Supplementary Information

Underlayer engineering into the Sn-doped hematite photoanode for facilitating carrier extraction

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Fig. S1. Typical SEM images of various underlayers [(c) TiO₂, (e) NiO, (g) ITO and (i) Al₂O₃] deposited on (a) FTO substrate, and the corresponding SEM images of the post-grown Sn doped hematite film [(b) FTO/Sn@ α -Fe₂O₃, (d) FTO/TiO₂/Sn@ α -Fe₂O₃, (f) FTO/NiO/Sn@ α -Fe₂O₃, (h) FTO/ITO/Sn@ α -Fe₂O₃ and (j) FTO/Al₂O₃/Sn@ α -Fe₂O₃].



Fig. S2. XRD patterns of $FTO/Sn@\alpha$ -Fe₂O₃, $FTO/TiO_2/Sn@\alpha$ -Fe₂O₃, $FTO/NiO/Sn@\alpha$ -Fe₂O₃, $FTO/ITO/Sn@\alpha$ -Fe₂O₃ and $FTO/Al_2O_3/Sn@\alpha$ -Fe₂O₃ photoanodes.



Fig. S3. Raman spectra of FTO/Sn@ α -Fe₂O₃, FTO/TiO₂/Sn@ α -Fe₂O₃, FTO/NiO/Sn@ α -Fe₂O₃, FTO/ITO/Sn@ α -Fe₂O₃ and FTO/Al₂O₃/Sn@ α -Fe₂O₃ photoanodes.



Fig. S4. (a) XPS spectra of FTO/Sn@ α -Fe₂O₃, FTO/TiO₂/Sn@ α -Fe₂O₃, FTO/NiO/Sn@ α -Fe₂O₃, FTO/ITO/Sn@ α -Fe₂O₃ and FTO/Al₂O₃/Sn@ α -Fe₂O₃ photoanodes. (b–d) are the Fe 2p, Sn 3d and O 1s spectra in varying-underlayer photoanodes, respectively. Note that both of the positions and intensities of the Fe 2p, Sn 3d and O 1s peaks for various samples show slight changes due to the element doping from the underlayer.



Fig. S5. (a) Reflectance, (b) transmittance and (c) absorption spectra of $FTO/Sn@\alpha-Fe_2O_3$, $FTO/TiO_2/Sn@\alpha-Fe_2O_3$, $FTO/NiO/Sn@\alpha-Fe_2O_3$, $FTO/ITO/Sn@\alpha-Fe_2O_3$ and $FTO/Al_2O_3/Sn@\alpha-Fe_2O_3$ photoanodes. Absorption is calculated by unit subtracting the sum of reflectance and transmittance.



Fig. S6. (a) *J-E* curves, (b) Mott-Schottky curves, (c) PEIS plots at 1.23 V_{RHE}, (d) transient current density at 1.5 V_{RHE} between light-ON and light-OFF states for the FTO/NiO/Sn@ α -Fe₂O₃ photoanodes with different thicknesses of NiO underlayer.



Fig. S7. (a) *J-E* curves, (b) Mott-Schottky curves, (c) PEIS plots at 1.23 V_{RHE}, (d) transient current density at 1.5 V_{RHE} between light-ON and light-OFF states for the FTO/ITO/Sn@ α -Fe₂O₃ photoanode with different thicknesses of ITO underlayer.



Fig. S8. (a) *J-E* curves, (b) Mott-Schottky curves, (c) PEIS plots at 1.23 V_{RHE}, (d) transient current density at 1.5 V_{RHE} between light-ON and light-OFF states for the FTO/Al₂O₃/Sn@ α -Fe₂O₃ photoanode with different thicknesses of Al₂O₃ underlayer.



Fig. S9. Onset potential is consistent with the C_{ss} peak and the R_{ct} valley for the (a) FTO/Sn@ α -Fe₂O₃, (b) FTO/NiO/Sn@ α -Fe₂O₃, (c) FTO/ITO/Sn@ α -Fe₂O₃ and (d) FTO/Al₂O₃/Sn@ α -Fe₂O₃ photoanodes.



Fig. S10. Fitting values of (a) R_{trap} and (b) C_{ss} based on the equivalent circuit model.



Fig. S11. The ratios of (a) R_{trap} , (b) C_{bulk} , (c) R_{ct} and (d) C_{ss} for the varying-underlayer photoanodes relative to the FTO/Sn@ α -Fe₂O₃ photoanode.



Fig. S12. IMPS plot at 1.23 V_{RHE} for FTO/Sn@ α -Fe₂O₃, FTO/TiO₂/Sn@ α -Fe₂O₃, FTO/NiO/Sn@ α -Fe₂O₃, FTO/ITO/Sn@ α -Fe₂O₃ and FTO/Al₂O₃/Sn@ α -Fe₂O₃ photoanodes under the illumination of an UV LED.



Fig. S13. (a) A ratio of K_{rec} for the varying-underlayer photoanodes relative to the FTO/Sn@ α -Fe₂O₃ photoanode. (b) The transfer rate constant (K_{tran}) based on the IMPS plots.