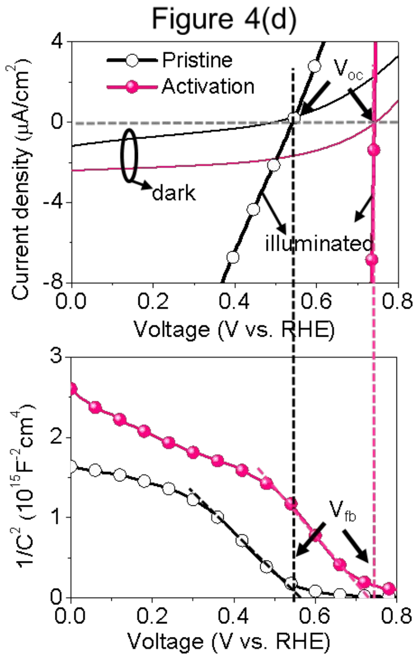

Figure S7. (Top) LSV curves of Figure 4d and (bottom) M-S plots for the $NiO_x/SiO_2/Si$ photocathode in pristine and tested samples after the activation. The V_{fb} values are well corresponded with V_{oc} values.

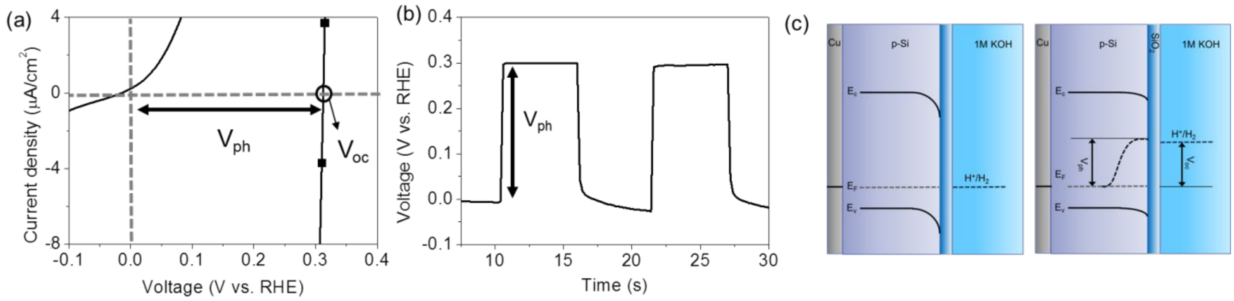

Figure S8. (a) The V_{oc} and (b) photovoltage characterization for electrolyte/SiO_2/p-Si photocathode with Schottky-type electrolyte/p-Si junction. (c) The energy band diagrams under dark (left) and illuminated (right) conditions.

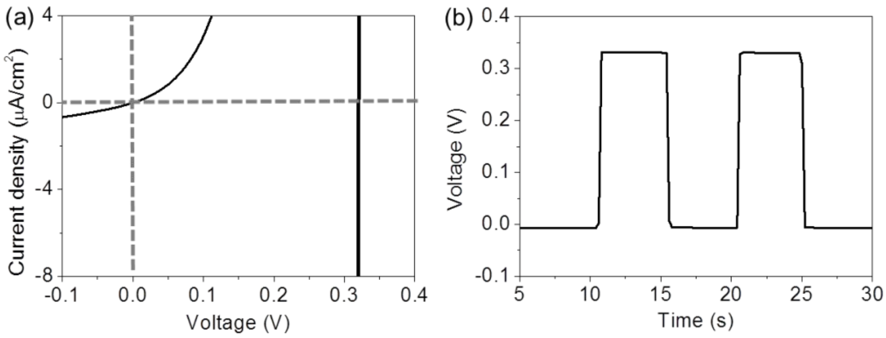

Figure S9. (a) The V_{oc} and (b) photovoltage characterizations of the solid-state NiO_x/SiO_2/p-Si sample with Schottky-type NiO_x/p-Si junction.

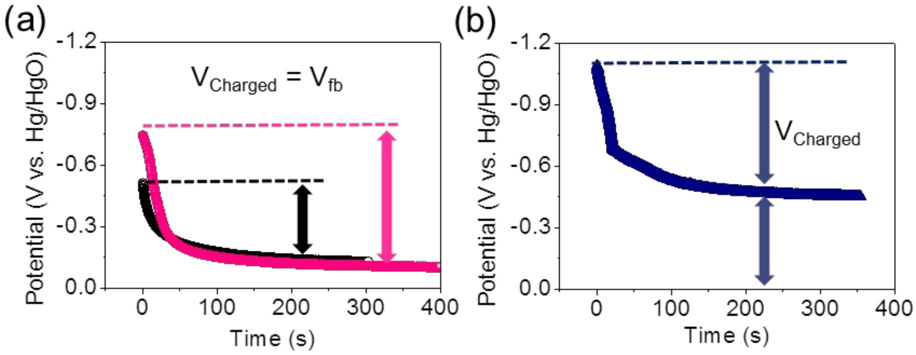

Figure S10. Discharge potential characteristics for (a) the NiO_x/SiO_2/Si and (b) the NiO_x/Ti/SiO_2/Si photocathodes. The NiO_x/SiO_2/Si shows discharge potential near the zero value. However, the potential for the NiO_x/Ti/SiO_2/Si is discharged at 0.45 V vs. Hg/HgO, possibly caused by the built-in potential developed at the Ti/p-Si junction.

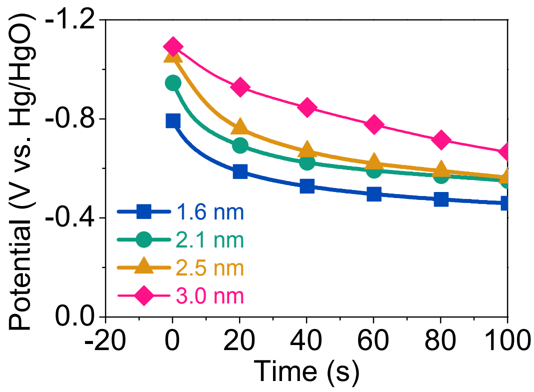

Figure S11. The electrochemical potential for the NiO_x/SiO_2/Si photocathode with varying SiO_2 thickness.

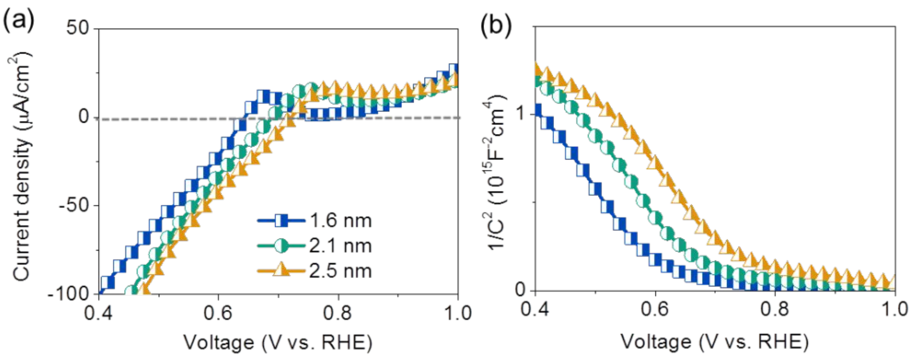

Figure S12. (a) V_{oc} and (b) V_{fb} characterizations for the 40-nm-thick $NiO_x/SiO_2/Si$ photocathode with varying SiO_2 thicknesses.

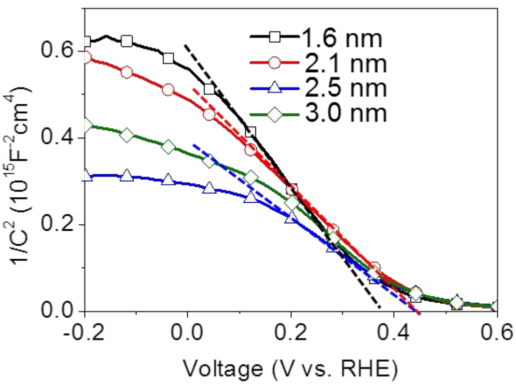

Figure S13. V_{fb} characterizations for the $NiO_x/Ti/SiO_2/Si$ photocathode (Schottky Ti/Si junction) with varying SiO_2 thicknesses.

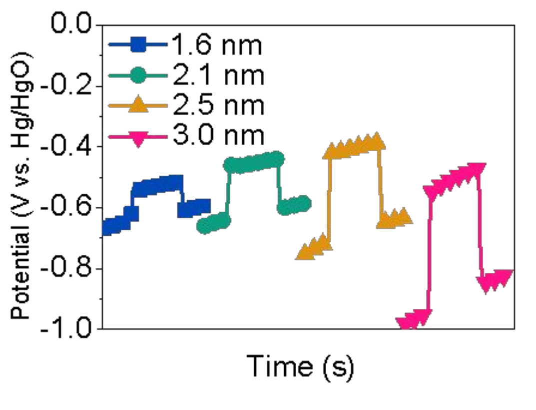

Figure S14. V_{ph} characterizations for the $NiO_x/SiO_2/Si$ photocathode with varying SiO_2 thicknesses.

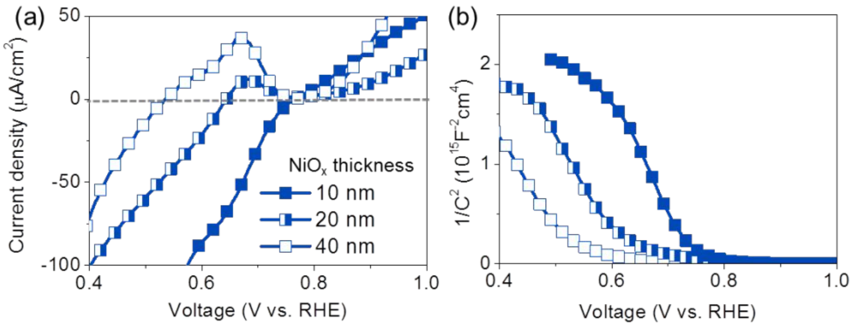

Figure S15. (a) V_{oc} and (b) V_{fb} characterizations for the $NiO_x/SiO_2/Si$ photocathode with varying NiO_x thickness.

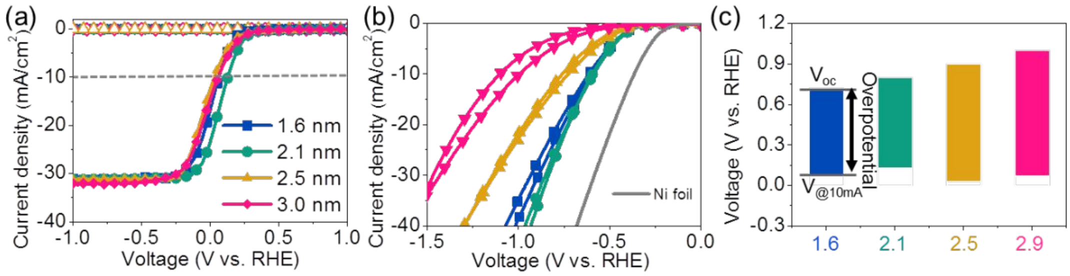

Figure S16. LSV curves of (a) the NiO_x/SiO_2/p-Si photocathode and (b) the $NiO_x/SiO_2/n^+$-Si electrode. (c) Plots showing summary of V_{oc}, potential at −10 mA/cm^2 ($V_{@10mA}$), and kinetic overpotential at −10 mA/cm^2. Gray curve in (b) is measured from NiO_x/Ni foil sample for characterizing the catalytic activity only. The $NiO_x/SiO_2/n^+$-Si electrode requires a large overpotential compared to the NiO_x/Ni foil because of the additional resistance of the SiO_2 layer. Thick SiO_2 achieves a high V_{oc}, but requires a large overpotential. Because of this tradeoff relation, the largest $V_{@10mA}$ value is achieved at the optimum thickness of 2.1 nm, as described in (c).