

Supplementary Information

Hydrogen Induced Interface Engineering in $\text{Fe}_2\text{O}_3\text{-TiO}_2$ Heterostructures for Efficient Charge Separation for Solar-driven Water Oxidation in Photoelectrochemical Cells

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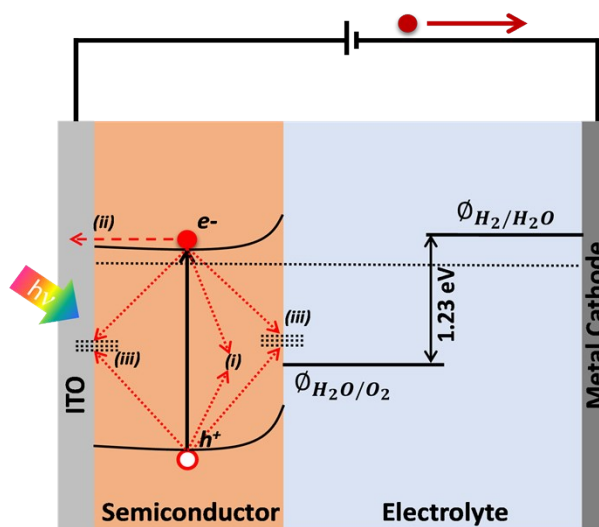


Figure S1: Schematic band alignment of hematite photoanode for PEC water oxidation. Creation of photogenerated electron-hole pair, migration of holes to the hematite surface for water oxidation to oxygen, and migration of electrons to the back charge collector metal cathode for water reduction to hydrogen. The four possible recombination sites that are unfavorable to complete the water oxidation and reduction in a PEC cell are: i) bulk charge recombination, ii) poor charge collection efficiency, iii) surface trapping and recombination and iv) interfacial carrier trapping and recombination.

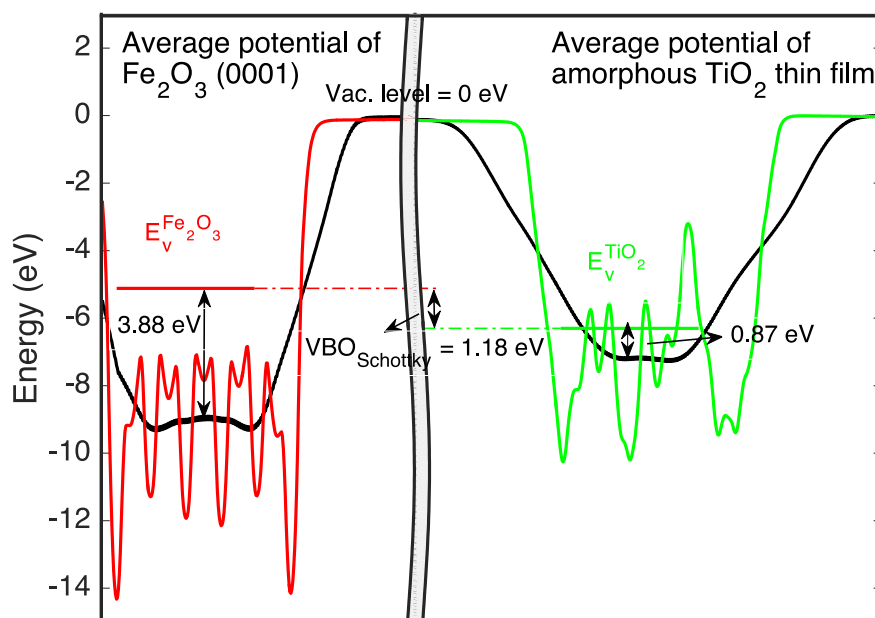


Figure S2: The calculated the VBO of individual systems of Fe_2O_3 (0001) and a- TiO_2 thin film.

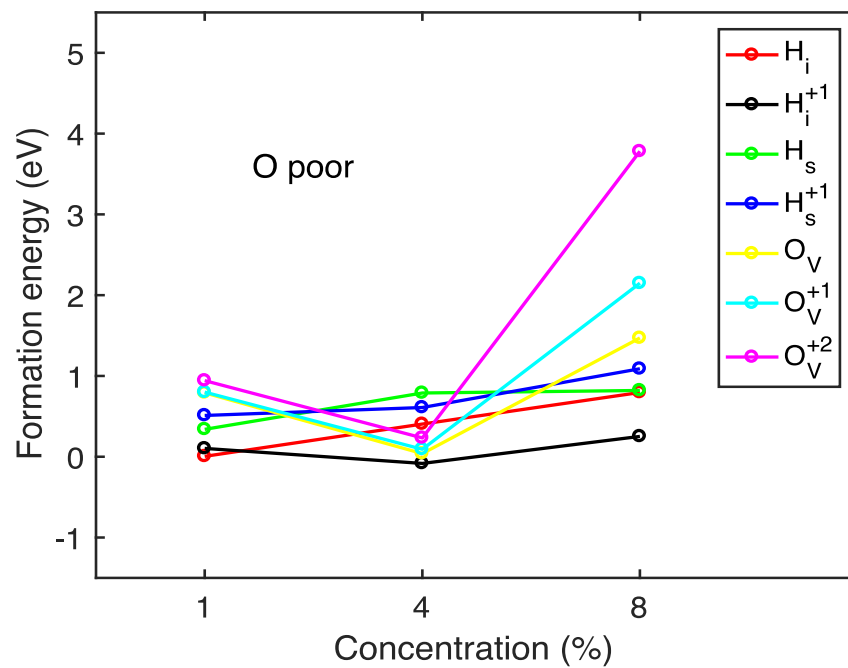


Figure S3: The calculated formation energy of various defects in anatase varying with the defect concentration under O-poor conditions. The Fermi energy is set to $E_f = 3.0$ eV

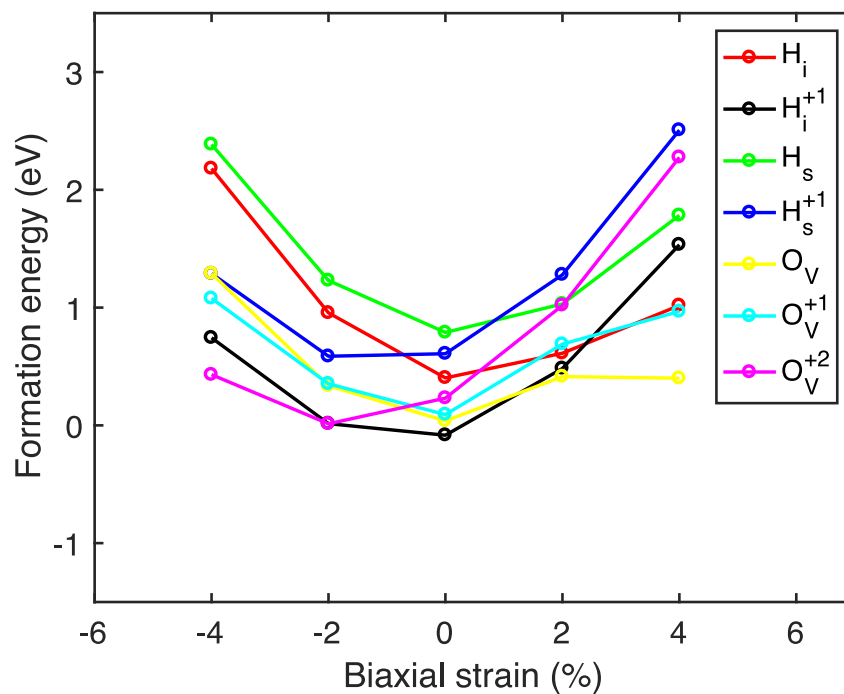


Figure S4: The calculated formation energy of different charged/neutral defects under biaxial strain from -4% to +4% under O-poor conditions. The Fermi energy is set to $E_f = 3.0$ eV.

Table S1. Formation energy of H interstitial, substitutional H and O vacancy in a-TiO₂ calculated with the PBE + U method.

H in a-TiO ₂	formation energy
H_i_2O	8.77
H_i_3O	-0.407
H_i_1x2	-1.04
H_i_1x3	-1.69
H_s	3.838
O_v	7.840

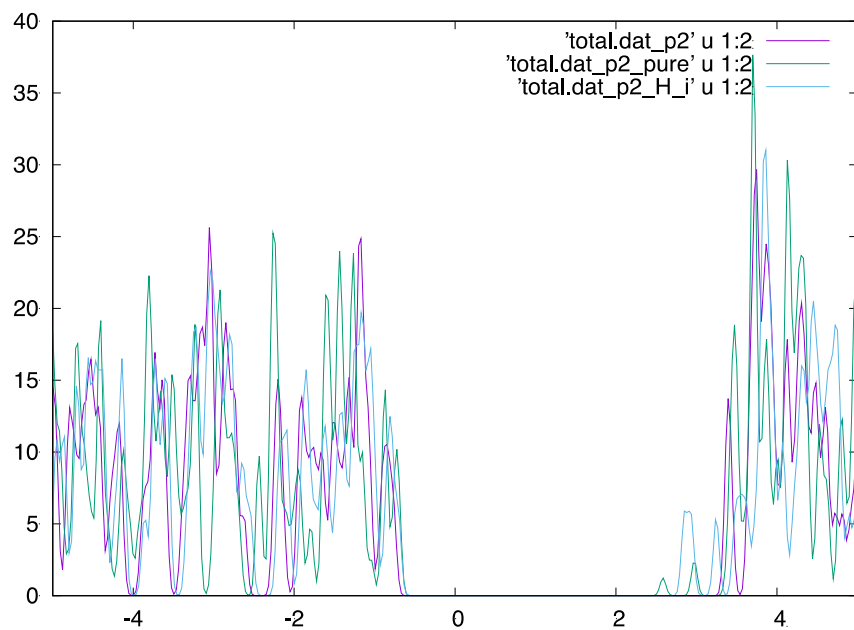


Figure S5: The DOS of pure anatase, H_i and H_i^+ doped anatase under 2% tensile biaxial strain.

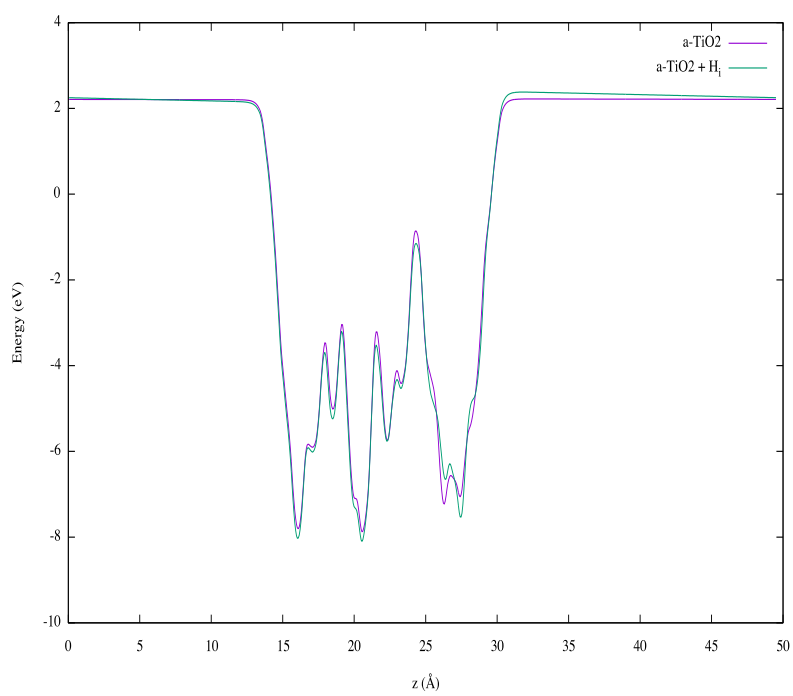


Figure S6: The calculated electrostatic potential of the H doped a-TiO₂ as compared with pristine a-TiO₂.

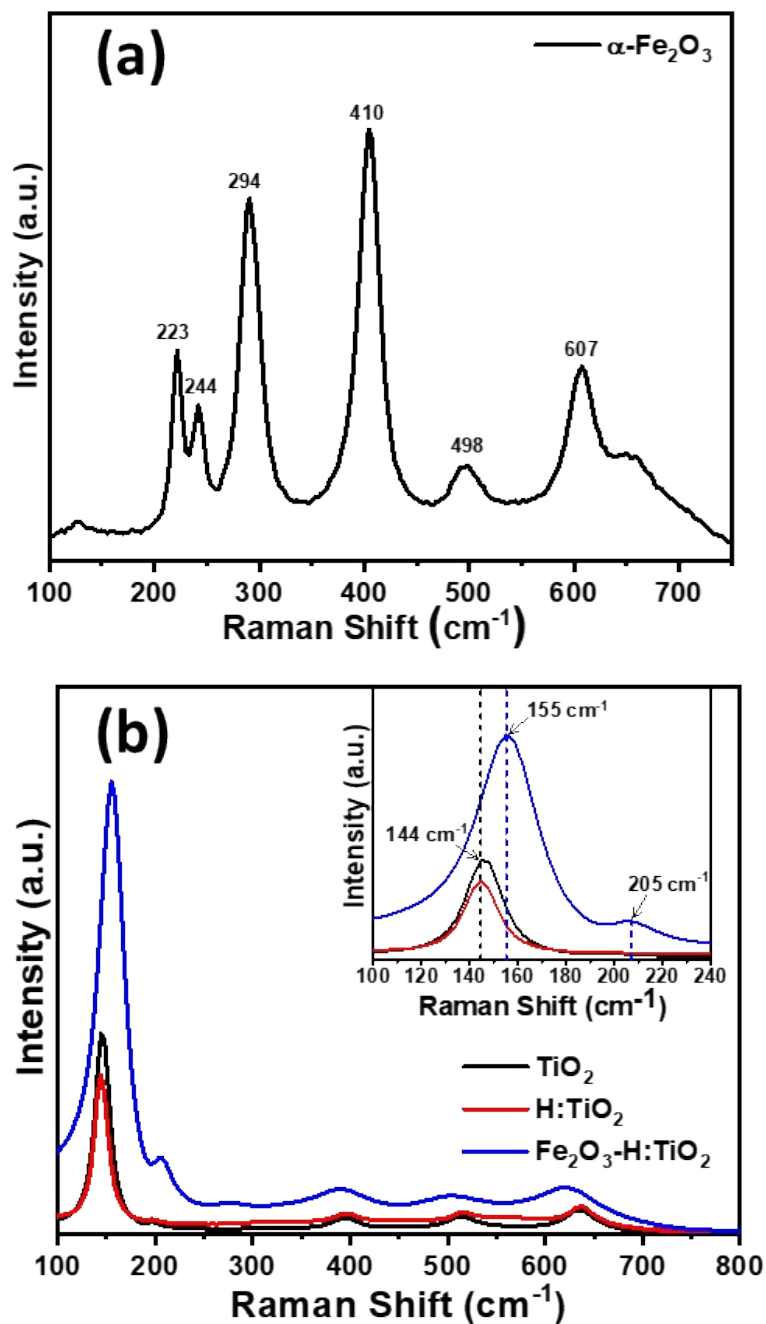


Figure S7. (a) Raman spectra of $\alpha\text{-Fe}_2\text{O}_3$, and (b) Raman spectra of TiO_2 , H:TiO_2 and $\text{Fe}_2\text{O}_3\text{-TiO}_2$ heterostructure thin films recorded from wavenumbers in the range of 100-900 cm^{-1} , Inset of (b) shows the no shift in E_g mode of TiO_2 upon hydrogen doping, however an up-shift of E_g mode of TiO_2 from 141 to 155 cm^{-1} can be seen in $\text{Fe}_2\text{O}_3\text{-TiO}_2$ heterostructure.

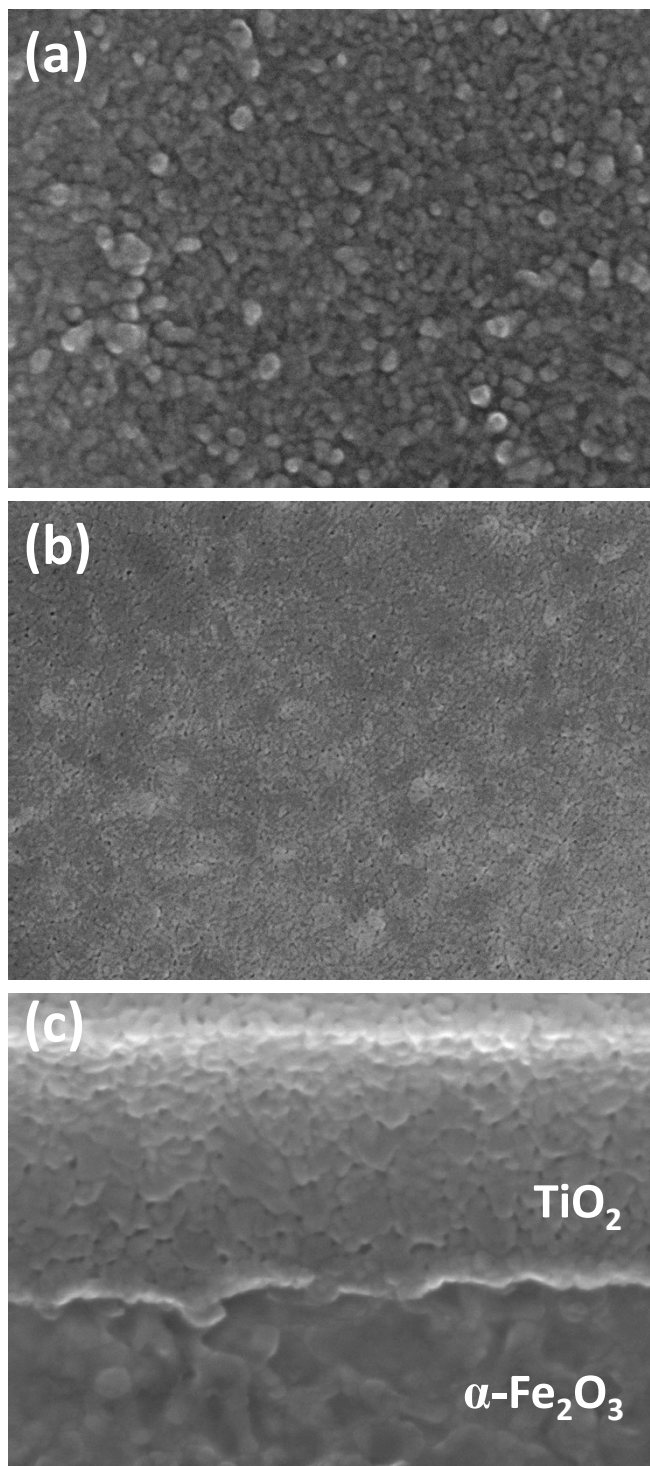


Figure S8: SEM images of pristine $\alpha\text{-Fe}_2\text{O}_3$ and (b) pristine TiO_2 and (c) $\text{Fe}_2\text{O}_3\text{-TiO}_2$ heterostructures annealed at 350 °C.

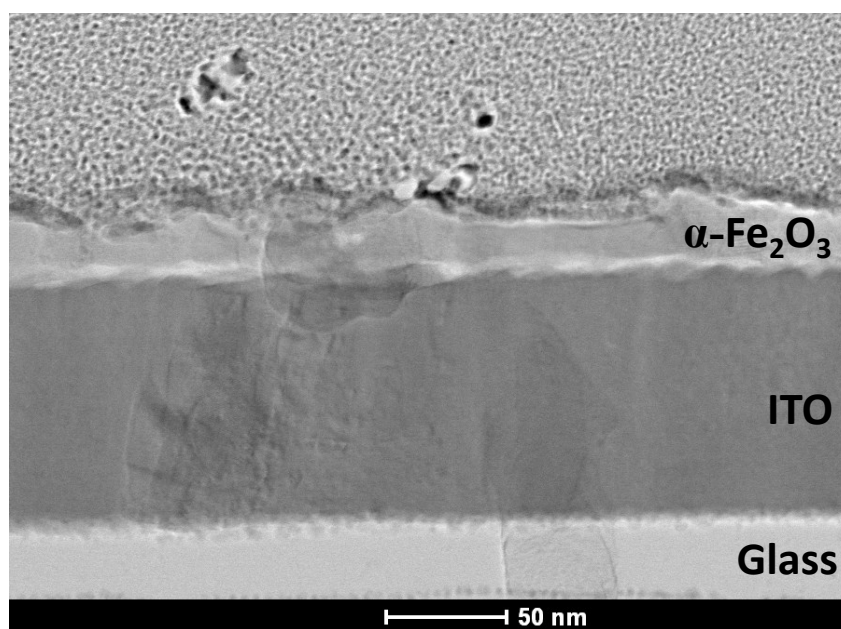


Figure S9: TEM images of pristine $\alpha\text{-Fe}_2\text{O}_3$ annealed at 350 °C.

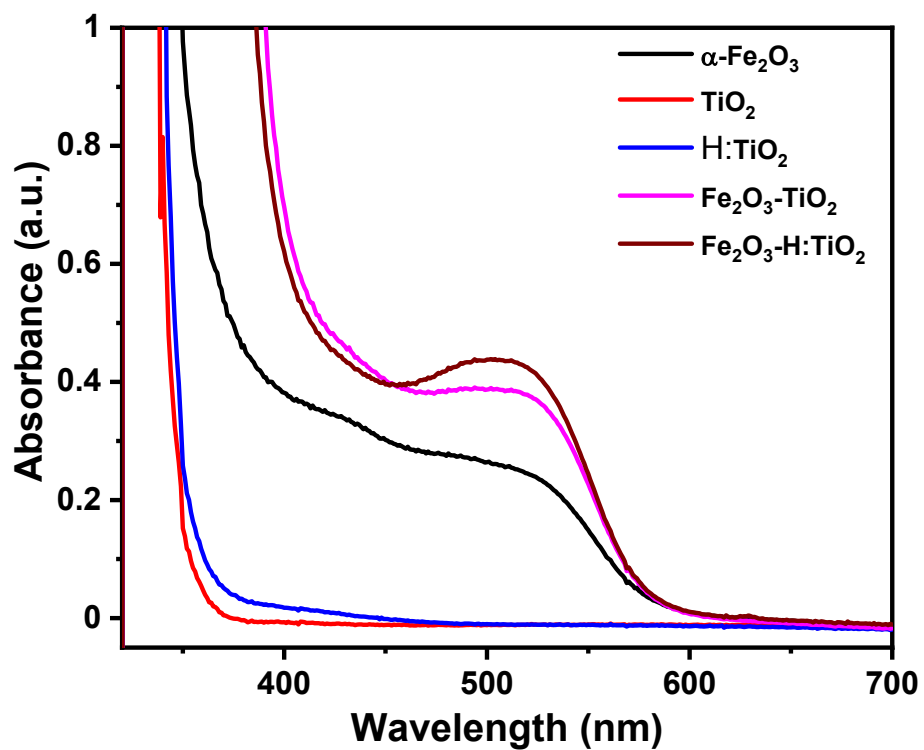


Figure S10: Optical absorption spectra of TiO₂, H:TiO₂, α -Fe₂O₃, Fe₂O₃-TiO₂, and Fe₂O₃-H:TiO₂ heterostructures.

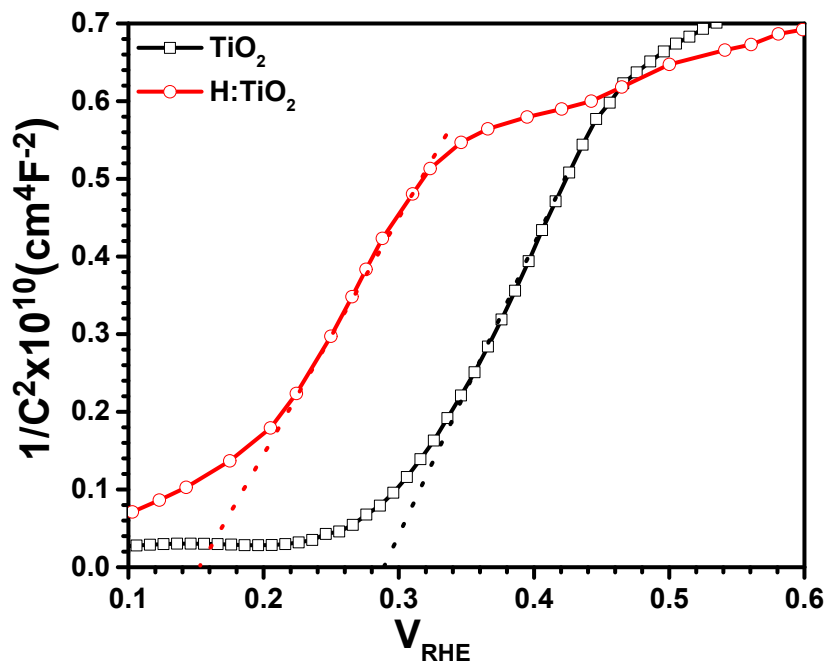


Figure S11: Mott-Schottky curves measured in dark condition for pristine and hydrogen doped TiO_2 photoanodes obtained at 1 kHz.

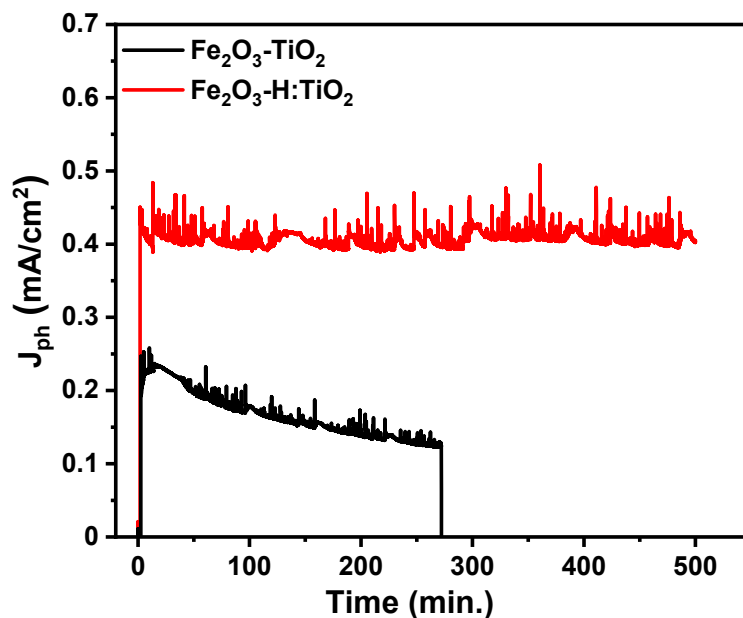


Figure S12: Long-term photoanode stability test of Fe₂O₃-TiO₂ and Fe₂O₃-H:TiO₂ heterostructure under 1 Sun illumination. In order to check the stability of the Fe₂O₃-H:TiO₂ heterostructure photoelectrodes, chronoamperometric studies were performed. A bias potential of 0.5 V_{RHE} in 0.1 M NaOH solution was applied to the photoelectrode and the photocurrent density is measured for 600 minutes. A stable photocurrent density was found. It is worth noting that the nominal decrease in photocurrent densities in this stability test measurements are achieved at 0.5 V_{RHE} applied biases.

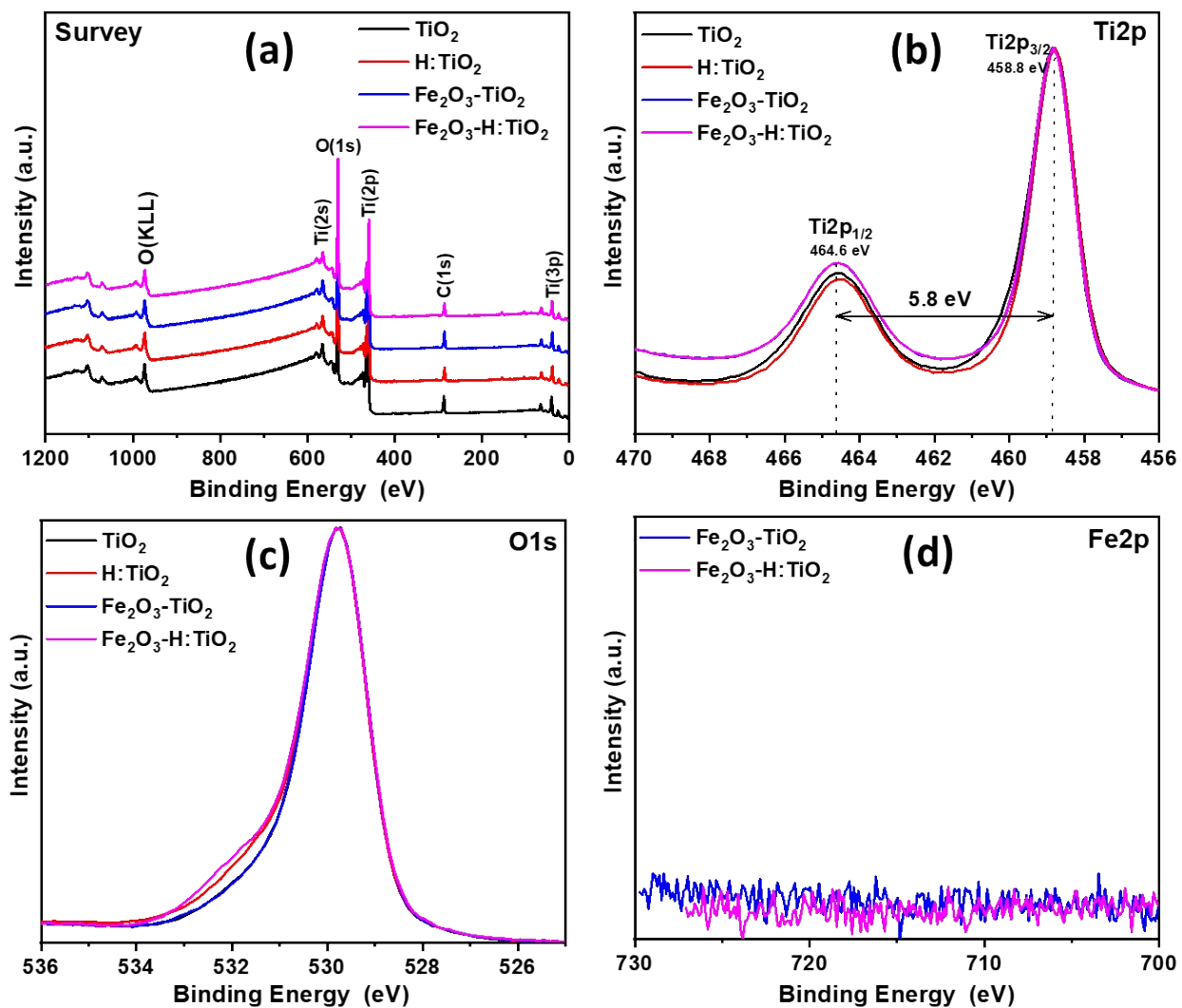


Figure S13: (a) XPS survey spectra (b) Ti2p core-level (c) O1s core-level spectra for the pristine TiO₂, H:TiO₂, Fe₂O₃-TiO₂, and Fe₂O₃-H:TiO₂ specimens and (d) Fe2p core-level spectra for Fe₂O₃-TiO₂, and Fe₂O₃-H:TiO₂ specimens.