Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

NiO_x-Fe_2O_3-coated p-Si photocathodes for enhanced solar water splitting in neutral pH water

Alireza Kargar,[a] Justin S. Cheung,[a] Chin-Hung Liu,[bc] Tae Kyoung Kim,[bc] Conor T. Riley,[d] Shaohua Shen,[e] Zhaowei Liu,[a] Donald J. Sirbuly,[d] Deli Wang[abf] and Sungho Jin*[bc]

*Corresponding author: jin@ucsd.edu

Optical absorption measurement:

Absorption measurements were obtained using a 150 mm integrating sphere connected to a LAMBDA 1050 UV/Vis/NIR spectrophotometer. Since the silicon transmittance (T) was found to be zero (Fig. S1a), the absorption (A) was calculated using; A(%) = 100-R(%) (R: reflectance). Fig. S1b shows the absorption spectra of bare and metal-oxide-coated Si substrates.

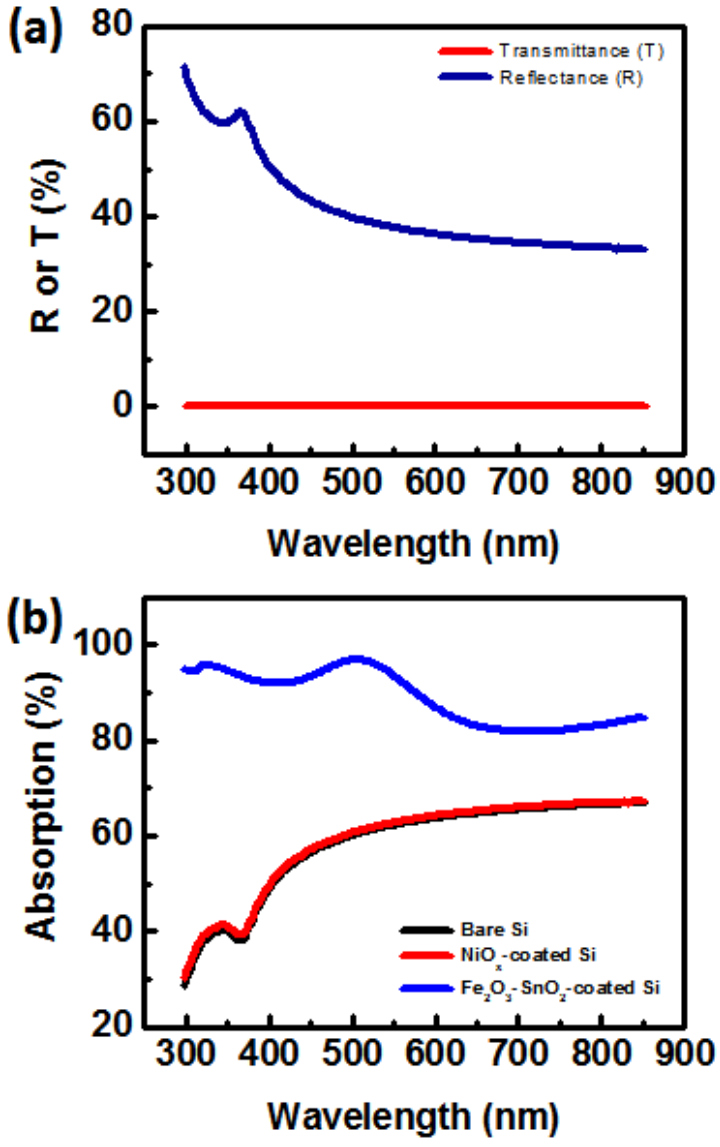

Fig. S1 (a) Transmittance and reflectance spectra of bare Si substrate. (b) Absorption spectra of bare and metal-oxide-coated Si substrates.

p-Si/n-SnO_2/n-Fe_2O_3 heterojunction band diagram:

The band gap of SnO_2 layer sputtered at a RF power of 400 W at room temperature was measured resulting in a band gap of 3.37 eV. The considered Si and Fe_2O_3 band gaps were 1.11 eV and 2.1 eV, respectively. To simulate the band diagram, the thicknesses of the Fe_2O_3 nanorod (NR) film and the SnO_2 seeding layer were considered as 141 nm and 82 nm, respectively, as measured for the sample using the SEM imaging (see the text). The electron affinities for Si, SnO_2, and Fe_2O_3 were considered as 4.05 eV, ~4.8 eV,[1,2] and ~4.7 eV,[1] respectively. The doping concentration of p-Si is in the range of 6.7×10^{14}–1.5×10^{16} cm^{-3} based on its resistivity of 1−20 Ωcm, and of sputtered SnO_2 is in range of 10^{19} cm^{-3}.[3] The effect of electrolyte pH was considered in the band diagram using the Nernst equation;

$$E(\mathrm{H^+/H_2}) = -0.059 \times \mathrm{pH} \quad (\mathrm{V\ vs\ NHE}) \tag{1}$$

where $E(\mathrm{H^+/H_2})$ is the Nernstian (thermodynamic) potential for hydrogen evolution (water reduction). Fig. S2 shows the approximate energy band diagram of the p-Si/n-SnO_2/n-Fe_2O_3 heterojunction at equilibrium condition and at dark for an electrolyte pH of 7.1 which was simulated using SCAPS (version 3.1.02) numerical simulation software.

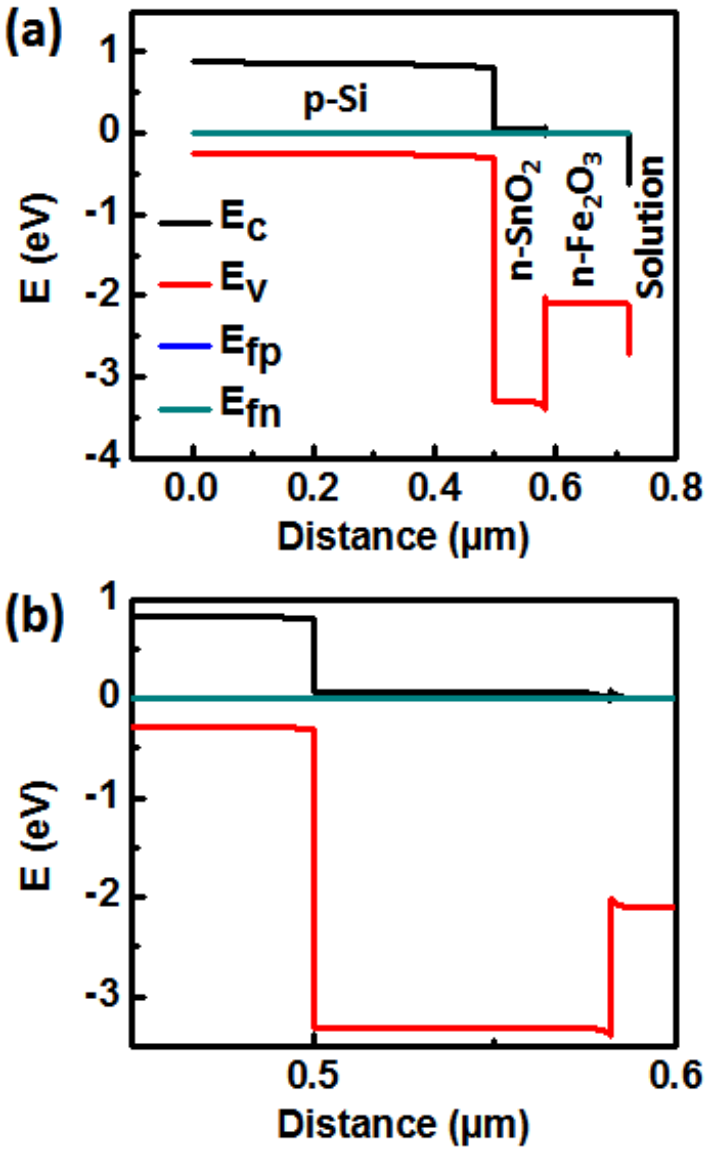

Fig. S2 (a) Approximate simulated energy band diagram of p-Si/n-SnO_2/n-Fe_2O_3 heterojunction at equilibrium condition and at dark for an electrolyte pH of 7.1. The considered thickness for planar Si substrate was 500 nm in the simulation. E_c, E_v, E_{fp}, and E_{fn} are conduction band, valance band, hole Fermi level, and electron Fermi level, respectively. Note that E_{fp} and E_{fn} overlap each other after alignment of energy levels. Energy levels are plotted with reference to vacuum level. Four different regions including p-Si, n-SnO_2, n-Fe_2O_3, and solution are labeled in (a). (b) Zoomed-in band diagram around p-Si/n-SnO_2 and n-SnO_2/n-Fe_2O_3 junctions.

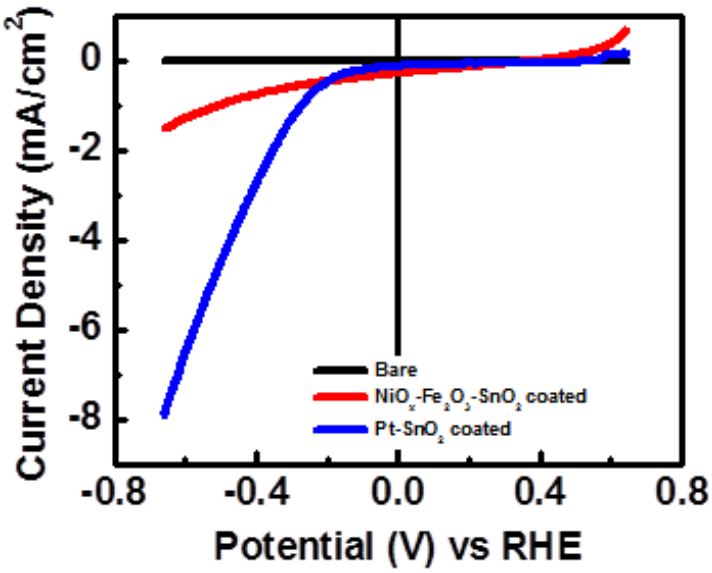

Fig. S3 Current density under illumination of bare and NiO_x-Fe_2O_3-SnO_2-coated p-Si photocathodes in comparison to Pt-SnO_2-coated p-Si photocathode measured in the neutral pH water. This figure is re-plotted of Fig. 4b (in the main text) in full scanned potential range to see the difference in current densities at high reversed biasing potentials.

References

1. M. Grätzel, *Nature*, 2001, **414**, 338-344.
2. Y. Cheng, R. Yang, J.-P. Zheng, Z. L. Wang and P. Xiong, *Mater. Chem. Phys.*, 2012, **137**, 372-380.
3. B. S. Tosuna, R. K. Feist, A. Gunawan, K. A. Mkhoyan, S. A. Campbell and E. S. Aydil, *Thin Solid Films*, 2012, **520**, 2554-2561.