Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Supplemental Information for**

**Hot Electron-Driven Photocatalytic Water Splitting**

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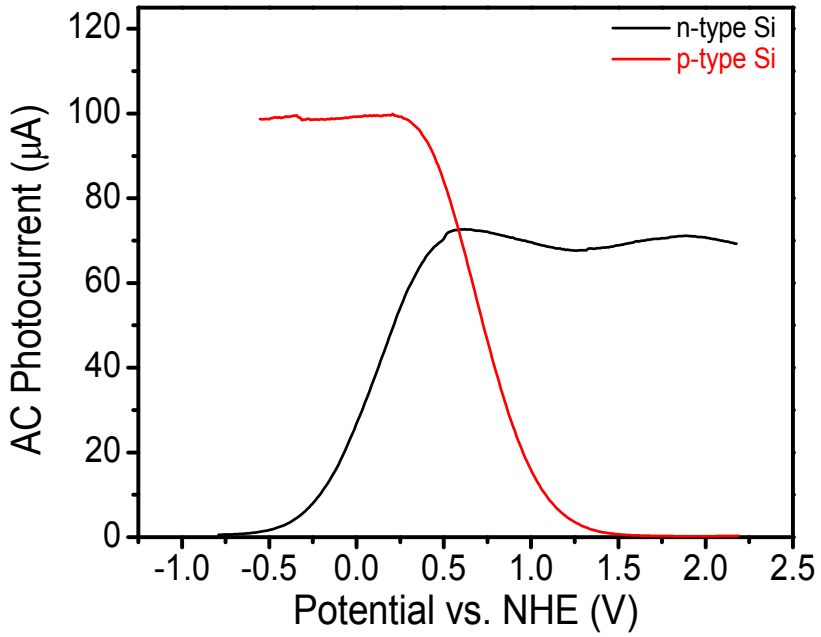


**Figure S1.** AC photocurrent plotted as a function of the reference potential for n- and p-type bulk Si photocatalysts in a 0.5M $H_2SO_4$ solution.

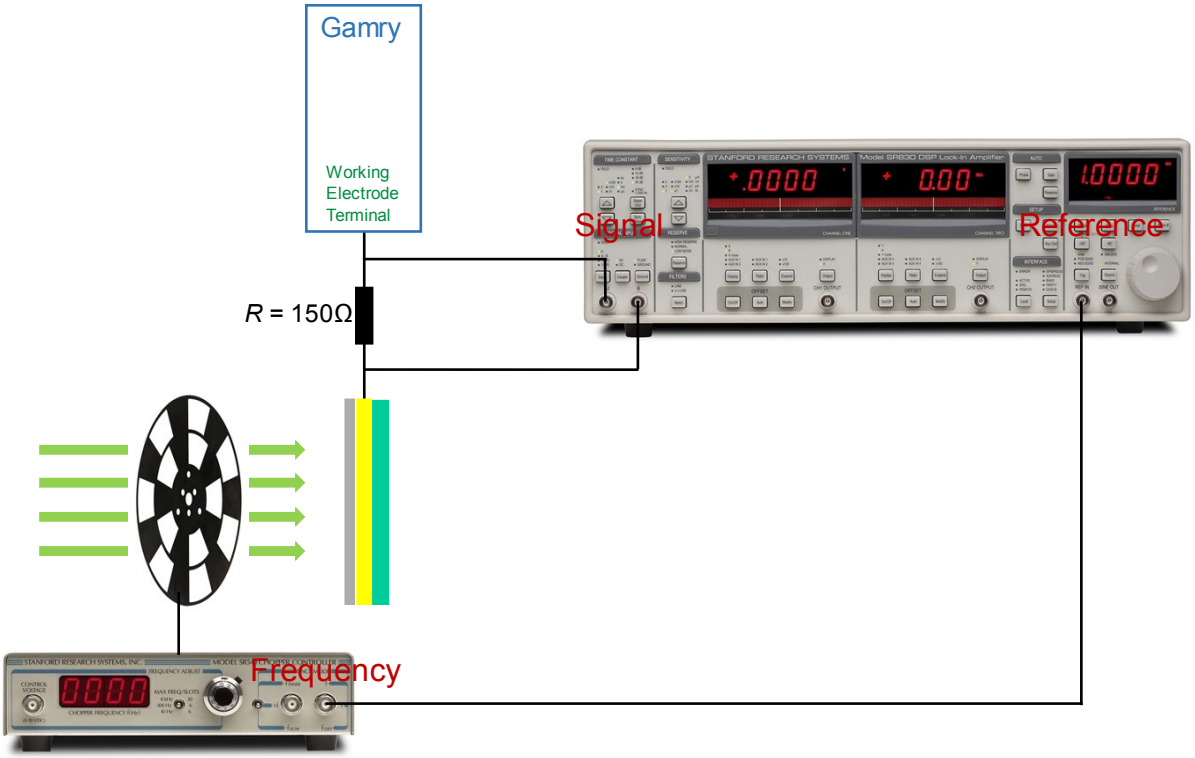


**Figure S2.** Schematic circuit diagram of the AC lock-in technique, in which the incident light is modulated by a chopper wheel and chopper controller, which provides a reference signal for the lock-in amplifier. This enables the lock-in amplifier to detect only voltages at the specific frequency of the modulated light, providing a very sensitive measure of the photoresponse of these photocatalytic surfaces. Here, the "signal" measured by the lock-in amplifier is the voltage drop across a known resistor (150Ω). This voltage drop is converted to photocurrent by diving the measured AC voltage by the known resistance (i.e., $I=V/R$).

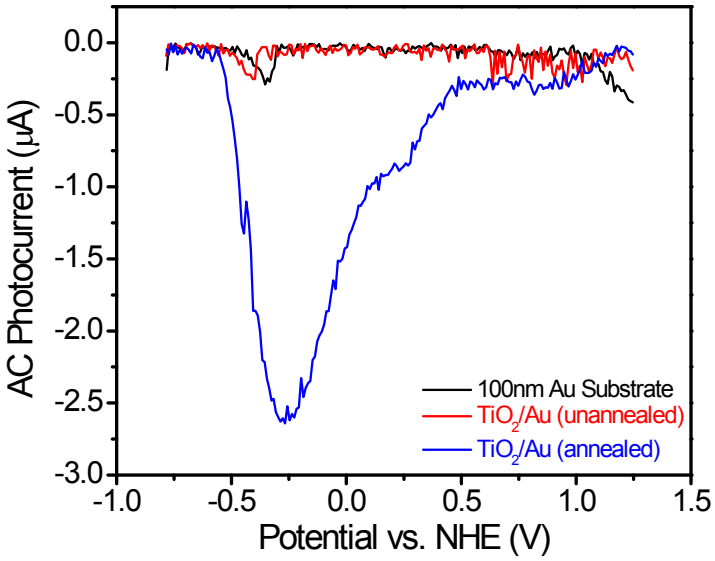


**Figure S3.** Additional datasets of the AC photocurrent plotted as a function of the reference potential for the hydrogen evolution reaction (HER), which show the same behavior observed in Figure 3 of the manuscript.

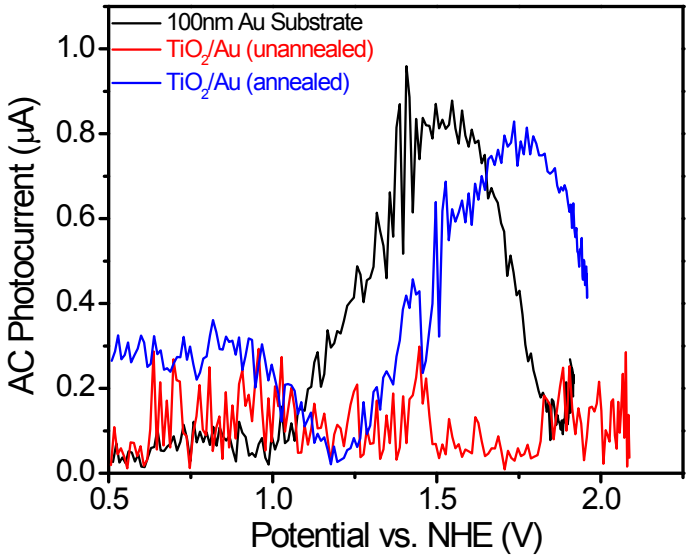


**Figure S4.** Additional datasets of the AC photocurrent plotted as a function of the reference potential for the oxygen evolution reaction (OER), which show the same behavior observed in Figure 4 of the manuscript.

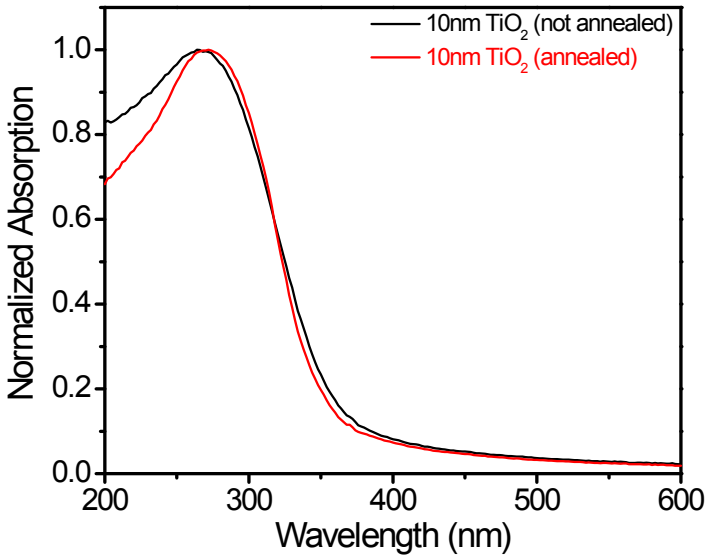


**Figure S5.** UV-vis absorption spectra of a 10nm thick $TiO_2$ film taken before and after annealing at 450°C for 30 min in an $O_2$ gas environment.