ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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p-Si/SnO_2/Fe_2O_3 Core/Shell/Shell Nanowire Photocathodes for Neutral pH Water Splitting

*Alireza Kargar, Sung Joo Kim, Paniz Allameh, Chulmin Choi, Namseok Park, Huisu Jeong, Yusin Pak, Gun Young Jung, Xiaoqing Pan, Deli Wang, and Sungho Jin**

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Band diagram of p-Si/n-SnO_2/n-Fe_2O_3 css-NW heterojunctions

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 as shown in Figure S1. The obtained SnO_2 band gap is consistent with that reported elsewhere.[1] The considered Si and Fe_2O_3 band gaps were 1.11 eV and 2.1 eV, respectively. To draw the band diagram, the Si NW radius, SnO_2 thickness, and Fe_2O_3 NC length were considered as 140 nm, 28 nm, and 136 nm, respectively, based on the measured thicknesses for the css(10m-Si/SnO_2/2h-Fe_2O_3) NWs (see the text). The electron affinities for Si, SnO_2, and Fe_2O_3 were considered as 4.05 eV, ~4.8 eV,[2,3] and ~4.7 eV,[2] 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}.[1] This causes that for the junction between p-Si and n-SnO_2, the depletion region mostly lies in the p-Si NW because of much higher doping concentration of n-SnO_2 layer. The effect of electrolyte pH was considered in the band diagram using the Nernst equation;

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

where $E(\mathrm{H^+/H_2})$ is the Nernstian (thermodynamic) potential for hydrogen evolution (water reduction). Figure S2-S3 show the approximate energy band diagrams of the p-Si/n-SnO_2/n-Fe_2O_3 css-NW heterojunctions at pre-equilibrium and equilibrium conditions, respectively, and at dark for an electrolyte pH of 7.25. The drawn band diagrams were confirmed by simulation using SCAPS (version 3.1.02) numerical simulation software.

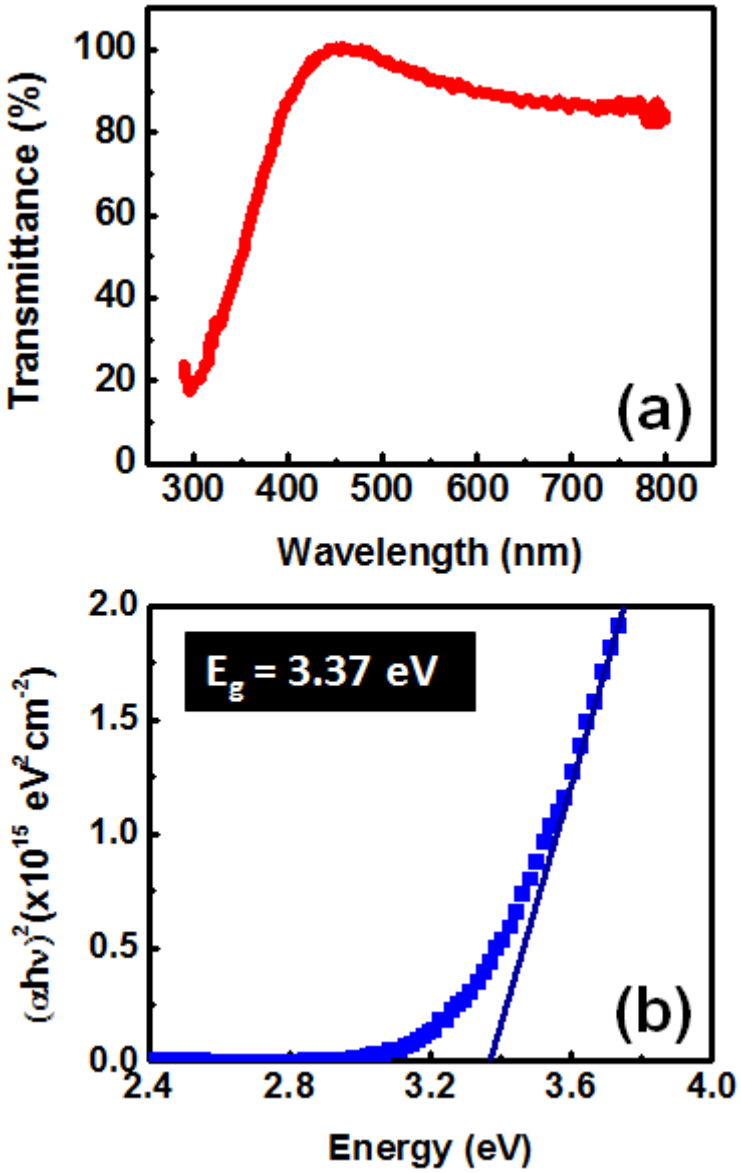

Figure S1. (a) Optical transmittance and (b) Tauc plot of 75 nm thick SnO_2 film sputtered at a RF power of 400 W at room temperature on glass. Extrapolated value gives a SnO_2 band gap of 3.37 eV.

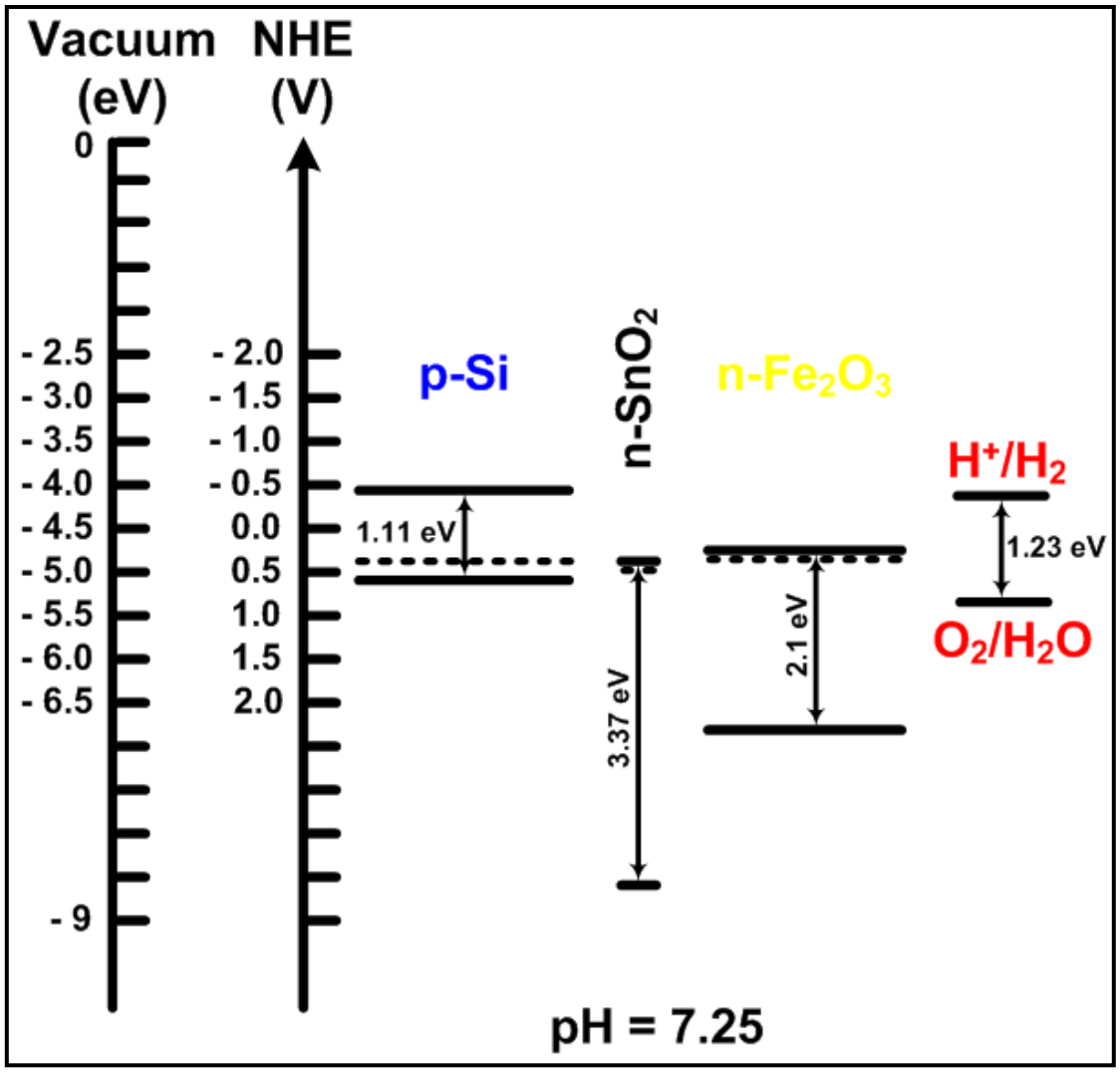

Figure S2. Approximate energy band diagram of p-Si/n-SnO_2/n-Fe_2O_3 css-NW hetero-junctions at pre-equilibrium condition and at dark for an electrolyte pH of 7.25.

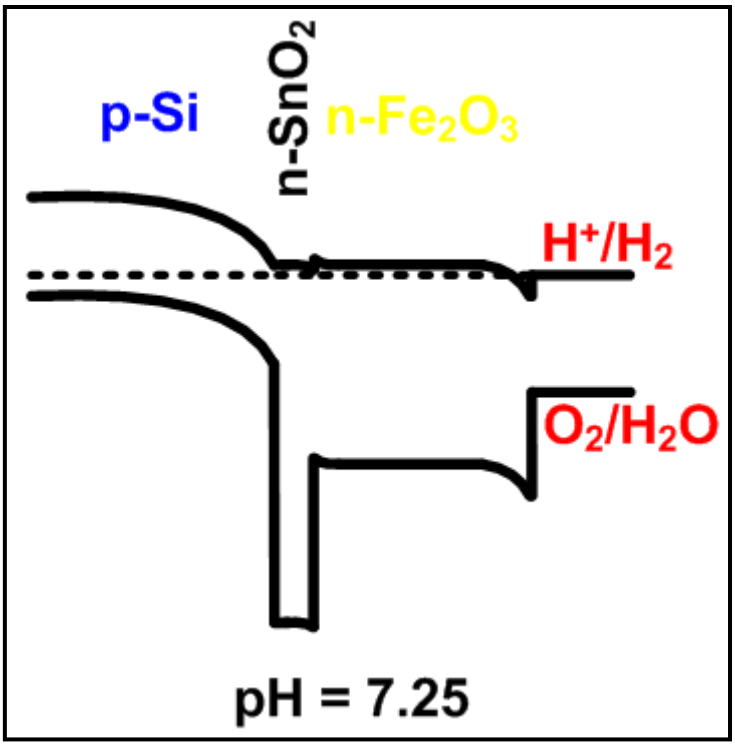

Figure S3. Approximate energy band diagram of p-Si/n-SnO_2/n-Fe_2O_3 css-NW hetero-junctions at equilibrium condition and at dark for an electrolyte pH of 7.25.

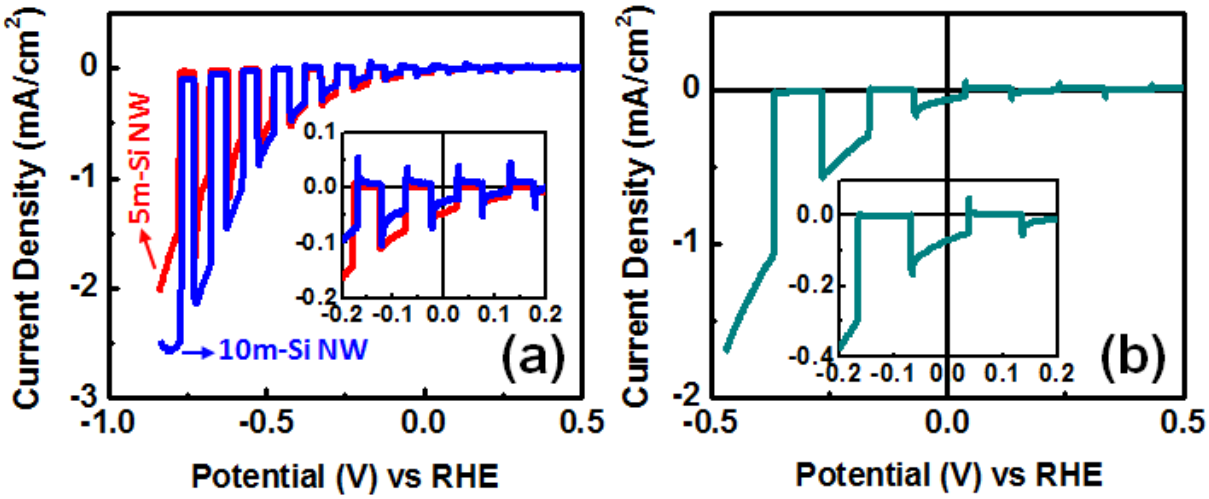

Figure S4. (a) Current density under chopped illumination of css(Si/SnO_2/2h-Fe_2O_3) NWs with different Si etching times. These curves are for the same samples shown in Figure 3b in the main text. (b) Current density under chopped illumination of css(10m-Si/SnO_2/2h-Fe_2O_3) NWs (the same sample shown in Figure 3c in the main text) measured in 1 M NaOH with pH = 13.5. The insets show the zoom-in plots around 0 V versus RHE.

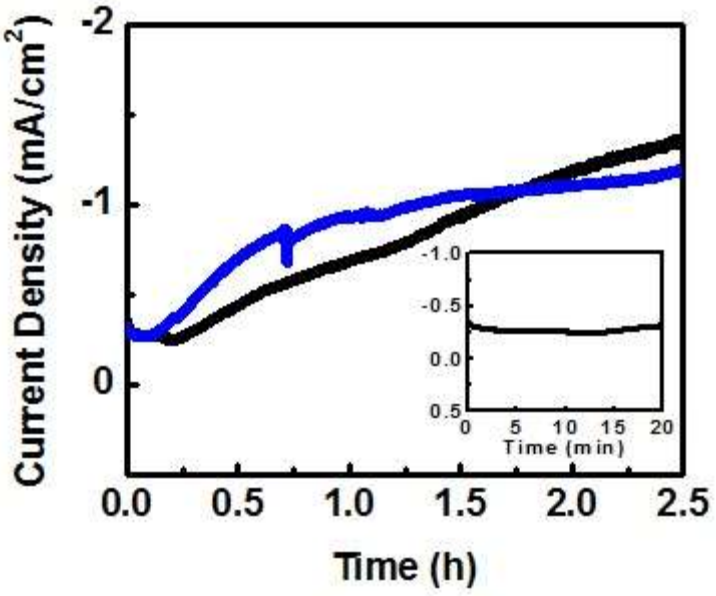

Figure S5. Current density under constant light illumination versus time (stability performance) at -0.33 V versus RHE and in neutral electrolyte of css(8.5m-Si(111)/SnO_2/2h-Fe_2O_3) NWs (blue curve; the same curve as shown in Figure 4a in the main text), and css(5m-Si(100)/SnO_2/2h-Fe_2O_3) NWs (black curve). Inset exhibits the enlarged first part (0-20 min) of black curve.

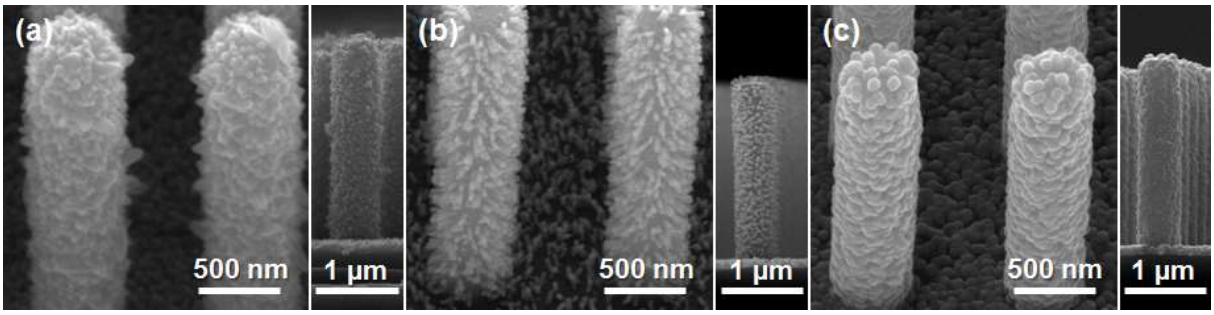

Figure S6. Comparison of different p-Si/metal-oxide NW photocathodes. SEM images of (a) $Si/SnO_2/Fe_2O_3$ css-NWs, (b) ZnO/Si branched NWs, and (c) TiO_2/Pt-coated ZnO/Si branched NWs. The p-Si(100) NW cores are from 10 mins etching for all the samples in (a)-(c) and they were fabricated under similar conditions. The Fe_2O_3 and ZnO growth times are 2 hrs and 5 mins, respectively. Insets in (a)-(c) show the cross-sectional view images of corresponding samples. The metal-oxide shell in (a)-(c) has almost similar thickness.

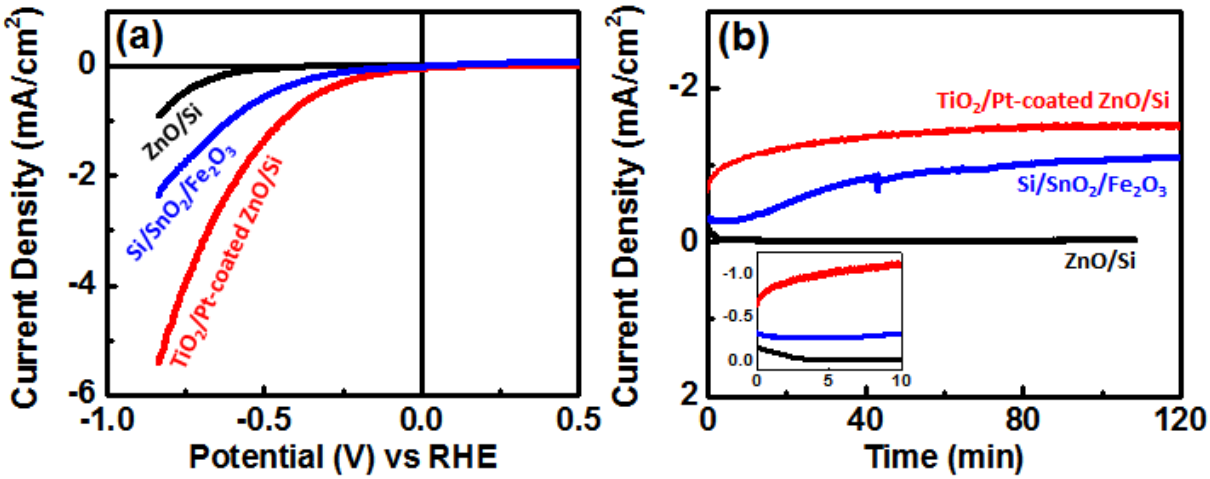

Figure S7. (a) Current density under illumination measured in the neutral electrolyte of $Si/SnO_2/Fe_2O_3$ css-NWs, ZnO/Si branched NWs, and TiO_2/Pt-coated ZnO/Si branched NWs (the corresponding samples shown in Figure S6). (b) Current density under constant illumination versus time at -0.33 V versus RHE and in the neutral solution of corresponding samples. Inset shows the enlarged first part (0-10 min) of the corresponding curves.

References

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