

Parallel multi-stacked photoanodes of Sb-doped p–n homojunction hematite with near-theoretical solar conversion efficiency

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The present manuscript addresses the study of high-efficient Fe₂O₃ photoanodes for water oxidation. The authors have carried out a systematic investigation optimizing the Sb content, generating donor species in the bulk and acceptor species at the surface, leading to an n-p type photoanode architecture. The reducing atmosphere of the first heating process and the fast annealing with microwave heating have also significantly contributed to the optimization of the photoanode. The authors have implemented a stacked configuration of six parallel photoanodes achieving a remarkable performance. However, there are some issues, which still need further elaboration before the manuscript can be further considered for publication in Nature Communications. More detailed comments are provided below:

- 1) The authors have carried out Mott-Schottky analysis, and the results are showed in Figure 2A. With the complex morphology of the films, the use of the conventional Mott-Schottky equation to do any estimation of flatband potential or donor/acceptor density is not adequate. Indeed, the authors report some very high values of donor density (1020 cm⁻³), which should be revised. It is possible that this donor density corresponds to the underlying FTO substrate. The authors are refereed to Chem. Sci., 2022,13, 4828-4837 and J. Mater. Chem. A, 2019,7, 26162-26176 for a clear understanding of the validity of the Mott-Schottky analysis for photoelectrochemical applications.
- 2) The spikes showed in Figure 3b would be better visualized in a potentiostatic experiment, showing photocurrent as a function of time for ON-OFF illumination cycles. In any case, the information that the authors want to convey is clear from the present Figure 3b.
- 3) The authors study the charge separation and charge transfer efficiencies using H₂O₂ as hole scavenger. However, they have previously commented that H₂O₂ deactivates the surface Sb^{<+3} species, deleteriously affecting the photoanode performance. A different hole scavenger (for example Na₂SO₃) would provide better results. Why did they use H₂O₂ in these experiments?
- 4) The authors have carried out an impedance spectroscopy study, but only two different potentials (1 and 1.23 V vs RHE) are investigated, and consequently, the obtained results are not very informative. A wider potential range with more potentials (0.5-1.5 V vs RHE, V step 50 mV for example) would be more adequate to rationally interpret the trends of capacitances and resistances, in line with the complementary characterizations employed in the study. In particular, information of surface states would be highly valuable to understand the contribution of surface Sb^{<+3} and NiFeOOH species.
- 5) The authors claim that "The carrier lifetime of p–n homojunction is ~190 ms at the transient when illumination is stopped, much shorter than those of bare Fe₂O₃ (~4.0 s) and PN-10-O (~4.6 s), and further decreases to ~96 ms with co-catalyst loading (Fig. 3f)". However, these lifetimes are different from the numbers included in the Figure 3f.
- 6) In page 19, the authors claim: "In particular, a parallel 6-stacked photoanode records J_{ph} of 373 over 10 mA cm⁻², which is by far closest to the theoretical value (12.6 mA cm⁻²),..." However, this claim would be correct for a single photoelectrode, not for a parallel configuration of 6 photoanodes. Consequently, the authors should modify this claim.
- 7) Also, in page 19, the authors claim: "The measured J_{ph} of the ith (i=2, 3, 4, 5, and 6) photoanode in 6-stacked configuration shows 1.99, 1.50, 1.02, 0.65 and 0.50 mA cm⁻² at 1.23 VRHE under standard condition, respectively (Fig. 4c), ...". These values are not clear from the figure 4c. Furthermore, there are 5 photocurrent values, and there should be 6 values.
- 8) The characterization of the IPCE for the stacked configuration is very interesting, but the representation selected by the authors to convey this information is not so visual. Maybe the authors could show IPCE versus wavelength for 1, 1+2, 1+2+3,

..., 1+2+3+4+5+6, to clearly visualize that the stacked configuration with 6 photoanodes achieves an IPCE close to 100% at all measured wavelengths. Additionally, they could calculate the integrated photocurrent and further validate the obtained photocurrent of 10 mA·cm⁻².

9) Figure 5 and Figure S34 have some similar figures. The authors may avoid duplicating the information in the main text and in the Supplementary Information.

10) The photoelectrochemical cell that the authors have employed (Supplementary figure 14) is not optimized for the field lines between anode and cathode and may face some mass transport issues. Did the authors investigate this issue? Additionally, how did they calibrate that the light intensity at the photoanode was 1 sun?

Reviewer #2

(Remarks to the Author)

The authors have made a nice approach to stack homo-type Sb-doped Fe₂O₃ photoanodes to enhance the overall photocurrent. The approach is neat and smart and the characterisation is well done, but generally there are very low degree of specific scientific novelty. Sb-doping of hematite has been done previously, for example in [ACS Appl. Mater. Interfaces 2018, 10, 19, 16467–16473]. Several other studies has also enlightened the role of Sb as dopant in similar applications. Therefore, even if the approach is neat and smart, and the concept itself is a good way to overcome the short diffusion length of charge carriers in hematite, I see not enough novelty to be published in Nature Communications. I would see that the study should be published in a more specialized journal where the concept itself is of interest for the readers.

Reviewer #3

(Remarks to the Author)

The author present a multi-stacked photoanodes. This effort is challenging. Indeed hematite is not optimum for a photoanodes. Hematite requires a suitable thickness to access strong light. the author use Sb and Fe₂O₃ to generate a strong p-n, but this is not enough.

The characterization is strong in all details. The device can work, but the photocurrent is low, mA 4,21. Moreover there is no discussion about the surface defects.

Best regards

Giovanni

Reviewer #4

(Remarks to the Author)

The authors have reported a parallel multi-stacked photoanodes of Sb doped hematite for PEC water oxidations. They proposed parallel-connected stack of six p–n homojunction hematite photoanodes records a near-theoretical J_{ph} of ~10 mA cm⁻² at 1.23 VRHE under standard PEC water splitting conditions, which sets a new benchmark of hematite photoanodes and promises its practical application for unbiased PEC water splitting. However, the manuscript needs further revisions to clarify the following points:

(1) The band alignment of PN-10 homojunction of Fig. 2 shows that the energy gap between CBM of Sb₃₊:Fe₂O₃ and VBM of Sb₅₊:Fe₂O₃ is only ~ 0.7 eV. Thus, the nonadiabatic coupling CBM of Sb₃₊:Fe₂O₃ and VBM of Sb₅₊:Fe₂O₃ is strong. In this case, the electrons in CBM of Sb₃₊:Fe₂O₃ can easily recombine with the holes in VBM of Sb₅₊:Fe₂O₃, resulting in fast charge recombination and short charge carrier lifetime. Why does the Sb doping can promote the charge separation in this situation?

(2) In page 17, the authors proposed that the fast OCP transient decay indicates a significant charge recombination when illumination is stopped, which implies on the other hand that the charge trapping is insignificant when illuminated. Please reveal in detail how does the charge trapping process occurs and provide the mechanism evidences?

(3) The XRD spectra of p–n homojunction hematite photoanodes in Supplementary Fig. 2 show that Sb doping can cause the formation of a new phase Fe₂Sb₂O₇. However, the peak of Fe₂Sb₂O₇(103) only exists in PN-40, why this peak does not exist in PN-20? Whether the peak of Fe₂Sb₂O₇(103) is corresponding to the peak of Fe₂O₃(110)? In addition, why the authors choose the Fe₂Sb₂O₇ as the XRD standard card? The stoichiometric ratios of Fe_xSb_yO_z in PN-5, PN-10, PN-20, PN-40 are Fe₂Sb₂O₇?

(4) Under normal circumstances, the calcination temperature from β-FeOOH to α-Fe₂O₃ is 500 or 550°C, why 400°C is chosen in this paper?

(5) In page 7 of Supplementary, please check whether the“(OC, 532.5–533.1 eV)²” is correct.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have convincingly addressed all raised issues and the manuscript can be accepted for publication.

Reviewer #4

(Remarks to the Author)

This paper is probably publishable, but should be reviewed again in revised form before it is accepted.

The authors proposed that the photogenerated holes can be quickly extracted by co-catalyst, is there any experimental evidence for that? In addition, photogenic holes participate in OER reaction very slowly. How does it inhibit charge recombination?

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)

Authors have addressed all my concerns, I recommend the manuscript for publication.

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Response to Editor and Reviewers' Comments

We would like to thank the editor and the reviewers for their careful evaluation of this work and for making valuable comments and suggestions, which were of great help in improving the quality of this work. All the comments have been accommodated as summarized in the following point-by-point responses. The revised parts of the manuscript have been highlighted.

Reviewer #1:

Comments to the Author: *The present manuscript addresses the study of high-efficient Fe₂O₃ photoanodes for water oxidation. The authors have carried out a systematic investigation optimizing the Sb content, generating donor species in the bulk and acceptor species at the surface, leading to an n-p type photoanode architecture. The reducing atmosphere of the first heating process and the fast annealing with microwave heating have also significantly contributed to the optimization of the photoanode. The authors have implemented a stacked configuration of six parallel photoanodes achieving a remarkable performance. However, there are some issues, which still need further elaboration before the manuscript can be further considered for publication in Nature Communications.*

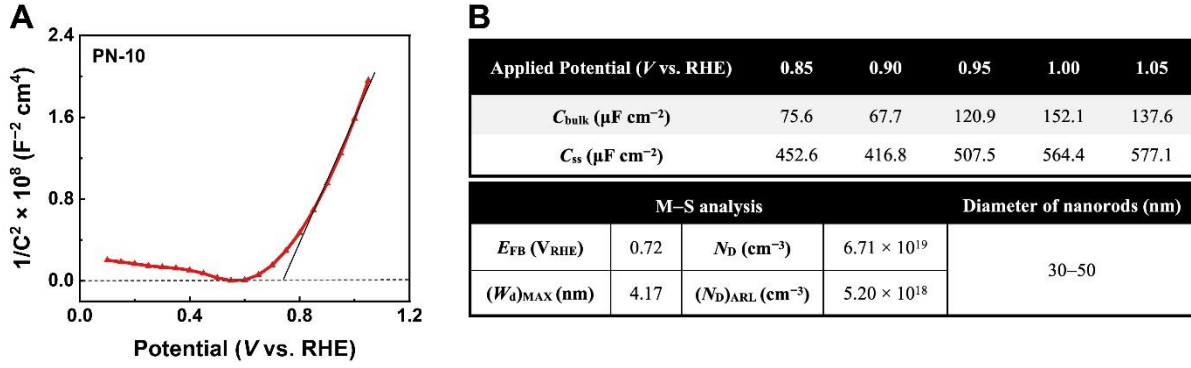
Response: We thank the reviewer for the positive comments that our investigation into the formation of p–n homojunction is a systematic investigation and the stacked configuration of six parallel photoanodes achieves a remarkable performance. All the comments are beneficial for improving this work's quality. The point-by-point response to each comment is the following.

Comment 1: *The authors have carried out Mott-Schottky analysis, and the results are showed in Figure 2A. With the complex morphology of the films, the use of the conventional Mott-Schottky equation to do any estimation of flatband potential or donor/acceptor density is not adequate. Indeed, the authors report some very high values of donor density (10^{20} cm^{-3}), which should be revised. It is possible that this donor density corresponds to the underlying FTO substrate. The authors are referred to Chem. Sci., 2022,13, 4828-4837 and J. Mater. Chem. A, 2019,7, 26162-26176 for a clear understanding of the validity of the Mott-Schottky analysis for photoelectrochemical applications.*

Response 1: We thank the reviewer for pointing out the long-standing issue that the conventional Mott–Schottky (M–S) equation has limitation in evaluating the flat-band potential or donor/acceptor density of the porous nanostructured photoelectrodes. We have carefully considered the reviewer’s comments and have made the following clarifications and revisions.

Based on Sivula’s editorial in *ACS Energy Lett.* **6**, 2549–2551 (2021), we performed a few sanity checks to correct and evaluate the validity of M–S results. Besides, we combined comprehensive resources explored in Hankin *et al.*’s work (*J. Mater. Chem. A* **7**, 26162–26176 (2019)) to carefully evaluate the flat band potential of Sb-doped hematite nanorods with different doping concentrations to reveal more information about the surface states.

Check the validity of M–S results. The derivation of the M–S equation is based on several fundamental assumptions (*J. Phys. D: Appl. Phys.* **11**, L63 (1978)). Yet, some of them are invalid at the porous nanostructured photoelectrode/electrolyte interfaces. Through the linear region of the M–S plot obtained on PN-10, we extracted the capacitance in the depletion layer (C_{bulk}) and the surface state capacitance (C_{ss}) at different applied potentials (0.85, 0.90, 0.95, 1.00 and 1.05 V_{RHE}), which are shown in Supplementary Fig. 7. The C_{bulk} is much smaller than the C_{ss} , thus the capacitance measured in M–S plot ($1/C = 1/C_{\text{bulk}} + 1/C_{\text{ss}}$) is considered to be mainly contributed by depletion layer capacitance (*J. Mater. Chem. A* **7**, 26162–26176 (2019), *ACS Energy Lett.* **6**, 2549–2551 (2021)). Therefore, the estimation of flat band potential (E_{FB}) and donor density (N_{D}) based on M–S analysis in this work is basically valid and meaningful. Moreover, the comparison of the maximum depletion layer width ($(W_{\text{d}})_{\text{MAX}}$) and the size of nanostructure is another necessary means of inspection. The diameter of PN-10 nanorods synthesized in this work is 30–50 nm, while the $(W_{\text{d}})_{\text{MAX}}$ is calculated to be 4.17 nm, using the N_{D} extracted from the M–S equation and the largest ($V - E_{\text{FB}}$) employed in the M–S fit in equation (2) (Supplementary Fig. 7). The small $(W_{\text{d}})_{\text{MAX}}$ ($4.17 \times 2 = 8.34$ nm) relative to the diameters of nanorods suggests that the semiconductor is not fully depleted over the potential region of the M–S plot. Thus, the C_{bulk} is measured correctly. Also, we calculated the analytical resolution limit of N_{D} ($(N_{\text{D}})_{\text{ARL}}$) by assuming the semiconductor is fully depleted, where the estimated N_{D} by M–S ($6.71 \times 10^{19} \text{ cm}^{-3}$) is an order of magnitude larger than the $(N_{\text{D}})_{\text{ARL}}$ ($5.20 \times 10^{18} \text{ cm}^{-3}$), demonstrating that donor density of Sb-doped hematite is reasonable and valid without corresponding to the underlying FTO substrate (*Chem. Sci.* **13**, 4828–4837 (2022)).



Supplementary Fig. 7| M-S analysis of PN-10. The extracted capacitance in the depletion layer (C_{bulk}) and extracted surface state capacitance (C_{ss}) from PEIS over the linear region of the M-S plot are listed in (B). The C_{bulk} is much smaller than the C_{ss} , indicating that the C in the M-S plot ($1/C = 1/C_{\text{bulk}} + 1/C_{\text{ss}}$) can be regarded as the capacitance in the depletion layer, which in turn proves the validity of M-S results^{2,3}.

The donor density (N_{D}) can be extracted from the equation⁴:

$$\left(\frac{A}{C}\right)^2 = \frac{2}{q\epsilon_r\epsilon_0 N_{\text{D}}} \left(V - E_{\text{FB}} - \frac{k_{\text{B}}T}{q}\right) \quad (1)$$

where A is the surface area of photoanode, C is the capacitance of the semiconductor depletion layer, V is the applied potential, E_{FB} is the flat band potential, $k_{\text{B}} = 1.38 \times 10^{-23} \text{ J K}^{-1}$, $T = 298 \text{ K}$, $q = 1.602 \times 10^{-19} \text{ C}$, $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$, and $\epsilon_r = 32$ for hematite.

The depletion layer width (W_{d}) can be calculated with the following equation⁵

$$W_{\text{d}} = \left(\frac{2\epsilon_r\epsilon_0(V - E_{\text{FB}})}{qN_{\text{D}}}\right)^{1/2} \quad (2)$$

The maximum value of W_{d} ($(W_{\text{d}})_{\text{MAX}}$) is obtained using the N_{D} extracted from the M-S equation and the largest $(V - E_{\text{FB}})$ employed in the M-S fit. Let us assume that the semiconductor is completely depleted, meaning that the width of the depletion layer reaches the scale of the nanorod diameter. In this case, the calculated N_{D} can be regarded as the analytical resolution limit of N_{D} ($(N_{\text{D}})_{\text{ARL}}$) on this nanostructured material. As the N_{D} extracted from M-S ($6.71 \times 10^{19} \text{ cm}^{-3}$) is much larger than the $(N_{\text{D}})_{\text{ARL}}$ ($5.20 \times 10^{18} \text{ cm}^{-3}$), it can be safely attributed to the donor density of Sb-doped hematite instead of that corresponding to the underlying FTO substrate⁶.

Refs:

2. Sivula, K. Mott–Schottky Analysis of Photoelectrodes: Sanity Checks Are Needed. *ACS Energy Lett.* **6**, 2549–2551 (2021).
3. Hankin, A., Bedoya-Lora, F. E., Alexander, J. C. *et al.* Flat band potential determination: avoiding the pitfalls. *J. Mater. Chem. A* **7**, 26162–26176 (2019).
5. Zhang, Z. J., Nagashima, H., Tachikawa, T. Ultra-Narrow Depletion Layers in a Hematite Mesocrystal-Based Photoanode for Boosting Multihole Water Oxidation. *Angew. Chem. Int. Ed.* **59**, 9047–9054 (2020).
6. Ravishankar, S., Bisquert, J., Kirchartz, T. Interpretation of Mott–Schottky plots of photoanodes for water splitting. *Chem. Sci.* **13**, 4828–4837 (2022).

The revised donor density of the optimized Sb-doped hematite has been added in the revised manuscript # (Supplementary Fig. 7).

(p. 10) “After oxidation, both of the negative slopes of PN-10-O and PN-40-O are weakened and even vanished (Supplementary Fig. 6), which indirectly demonstrates the existence of $\text{Sb}^{<3+}$ species. The donor density (N_D) of the optimized PN-10 photoanode was calculated to be $6.71 \times 10^{19} \text{ cm}^{-3}$, and the validity of this M–S was evaluated in Supplementary Fig. 7.”

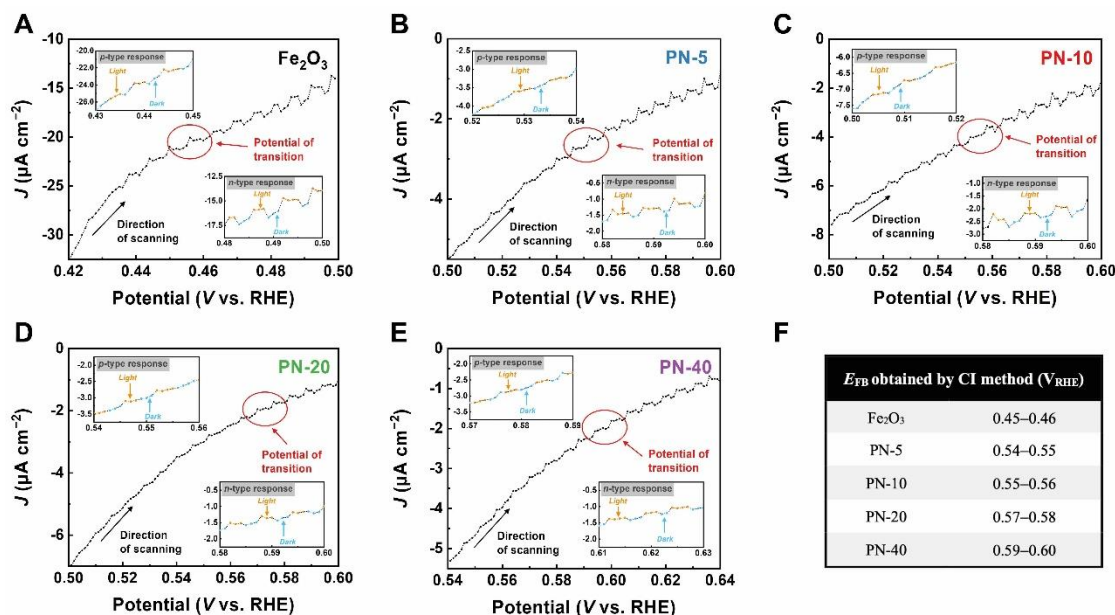
Determination of the flat band potential of Sb-doped hematite nanorods with different doping concentrations. When it comes to determining flat band potentials of different Sb-doped hematite nanorods, the significant doping effect on the surface would affect the capacitance of the interface and impair the validity of M–S results, leading to a significant deviation of E_{FB} values. However, the chopped illumination (CI) method was found to give reproducible and the most accurate results on hematite (*J. Mater. Chem. A* **7**, 26162–26176 (2019)), where the transition potential from cathodic to anodic photocurrents during a slow potentiodynamic scan under chopped illumination is determined to be the E_{FB} value, which is not compromised by substantial rates of Faradaic processes (*J. Electrochem. Soc.* **126**, 419 (1979)). E_{FB} values determined by M–S and CI methods on PN-5 and PN-10 photoanodes are well consistent with each other. For PN-5 photoanode, E_{FB} determined by M–S and CI are 0.61 and 0.54–0.55 V_{RHE} , respectively. For PN-10 photoanode, E_{FB} determined by M–S and CI are 0.72 and 0.55–0.56 V_{RHE} , respectively. These results in turn demonstrate the feasibility and reasonability of M–S analysis in low concentrations of Sb-doped hematite. However, M–S analysis becomes unsuitable for determining E_{FB} in the case of heavier doping because the E_{FB} values are higher than V_{on} of photoanodes, which is not possible. Based on

CI-determined E_{FB} values, the OER overpotentials were re-calculated with reference to V_{on} , and the detailed information is added to the revised manuscript # (Supplementary Fig. 19).

(P. 14) “Actually, the practical V_{on} of photoanodes is always more positive than its flat band potential (E_{FB}) owing to a required kinetic overpotential for oxygen evolution reaction (OER)⁵². Generally, heavy surface doping significantly affects the semiconductor/electrolyte interface and impairs the validity of M–S results for E_{FB} determination. Hence, a more accurate method of chopped illumination (CI) is proposed here, which is not compromised by substantial rates of Faradaic processes⁵³. As shown in Supplementary Fig. 19, E_{FB} shifts positively with heavier doping of Sb, and all Sb-doped Fe_2O_3 samples show an increased difference (>320 mV) between V_{on} and E_{FB} relative to that of bare Fe_2O_3 (290–300 mV). However, PN-10 with optimum Sb doping concentration (320–330 mV) has the smallest overpotential among all Sb-doped Fe_2O_3 samples (370–380 mV for PN-5, 390–400 mV for PN-20, and 430–440 mV for PN-40).”

Refs:

53. Wilhelm, S. M., Yun, K. S., Ballenger, L. W. et al. Semiconductor Properties of Iron Oxide Electrodes. *J. Electrochem. Soc.* **126**, 419 (1979).



Supplementary Fig. 19| Determination of flat band potential (E_{FB}) by chopped illumination (CI) method.

Comment 2: The spikes showed in Figure 3b would be better visualized in a potentiostatic experiment, showing photocurrent as a function of time for ON-OFF illumination cycles. In any case, the information that the authors want to convey is clear from the present Figure 3b.

Response 2: Thanks for the reviewer's suggestion. We have measured transient photocurrents in a potentiostatic experiment, showing photocurrent as a function of time at different potentials, which could better visualize the spikes and reflect the surface properties of different photoanodes. The chronoamperometry measurements under chopped illumination have been added in the revised manuscript # (Fig. 3b)

(P. 15) “The $J-t$ curves under chopped illumination at a potential close to V_{on} exhibit dramatically-reduced transient photocurrents upon light-on for the PN-10 photoanode relative to those of bare Fe_2O_3 and PN-10-O (Fig. 3b), indicating that hole accumulation on the surface was lessened because of the passivated surface. In contrast, the transient photocurrent of PN-10 upon light-off does not present this behavior, but instead shows apparently cathodic transient peaks similar to that of PN-10-O, indicating the significant recombination of the separated holes with electrons. This phenomenon was demonstrated to be related to the p -type transport behavior near to surface region⁵⁷. Consequently, $p-n$ homojunction under light irradiation could provide additional driving force for charge separation and accelerate hole injection to mitigate hole accumulation. As shown in Fig. 3a, $NiCoFe(OOH)_x$ has no significant effect on the improvement of V_{on} . However, the anodic transient photocurrent after $NiCoFe(OOH)_x$ loading on PN-10 at a potential close to V_{on} ($0.9 V_{RHE}$) is remarkably increased, which implies the function of hole extraction of the $NiCoFe(OOH)_x$ co-catalyst.”

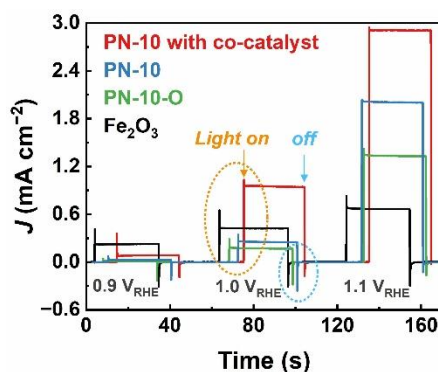


Fig. 3b| $J-t$ curves of bare Fe_2O_3 , PN-10-O, PN-10, and PN-10 with co-catalyst under chopped illumination.

Comment 3: The authors study the charge separation and charge transfer efficiencies using H_2O_2 as a hole scavenger. However, they have previously commented that H_2O_2 deactivates the surface $\text{Sb}^{<3+}$ species, deleteriously affecting the photoanode performance. A different hole scavenger (for example Na_2SO_3) would provide better results. Why did they use H_2O_2 in these experiments?

Response 3: We thank for the reviewer's advice to choose a different hole scavenger for better results. As claimed in the manuscript, we used H_2O_2 to eliminate the surface $\text{Sb}^{<3+}$ species and obtain PN-10-O counterpart, where PN-10 was kept in 30% H_2O_2 solution for 30 min to achieve the desired effect. During the measurement of charge separation efficiencies in 1 M NaOH with the addition of 0.5 M H_2O_2 , the preprocessing and potentiometric scanning process took only a few minutes, which would not significantly affect photoanode performance. As suggested, we have investigated the photoanode performance in 1 M NaOH by adding Na_2SO_3 or H_2O_2 . As shown in Fig. R1A, the difference between J_{ph} measured in 1 M NaOH + 0.5 M H_2O_2 electrolyte and 1 M NaOH + 0.5 M Na_2SO_3 electrolyte is not significant from V_{on} to the potential of water oxidation (0.9–1.3 V_{RHE}), indicating that 0.5 M H_2O_2 did not have any deleterious effect on the photoanode performance. Consequently, the hole scavengers on the evaluation of charge separation efficiencies in Fig. R1B are quite close. In any case, we agree with the reviewer's statement in principle that Na_2SO_3 would provide better results by avoiding mixed effects. Following the referee's suggestion, the measurements and results have been added in the revised manuscript, and the charge separation efficiencies based on 1 M NaOH + 0.5 M Na_2SO_3 electrolyte have been re-calculated and clarified # (Fig. 3d and e, Supplementary Fig. 22).

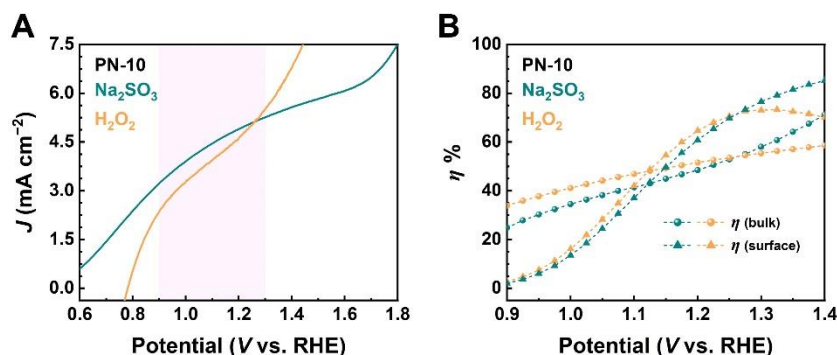
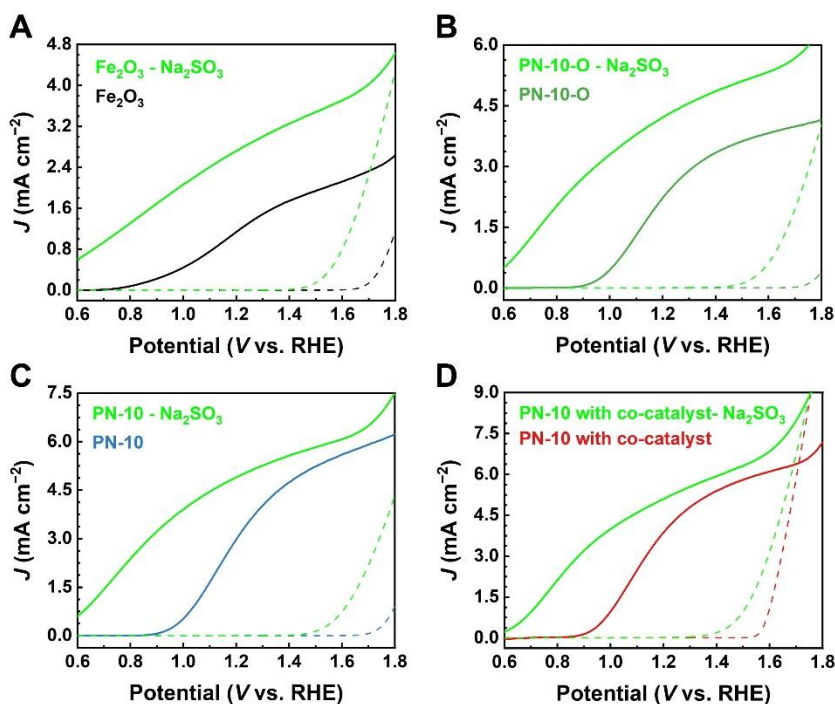


Fig. R1| J - V curves (A) and the obtained η_{bulk} and η_{surface} values (B) of PN-10 with the addition of Na_2SO_3 or H_2O_2 .

(P. 16) “Bulk (η_{bulk}) and surface (η_{surface}) charge separation efficiencies were determined in the same electrolyte with addition of Na_2SO_3 as a hole scavenger (Supplementary Fig. 22). In Fig. 3d, η_{bulk} of PN-10 achieves a record high value of $\sim 52.7\%$ at $1.23 \text{ V}_{\text{RHE}}$ among recent reports (Supplementary Table 4), ~ 2 times higher than that of bare Fe_2O_3 . PN-10-O generates a little smaller η_{bulk} of $\sim 46.5\%$, still much higher than that of bare Fe_2O_3 . The high η_{bulk} values of PN-10 and PN-10-O are attributed to the gradient doping of Sb^{5+} and Sn^{4+} ions, and the additional driving force of *in situ* formed *p-n* homojunction without interfacial defects. Doping and *p-n* homojunction also reduce the photocurrent gap between front and back illumination, indicating improved bulk electron transport (Supplementary Fig. 23). As expected, η_{bulk} does not show any effect of co-catalyst loading. In Fig. 3e, η_{surface} of both PN-10-O and PN-10 are much higher than that of bare Fe_2O_3 with an improvement over 27% at $1.23 \text{ V}_{\text{RHE}}$ after surface Sb doping. Notably, different Sb ion valence states on the PN-10-O and PN-10 surfaces generate different surface charge separation efficiency. η_{surface} of PN-10 is almost the same as that of PN-10-O at low potentials ($0.9\text{--}1.05 \text{ V}_{\text{RHE}}$), while it starts to exceed when applied potential increases further, indicating that $\text{Sb}^{<3+}$ species plays an important role at high applied potentials (especially for potentials over $1.23 \text{ V}_{\text{RHE}}$). With co-catalyst modification, however, η_{surface} is significantly improved in the whole potential range owing to more efficient hole extraction and utilization, reaching $\sim 80\%$ at $1.23 \text{ V}_{\text{RHE}}$ and $\sim 90\%$ at $1.4 \text{ V}_{\text{RHE}}$. “



Supplementary Fig. 22| PEC performance of photoanodes measured in 1 M NaOH solution with addition of Na₂SO₃ as a hole scavenger.

J–*V* curves of bare Fe₂O₃ (A), PN-10-O (B), PN-10 (C), and PN-10 with co-catalyst (D) measured in 1 M NaOH electrolyte with and without addition of 0.5 M Na₂SO₃. Bulk and surface charge separation efficiencies are determined according to the following equations:

$$\eta_{\text{bulk}} = \frac{J_{\text{Na}_2\text{SO}_3}}{J_{\text{abs}}} \quad (4)$$

$$\eta_{\text{surface}} = \frac{J_{\text{H}_2\text{O}}}{J_{\text{Na}_2\text{SO}_3}} \quad (5)$$

where η_{bulk} denotes the fraction of holes that reaches the electrode/electrolyte interface without recombination in the bulk, while η_{surface} represents the fraction of those holes at the interface that are successfully injected to participate in OER. $J_{\text{H}_2\text{O}}$ and $J_{\text{Na}_2\text{SO}_3}$ are photocurrent densities of water oxidation in 1 M NaOH without and with addition of Na₂SO₃, respectively. J_{abs} is the expected photocurrent when absorbed photons are completely converted into current. J_{abs} of bare Fe₂O₃, PN-10-O, PN-10 and PN-10 with co-catalyst are 10.4 (<608 nm), 9.3 (<599 nm), 9.5 (<599 nm) and 9.9 (<602 nm) mA cm⁻², respectively.

Comment 4: The authors have carried out an impedance spectroscopy study, but only two different potentials (1 and 1.23 V vs RHE) are investigated, and consequently, the obtained results are not very informative. A wider potential range with more potentials (0.5-1.5 V vs RHE, *V* step 50 mV for example) would be more adequate to rationally interpret the trends of capacitances and resistances, in line with the complementary characterizations employed in the study. In particular, information of surface states would be highly valuable to understand the contribution of surface Sb^{<3+} and NiFeOOH species.

Response 4: We thank the reviewer's valuable comment that the PEIS study with more potentials would be more informative and be valuable to understand the contribution of surface Sb^{<3+} and NiCoFe(OOH)_x species. We have carried out PEIS study with a wider potential range from 0.8 (close to *V*_{on}) to 1.5 V_{RHE} with a step of 50 mV. Note that at potentials lower than 0.7 V_{RHE} for bare Fe₂O₃ and potentials lower than 0.8 V_{RHE} for PN-10-O, PN-10 and PN-10 with co-catalyst, the photoanodes could not effectively respond to illumination and generate a certain photocurrent.

PEIS measurements in the potential range capable of generating photocurrents reveal the PEC properties of different photoanodes. The changes of resistances and capacitances with the increase of potential rationally provide more information on the beneficial contribution of gradient Sb doping, p - n homojunction, surface $\text{Sb}^{<3+}$ species, and co-catalyst. The measurements and results have been added in the revised manuscript # (Fig. 4, Supplementary Fig. 27, and Supplementary Table 5).

(p. 19-20) “Photoelectrochemical impedance spectroscopy (PEIS) at different potentials from 0.8 (close to V_{on}) to 1.5 V_{RHE} (with a step of 50 mV) reveals the trends of capacitances and resistances, which provide insights into the contribution of gradient Sb doping, p - n homojunction and co-catalyst to PEC performance (Supplementary Fig. 27). The obtained data were fitted to a typical two-RC-unit equivalent circuit model to decouple charge trapping and charge transfer resistances (Supplementary Table 5). In Fig. 4a, the maximum capacitances in the bulk (C_{bulk}) of PN-10-O, PN-10, and PN-10 with co-catalyst reach up to 4 times that of bare Fe_2O_3 , which is ascribed to the additional driving force provided by gradient dopants of Sb^{5+} and Sn^{4+} ions. Moreover, the additional driving force results in an obvious peak of C_{bulk} values at the potential range of 1.0–1.15 V_{RHE} , where C_{bulk} initially increases at a remarkable rate and declines rapidly when applied potential further increases due to the enhanced charge extraction and the lower accumulation of photogenerated holes^{64,65}. However, this behavior cannot be observed on bare Fe_2O_3 , where C_{bulk} of bare Fe_2O_3 shows rapid decay in the whole potential range. Notably, the potentials of maximum C_{bulk} value for p - n homojunctions (PN-10 and PN-10 with co-catalyst) are smaller than that of PN-10-O by 100–150 mV, indicating that the p - n homojunction can effectively separate the photo-generated electron and hole with a small bias. The surface-state capacitance (C_{ss}) of PN-10-O with surface composition of “ $\text{Sb}^{5+} + \text{Sb}^{3+}$ ” slightly increases compared to that of bare Fe_2O_3 , while C_{ss} of PN-10 significantly increases to ~ 2 times that of PN-10-O by surface composition of “ $\text{Sb}^{<3+} + \text{Sb}^{3+}$ ” (Fig. 4b). The higher C_{ss} comes from the contribution of the surface $\text{Sb}^{<3+}$ species, which helps to reduce charge recombination as mentioned above. The additional co-catalyst modification further enhances C_{ss} at potentials higher than water-oxidation potential (1.23 V_{RHE}), indicating a significant contribution of co-catalyst to OER.

Fig. 4c shows that trapping resistance (R_{trap}) values of PN-10-O, PN-10, and PN-10 with co-catalyst decrease greatly relative to that of bare Fe_2O_3 in the whole potential range of 0.8–1.5 V_{RHE}

owing to the enhanced bulk separation efficiency by high valence doping effect. With the increase of potential, the charge transfer resistance (R_{ct}) of all Sb-doped photoanodes decreases significantly owing to the enhanced surface conductivity. At potential of 0.9 V_{RHE} close to V_{on} , R_{ct} of PN-10-O is still much higher than that of bare Fe₂O₃, while R_{ct} of PN-10 and PN-10 with co-catalyst are comparable or even lower than that of bare Fe₂O₃. The huge different R_{ct} values near V_{on} of PN-10-O and PN-10 reflect the beneficial role of surface Sb^{<3+} species, which eventually enables higher J_{ph} .

Charge transfer through surface states is assumed as the predominant mechanism for surface charge transfer of OER⁵⁹. Thus, the proportion of charge transfer through surface states determines the rate of water oxidation on hematite photoanodes. Assuming that the rates of charge transfer and trapping are inversely proportional to their respective resistances, the charge transfer efficiency (η_{ct}) can be estimated through the equation^{66,67}:

$$\eta_{ct} = \frac{k_{ct}}{k_{ct} + k_{trap}} = \frac{R_{trap}}{R_{ct} + R_{trap}} \quad (1)$$

where k_{ct} and k_{trap} are the rate constants of charge transfer and trapping, respectively. Fig. 4d shows the η_{ct} values at different potentials of 0.8–1.5 V_{RHE}. The η_{ct} value of PN-10-O remains lower than that of bare Fe₂O₃ at potentials <1.15 V_{RHE} and becomes only a little better at higher potentials. At ~1.0 V_{RHE}, however, η_{ct} of PN-10 starts to exceed that of bare Fe₂O₃ and significantly increases up to ~80% at 1.23 V_{RHE}. The turning potential of 1.0 V_{RHE} is consistent with the potential at which J_{ph} of PN-10 exceeds that of bare Fe₂O₃. Therefore, these results indicate that high J_{ph} of PN-10 is generated by the contribution of surface Sb^{<3+} species instead of Sb³⁺ or Sb⁵⁺ ions. Further, co-catalyst modification enhances η_{ct} of PN-10 at all potentials.”

Refs:

59. Klahr, B., Gimenez, S., Fabregat-Santiago, F. et al. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with “Co–Pi”-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **134**, 16693–16700 (2012).

64. Wang, H. X., Wang, Y., Lin, Y. M. et al. Impact of NiCo₂O₄/SrTiO₃ *p–n* Heterojunctions on the Interface of Photoelectrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **15**, 28739–28746 (2023).

65. Ros, C., Andreu, T., David, J. et al. Degradation and regeneration mechanisms of NiO protective layers deposited by ALD on photoanodes. *J. Mater. Chem. A* **7**, 21892–21902 (2019).

66. Monllor-Satoca, D., Bärtsch, M., Fàbrega, C. et al. What do you do, titanium? Insight into the role of titanium oxide as a water oxidation promoter in hematite-based photoanodes. *Energy Environ. Sci.* **8**, 3242–3254 (2015).

67. Zhang, J. F., García-Rodríguez, R., Cameron, P. et al. Role of cobalt–iron (oxy)hydroxide (CoFeO_x) as oxygen evolution catalyst on hematite photoanodes. *Energy Environ. Sci.* **11**, 2972–2984 (2018).

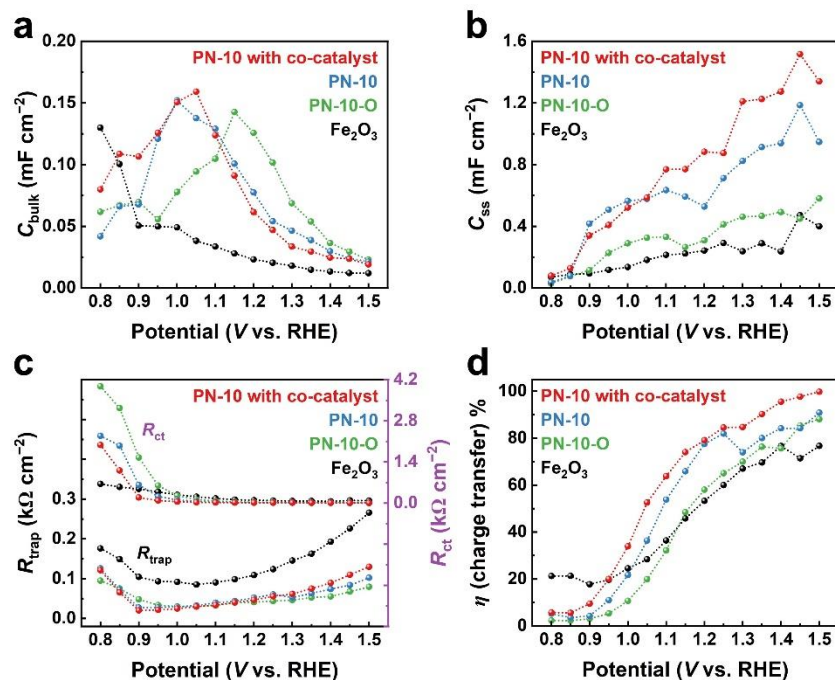
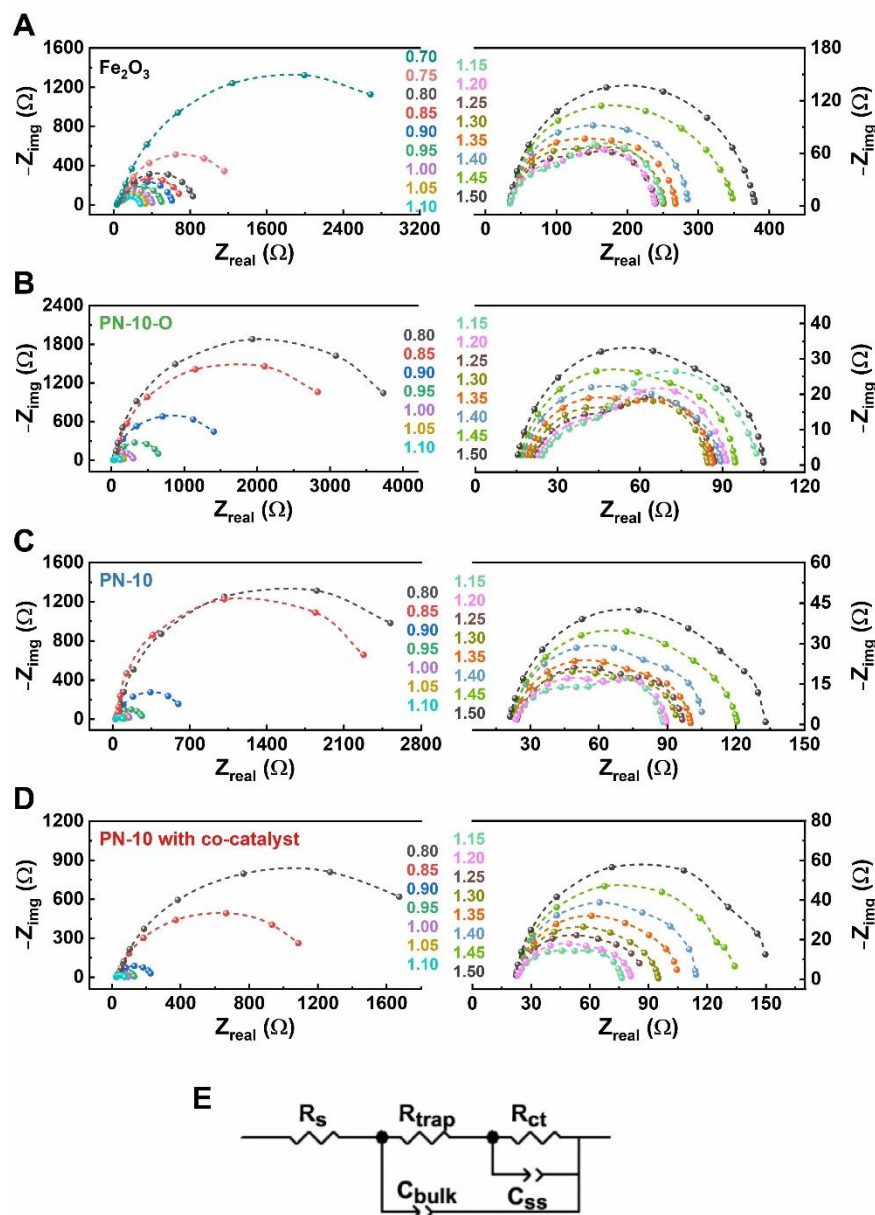


Fig. 4| PEIS of bare Fe_2O_3 , PN-10-O, PN-10 and PN-10 with co-catalyst photoanodes. (a) Bulk capacitance, (b) surface-state capacitance, (c) trapping resistance, and (d) charge transfer efficiency.



Supplementary Fig. 27| Nyquist plots at different potentials of bare Fe_2O_3 (A), PN-10-O (B), PN-10 (C), and PN-10 with co-catalyst (D). A typical two-RC-unit equivalent circuit model (E). The fitting results are listed in Supplementary Table 5. R_s refers to the whole series resistance ascribed to the electrolyte, external contact and conductive substrate; R_{trap} refers to the charge trapping resistance in the semiconductor; R_{ct} refers to the charge transfer resistance of semiconductor/electrolyte interface; C_{bulk} refers to the capacitance in the depletion layer; C_{ss} refers to the capacitance of semiconductor/electrolyte interface.

More measurements and discussions on the beneficial roles of Sb^{3+} and $\text{NiCoFe}(\text{OOH})_x$ (Fig. 3c, Supplementary Fig. 24, etc.) have also been added to the **“Photoelectrochemical water oxidation over modified photoanodes”** section in the revised manuscript to make the evaluation of photoanode PEC performance more comprehensive.

Comment 5: *The authors claim that “The carrier lifetime of p - n homojunction is ~ 190 ms at the transient when illumination is stopped, much shorter than those of bare Fe_2O_3 (~ 4.0 s) and PN-10-O (~ 4.6 s), and further decreases to ~ 96 ms with co-catalyst loading (Fig. 3f).”. However, these lifetimes are different from the numbers included in the Figure 3f.*

Response 5: We thank for the reviewer’s comment and we are sorry for this mistake. In Fig. 3f (variable carrier lifetime τ_n versus. V_{RHE}), the carrier lifetime is determined by the average of the minimum lifetime and the transient lifetime with reference to A. Zaban’s study (*ChemPhysChem* 4, 859 – 864 (2003)). The carrier lifetime values have been carefully recalculated and checked, and the results have been added in the revised manuscript #.

(p. 18) “The carrier lifetime of p - n homojunction is ~ 1.3 s at the transient when illumination is stopped, much shorter than those of bare Fe_2O_3 (~ 3.1 s) and PN-10-O (~ 7.2 s), and further decreases to ~ 245 ms with co-catalyst loading (Fig. 3f).”

Comment 6: *In page 19, the authors claim: “In particular, a parallel 6-stacked photoanode records J_{ph} of over 10 mA cm^{-2} , which is by far closest to the theoretical value (12.6 mA cm^{-2}),...” However, this claim would be correct for a single photoelectrode, not for a parallel configuration of 6 photoanodes. Consequently, the authors should modify this claim.*

Response 6: Thanks for the reviewer’s comment and we are sorry for this mistake. The claim has been modified in the revised manuscript #.

(p. 23) “In particular, a parallel 6-stacked photoanode records J_{ph} of over 10 mA cm^{-2} , which is by far closest to the theoretical value of a single hematite photoanode (12.6 mA cm^{-2}), which sets a new record for hematite HMP and is also superior to any type of hematite photoanodes and other multi-stacked photoelectrodes (see Supplementary Table 6 for benchmarking).”

Comment 7: Also, in page 19, the authors claim: “The measured J_{ph} of the i th ($i=2, 3, 4, 5$, and 6) photoanode in 6-stacked configuration shows 1.99, 1.50, 1.02, 0.65 and 0.50 mA cm^{-2} at 1.23 V_{RHE} under standard condition, respectively (Fig. 4c),...”. These values are not clear from the figure 4c. Furthermore, there are 5 photocurrent values, and there should be 6 values.

Response 7: We thank the reviewer’s advice. The plotting of Fig. 5c has been optimized to make the J_{ph} values for all photoanodes clear for readers. The relevant elaboration has also been modified in the revised manuscript # (Fig. 5c).

(p. 23) “The measured J_{ph} of the i th ($i=1, 2, 3, 4, 5$, and 6) photoanode in 6-stacked configuration shows 4.21, 1.99, 1.50, 1.02, 0.65, and 0.50 mA cm^{-2} at 1.23 V_{RHE} under standard condition, respectively (Fig. 5c), representing each contribution, which also demonstrates that sixth one is almost maximum owing to its very limited contribution.”

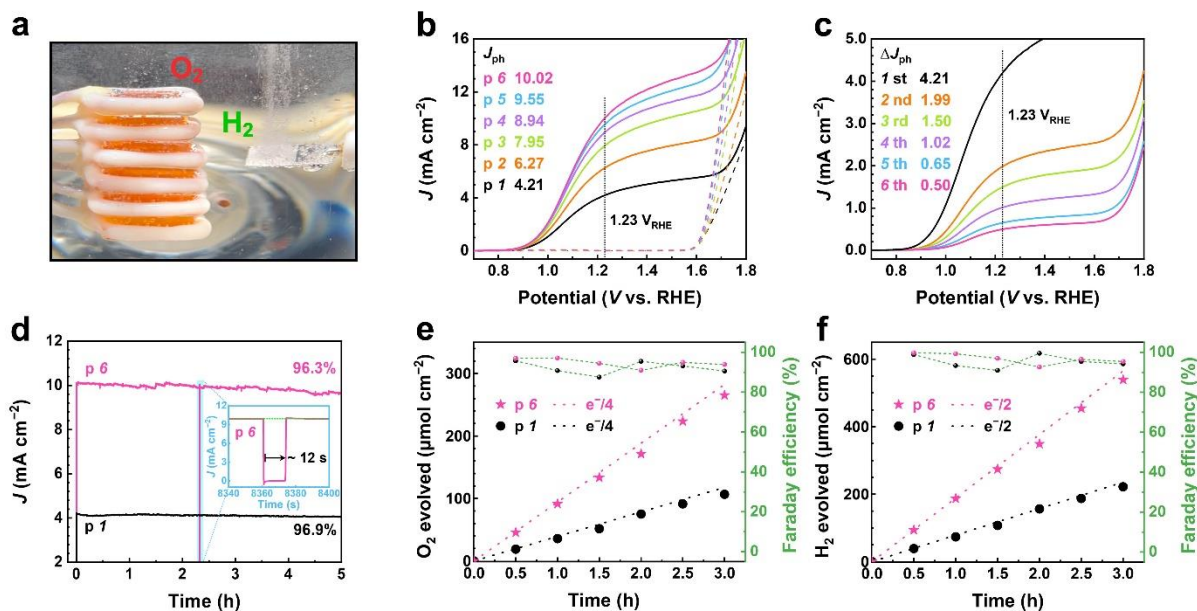


Fig. 5| Photoelectrochemical performance of parallel multi-stacked photoanode using co-catalyst-loaded PN-10 films. (a) Schematic of a parallel 6-stacked photoanode at work. J - V curves of **(b)** parallel n -stacked ($n=1, 2, 3, 4, 5$ and 6) photoanodes and **(c)** the i th ($i=1, 2, 3, 4, 5$, and 6) photoanodes in 6-stacked configuration. **(d)** Stability of single PN-10 and parallel 6-stacked photoanode. **(e)** O_2 and **(f)** H_2 evolution from PEC water splitting of photoanodes at 1.23 V_{RHE} .

Comment 8: The characterization of the IPCE for the stacked configuration is very interesting, but the representation selected by the authors to convey this information is not so visual. Maybe the authors could show IPCE versus wavelength for 1, 1+2, 1+2+3, ..., 1+2+3+4+5+6, to clearly visualize that the stacked configuration with 6 photoanodes achieves an IPCE close to 100% at all measured wavelengths. Additionally, they could calculate the integrated photocurrent and further validate the obtained photocurrent of 10 mA cm^{-2} .

Response 8: We thank the reviewer's advice. As shown in Supplementary Fig. 37A, the IPCE value drops sharply beyond 400 nm due to hematite's indirect band transition (*Appl. Catal., B* **95**, 423–429 (2010)), and the IPCE values in the long-wavelength region cannot be close to 100% even for a stack configuration. However, the increase of IPCE for each stacked configuration ($p1=1$, $p2=1+2$, $p3=1+2+3$, $p4=1+2+3+4$, $p5=1+2+3+4+5$, $p6=1+2+3+4+5+6$) at all measured wavelengths is clearly shown in Supplementary Fig. 37A. Moreover, we have normalized the IPCEs of multi-stacked photoanodes at diverse wavelengths to visualize the contribution from the stack configuration in long-wavelength light absorption (Fig. 6c). Besides, the integrated photocurrent density by IPCE of the 6-stacked photoanode has been calculated, which is consistent with the experimentally measured values. The results and relevant elaboration have been added to the revised manuscript # (Fig. 6c, Supplementary Fig. 37).

(p.25-26) “Fig. 6c shows the normalized IPCEs of multi-stacked photoanodes at wavelengths of 350 – 600 nm. At long wavelengths (450 – 600 nm), the succeeding 4th, 5th, and 6th photoanodes in the stack still enhance the IPCE values considerably and contribute to a high J_{ph} of the 6-stacked photoanode. The IPCE increase of the 6-stacked photoanode relative to that of a single one is 130%, 140%, 200%, and 220% at 400, 450, 500, and 550 nm, respectively (Supplementary Fig. 37A). Even at the absorption edge (600 nm), the IPCE also increases by 50%. Moreover, the integrated IPCE concerning the AM 1.5 G spectrum at 1.23 V_{RHE} yields a solar photocurrent density (J_{sc}) of 9.89 mA cm^{-2} for the 6-stacked photoanode (Supplementary Fig. 37B), which is consistent with the experimentally measured value at 1.23 V_{RHE} ($\sim 10 \text{ mA cm}^{-2}$) (Fig. 5b). The remarkable enhancement of light absorption and IPCE in the long-wavelength region demonstrates the vital function and effectiveness of HMP, potentially explaining the near-theoretical J_{ph} by the parallel 6-stacked photoanode.”

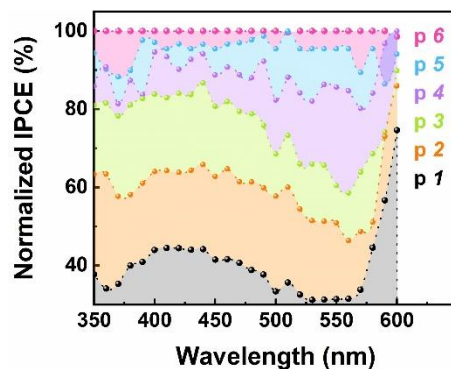
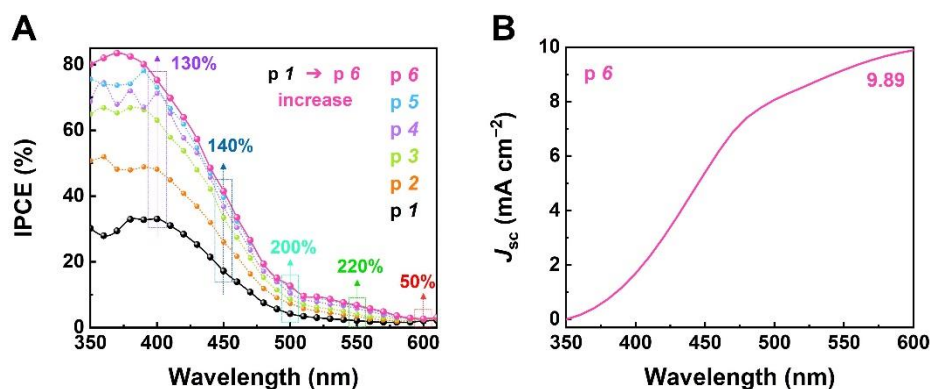


Fig. 6c| Normalized IPCEs at 1.23 V_{RHE} at specific wavelengths from 350 to 600 nm of parallel multi-stacked photoanodes.



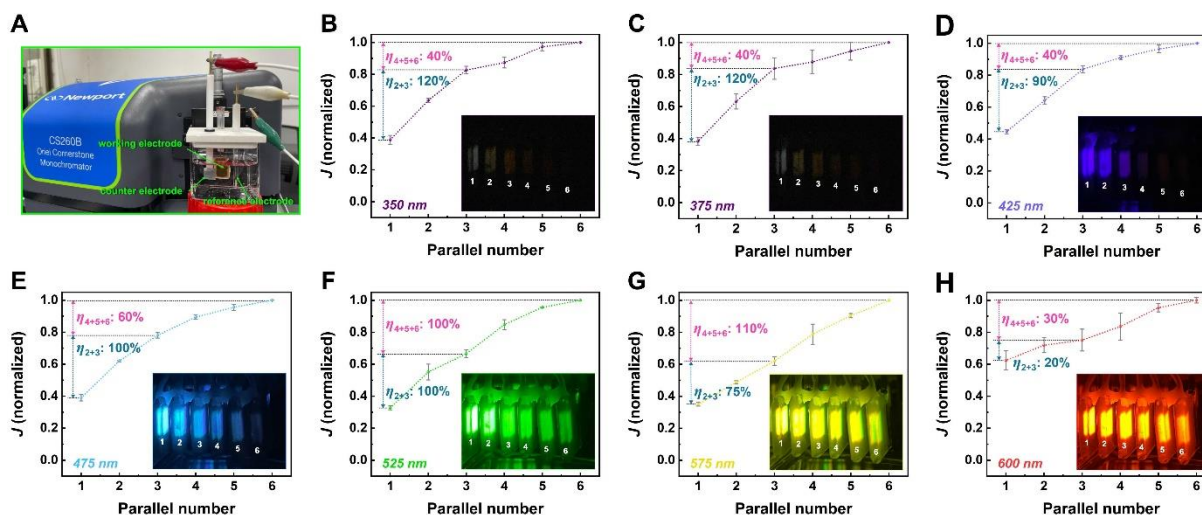
Supplementary Fig. 37| IPCEs measured at 1.23 V_{RHE} and solar photocurrent density (J_{sc}) by IPCE. The IPCE measurement was carried out with a 300 W Xe lamp (equipped with AM 1.5 G filter) and a monochromator (Newport, CS260B) with a bandwidth of 10 nm (Supplementary Fig. 39A). IPCE can be calculated from the measured current density according to the following equation:

$$IPCE = \frac{1240 \times J \text{ (mA cm}^{-2}\text{)}}{P_{\text{light}} \text{ (mW cm}^{-2}\text{)} \times \lambda \text{ (nm)}} \quad (8)$$

where J is the measured current density at specific wavelength, λ is the specific wavelength of incident light, and P_{light} is the corresponding calibrated illumination power. The integrated IPCE with respect to the AM 1.5 G spectrum at 1.23 V_{RHE} provides J_{sc} of 9.89 mA cm⁻² for the 6-stacked photoanode, close to J_{ph} of ~10 mA cm⁻² measured in Fig. 5b.

Comment 9: Figure 5 and Figure S34 have some similar figures. The authors may avoid duplicating the information in the main text and in the Supplementary Information.

Response 9: Thanks for the reviewer's advice and we have modified Supplementary Fig. 38 in the revised manuscript.



Supplementary Fig. 38| Normalized photocurrent densities of 6-stacked photoanode excited by diverse monochromatic lights. IPCE measurements of photoelectrodes using a three-electrode PEC cell in this work (A). The normalized photocurrent densities excited by diverse monochromatic lights (350, 375, 425, 475, 525, 575, and 600 nm) (B–H).

Comment 10: The photoelectrochemical cell that the authors have employed (Supplementary figure 14) is not optimized for the field lines between anode and cathode and may face some mass transport issues. Did the authors investigate this issue? Additionally, how did they calibrate that the light intensity at the photoanode was 1 sun?

Response 10: We thank the reviewer for mass transport issues. Further experiments on the mass transport have been carried out. The photocurrent densities of the same PN-10 photoanode and parallel 6-stacked photoanode were measured in the static and flowing electrolytes with the PEC cell used in this work (Supplementary Fig. 14), respectively. As shown in Fig. R2A, the flowing of the electrolyte slightly disturbed the J – V curve during the linear scanning of potential, but did not influence the J_{ph} value of single photoanode significantly. In this case, the anode and cathode are small and placed relatively close together so that the impact of mass transport issues is

negligible. However, the mass transport issue is magnified on the stacked photoanode and should be carefully considered in further industrial applications. The J - V curve is apparently disturbed and the J_{ph} values obtained at high potentials slightly decrease in the flowing electrolyte (Fig. R2B). This phenomenon may arise from the different distances between single photoanode and cathode in the stack configuration.

In our work, the light source we used is the Sol3A Class AAA Solar Simulator with a 450 Watt Xenon (94023A) from NewportTM (Fig. R2C), which has been carefully commissioned and maintained. The light intensity is calibrated to 100 mW cm^{-2} using a standard silicon solar cell calibration device.

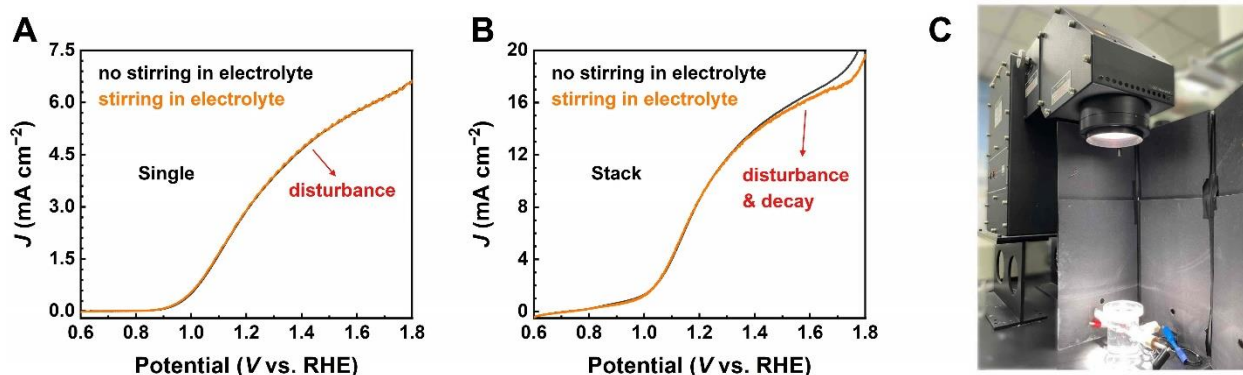


Fig. R2| Experiments on the mass transport of single photoanode (A), stack configuration (B), and Sol3A Class AAA Solar Simulator from NewportTM used in our work (C).

Reviewer #2:

Comments to the Author: *The authors have made a nice approach to stack homo-type Sb-doped Fe₂O₃ photoanodes to enhance the overall photocurrent. The approach is neat and smart and the characterisation is well done, but generally there are very low degree of specific scientific novelty. Sb-doping of hematite has been done previously, for example in [ACS Appl. Mater. Interfaces 2018, 10, 19, 16467–16473]. Several other studies has also enlightened the role of Sb as dopant in similar applications. Therefore, even if the approach is neat and smart, and the concept itself is a good way to overcome the short diffusion length of charge carriers in hematite, I see not enough novelty to be published in Nature Communications. I would see that the study should be published in a more specialized journal where the concept itself is of interest for the readers.*

Response: We greatly thank the reviewer for acknowledging that the authors have made a nice approach to stack homo-type Sb-doped Fe₂O₃ photoanodes to enhance the overall photocurrent; The approach is neat and smart and the characterization is well done; The concept itself is a good way to overcome the short diffusion length of charge carriers in hematite. Even though Sb dopant had been applied in other studies, in our case, however, it displays extraordinary function and distinctive performance. Here we would like to address the concern of novelty issue fully and provide additional context to highlight the unique and significant contributions of this work.

(1) Discovery of uncommon Sb^{<3+} ions. In this work, the presence of Sb^{<3+} species was carefully identified on the surface of Sb:Fe₂O₃ nanorods prepared with hybrid microwave annealing (HMA), which is uncommon and has not been previously reported. Moreover, the crucial role of Sb^{<3+} for the formation of *p–n* homojunction and the improvement of photoelectrochemical performance of the photoanode were demonstrated, which provides valuable insight into constructing more efficient photoelectrodes. See more clarifications in “**Photoelectrochemical water oxidation over modified photoanodes**” Section including some critical measurements of charge separation efficiencies, OCP-derived carrier lifetimes, and PEIS in a wide potential range.

(2) Novel method for constructing *p–n* homojunction and inducing gradient dopants. Constructing *p–n* homojunction based on hematite photoanodes is quite challenging, generally using sophisticated instruments and precisely controlled dopants with different elements (Mg-doped *p–n* homojunction by ALD: *J. Am. Chem. Soc.* **134**, 5508-5511 (2012); *p–n* homojunction

by intrinsic and extrinsic doping: *Chem. Eng. J.* **435**, 135016 (2022)). Here, we proposed a novel and facile method of extrinsic Sb doping combined with highly efficient HMA to prepare a distinctive p - n homojunction photoanode. Additionally, the gradient doping in this work is realized through the gradient contribution of valence states of a single Sb dopant instead of that of the dopant amount, which is innovative and difficult to realize. This approach allows for the controlled valence states through the reducing atmosphere and rapid high-temperature treatment, leading to significant advancements in the field. The optimized p - n homojunction photoanode achieves a J_{ph} of 3.33 mA cm^{-2} and a record η_{bulk} of over 50% in the absence of co-catalyst, which is superior or comparable to the state-of-the-art hetero-/homo-junction hematite photoanodes with other dopants (Fig. R3).

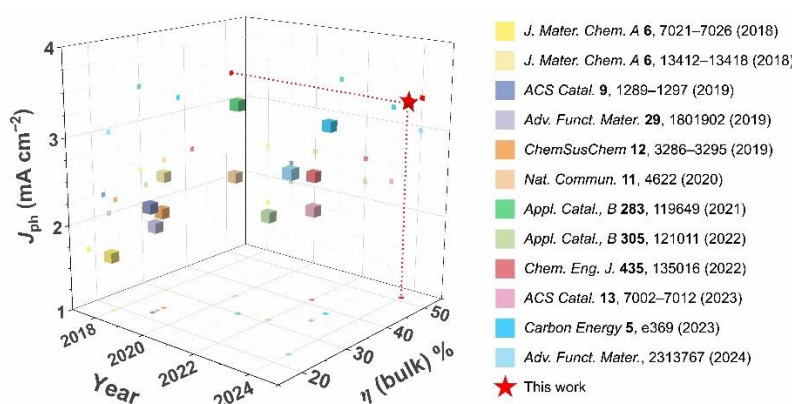


Fig. R3| Comparison of J_{ph} and bulk charge separation efficiency (η_{bulk}) measured at 1.23 V_{RHE} in our work with previously-reported hetero-/homo-junction hematite photoanodes.

(3) Impact of Sb on film transparency. While Sb is known as a beneficial dopant that can significantly improve the PEC performance of photoanodes at low doping concentrations (Sb-doped Fe_2O_3 : *ACS Appl. Mater. Interfaces* **10**, 16467–16473 (2018); Sb-doped SnO_2 : *Small* **18**, 2105026 (2022)), our study uniquely demonstrates that it also alters the transparency of hematite films. This property is crucial for addressing the light transmission issues in stacked photoelectrodes for PEC water splitting, marking the first instance of solving transparency challenges of hematite film through doping rather than reducing film thickness.

(4) Breakthroughs in PEC water splitting and relevance to Nature Communications. Nature Communications is known for publishing significant advancements in various scientific fields.

The results in this work represent significant breakthroughs of hematite-based photoanodes and are superior to other multi-stacked photoelectrodes in PEC water splitting (Fig. R4), with several innovative methods and first-of-its-kind discoveries, making it relevant and valuable to the broad readership of Nature Communications. We believe our study will garner considerable attention in Nature Communications, contributing broadly to the field and beyond.

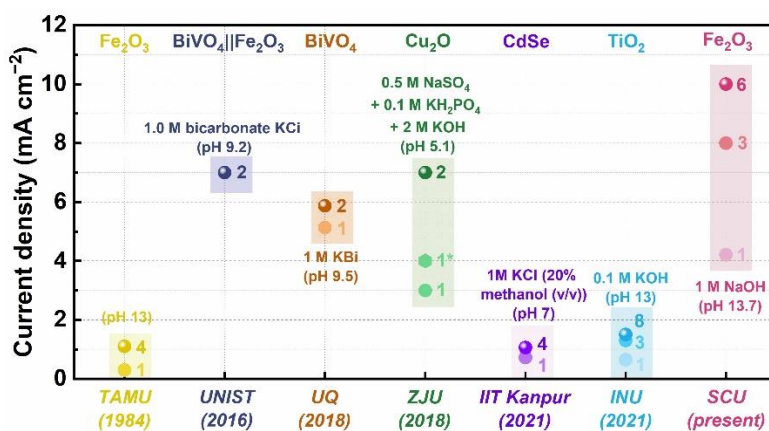


Fig. R4| Reports on multi-stacked photoelectrodes.

We are hopeful that these points could adequately address the reviewer's concerns and demonstrate the novelty and significance of our work.

Reviewer #3:

Comments to the Author: The author presents a multi-stacked photoanode. This effort is challenging. Indeed hematite is not optimum for photoanodes. Hematite requires a suitable thickness to access strong light, the author uses Sb and Fe₂O₃ to generate a strong p–n, but this is not enough. The characterization is strong in all details. The device can work, but the photocurrent is low, 4.21 mA. Moreover, there is no discussion about the surface defects.

Response: We thank the reviewer for recognizing that our multi-stacked photoanodes are challenging, and the characterization is strong in all details. He/she also noted that the photocurrent is still low, and discussion on surface defects is absent in the manuscript. We would like to further clarify our numerous efforts and achievements in enhancing the photocurrent density of hematite photoanodes and have conducted a more in-depth evaluation of the surface states of the photoanodes to better understand the contribution of surface Sb^{<3+} and NiCoFe(OOH)_x species to the improvement of PEC performance.

(1) Photocurrent density of hematite photoanode. We acknowledge that the photocurrent density of hematite photoanode is still lower than its theoretical value (~12.6 mA cm⁻²) due to its short hole diffusion length and a low light absorption coefficient (~10⁴ cm⁻¹). On the other hand, BiVO₄ (*eScience*, 100242 (2024)) and Ta₃N₅ (*Nat. Catal.* **3**, 932–940 (2020)) photoanodes have approached their respective theoretical values after extensive studies. More importantly, hematite offers unique advantages, including low cost, facile preparation, and excellent stability in aqueous solutions, making it still an attractive photoanode material and promising for commercialization. Although the PEC performance of hematite photoanodes is not the most outstanding among many metal oxide photoanodes, it could contribute to a stacked configuration significantly (*Nat. Commun.* **7**, 13380 (2016)). In our work, we designed a homo-type multiple photoelectrode “HMP” based on a unique hematite photoanode to compensate for the low utilization of long-wavelength light by a single electrode, in which the PEC performance and transmittance of the single hematite photoanode were optimized simultaneously. The concept demonstrates the successful practice of this stacked configuration in breaking the limitation of hematite photoanodes.

(2) Enhancements in several aspects through Sb doping. Sb doping enhances light absorption in the short-wavelength region and increases light transmittance in the long-wavelength region on

the thin film hematite photoanode, whose thickness is smaller than 400 nm (Fig. R5). In addition, extrinsic Sb doping by HMA results in valence-gradient doping and then constructs a p - n homojunction, facilitating charge separation. The prepared highly efficient and highly transparent photoanode achieves a high J_{ph} of 4.21 mA cm^{-2} , comparable to the recently advanced hematite photoanodes (*Nat. Commun.* **12**, 4309 (2021); *ACS Energy Lett.* **9**, 3169–3176 (2024)). Although the J_{ph} of a single photoanode remains far below the theoretical value, our stacked configuration of HMP significantly improves light utilization in the whole absorption range, achieving a J_{ph} near the theoretical limit of a single hematite photoanode with an irradiation area of 1 cm^2 . This is another effective way to increase the J_{ph} of hematite photoanodes per unit area of solar irradiation and is crucial in the development of unassisted PEC systems.

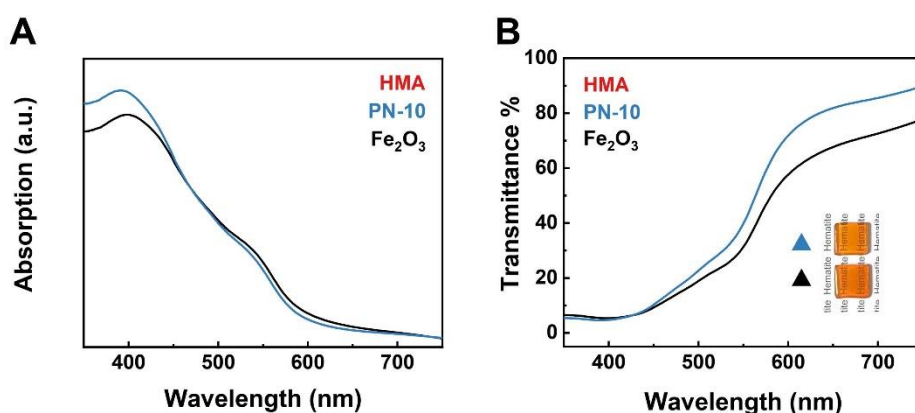


Fig. R5| UV-vis absorption (A) and transmittance spectra (B) of bare Fe₂O₃ and PN-10 by HMA.

(3) Evaluation of surface states. As suggested, we have evaluated the surface states of different photoanodes and discussed the beneficial roles of surface Sb^{3+} and $\text{NiCoFe}(\text{OOH})_x$ species in detail, which contributes to the significant improvement in PEC performance.

We have added more measurements in the revised manuscript, including the electrochemically active surface area (ECSA) (Fig. 3c), analysis of the second-order differentiation of the J - V curves (Supplementary Fig. 24), and analysis of the PEIS over a wider range of potentials (Fig. 4), as shown below:

(p. 15-16) “The electrochemically active surface area (ECSA) of different photoanodes with the same geometric area of 1 cm^2 was calculated by dividing the double-layer capacitance (C_{dl}) extracted from cyclic voltammograms (CV) by the specific capacitance of the active material under

identical electrolyte conditions ($C_s = 40 \mu\text{F cm}^{-2}$ in 1 M NaOH⁵⁸) (Supplementary Fig. 21). In Fig. 3c, surface Sb doping increases the C_{dl} of bare Fe_2O_3 photoanode ($25.9 \mu\text{F}$) by more than 50%, $40.6 \mu\text{F}$ for PN-10-O and $45.9 \mu\text{F}$ for PN-10. PN-10 shows a little higher C_{dl} than PN-10-O, indicative of a possible role of $\text{Sb}^{<3+}$ species in providing additional active sites. Importantly, C_{dl} of PN-10 is remarkably increased to $78.9 \mu\text{F}$ by more than 70% after co-catalyst loading, which reveals the promotion of hole utilization by co-catalyst. Accordingly, the ECSA values for bare Fe_2O_3 , PN-10-O, PN-10, and PN-10 with co-catalyst are determined to be 0.65, 1.02, 1.15, and 1.97 cm^2 , respectively. The increased active area for electrochemical adsorption of ions demonstrates a great number of active sites for water oxidation.”

Refs:

58. McCrory, C. C. L., Jung, S., Peters, J. C. et al. Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction. *J. Am. Chem. Soc.* **135**, 16977–16987 (2013).

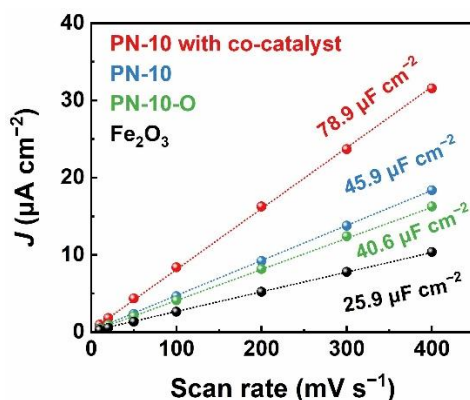


Fig. 3c| Double layer capacitance (C_{dl}) extracted from cyclic voltammograms (CV).

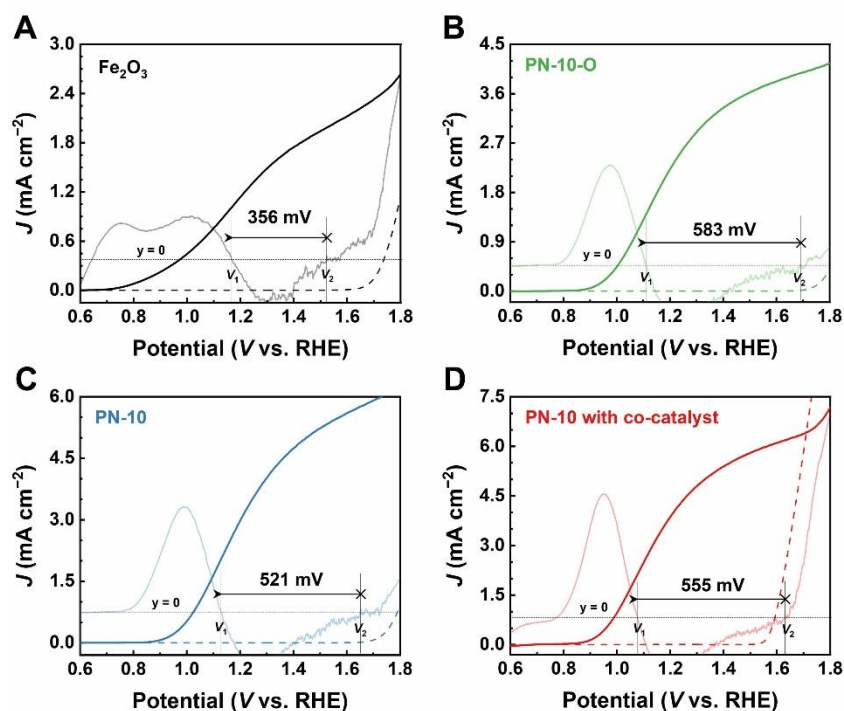
(p. 17) “The OER proceeds mainly *via* surface states and direct transfer from the valence band at moderately and highly anodic potentials in the PEC cells, respectively⁵⁹. Iandolo and Hellman used first-principle calculations to investigate surface states on hematite under photoelectrochemical conditions and further demonstrated that increasing the potential could empty the surface states⁶⁰, which explains why the J_{ph} of water photo-oxidation increases slowly (smaller slope of J – V curves) with the increase of potential. With the increase of applied potential, the surface states will gradually fade at about 1.1 V_{RHE} (V_1) until they reach a certain potential (V_2) where the surface states are completely emptied (Supplementary Fig. 24). The difference of potentials ($\Delta V = V_2 - V_1$) can reflect the surface-state density for different samples to a certain

extent. ΔV of bare Fe_2O_3 is determined to be 356 mV, while those of PN-10-O and PN-10 significantly increase to over 500 mV. The significantly increased ΔV after Sb doping suggests that extrinsic doping *via* surface spin-coating method and post-annealing indeed increases the surface states of Fe_2O_3 , which results in more positive V_{on} of PN-10-O and PN-10, consistent with the general understanding of doping effects. Notably, with the presence of Sb^{3+} species on the surface, different surface composition and electronic structure of PN-10 result in a reduced surface-state density compared to that of PN-10-O (ΔV : PN-10 vs. PN-10-O, 521 mV vs. 583 mV), which contributes to the enhanced surface charge separation and higher J_{ph} of PN-10. After co-catalyst modification, ΔV of PN-10 increases to 555 mV owing to the hole extraction function of $\text{NiCoFe}(\text{OOH})_x$ co-catalyst as mentioned above (Fig. 3a)."

Refs:

59. Klahr, B., Gimenez, S., Fabregat-Santiago, F. et al. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with "Co-Pi"-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **134**, 16693–16700 (2012).

60. Iandolo, B., Hellman, A. The Role of Surface States in the Oxygen Evolution Reaction on Hematite. *Angew. Chem. Int. Ed.* **53**, 13404–13408 (2014).



Supplementary Fig. 24| Evaluation of surface-state density. J - V curves and corresponding second-order differential curves (math.) of bare Fe_2O_3 (A), PN-10-O (B), PN-10 (C), and PN-10 with co-catalyst (D) measured in 1 M NaOH electrolyte.

(p. 19-20) “Photoelectrochemical impedance spectroscopy (PEIS) at different potentials from 0.8 (close to V_{on}) to 1.5 V_{RHE} (with a step of 50 mV) interprets the trends of capacitances and resistances, which provide insights into the contribution of gradient Sb doping, p - n homojunction and co-catalyst to PEC performance (Supplementary Fig. 27). The obtained data were fitted to a typical two-RC-unit equivalent circuit model to decouple charge trapping and charge transfer resistances (Supplementary Table 5). In Fig. 4a, the maximum capacitances in the bulk (C_{bulk}) of PN-10-O, PN-10, and PN-10 with co-catalyst reach up to 4 times that of bare Fe_2O_3 , which is ascribed to the additional driving force provided by gradient dopants of Sb^{5+} and Sn^{4+} ions. Moreover, the additional driving force results in an obvious peak of C_{bulk} values at the potential range of 1.0–1.15 V_{RHE} , where C_{bulk} initially increases at a remarkable rate and declines rapidly when applied potential further increases due to the enhanced charge extraction and the lower accumulation of photogenerated holes^{64,65}. However, this behavior cannot be observed on bare Fe_2O_3 , where C_{bulk} of bare Fe_2O_3 shows rapid decay in the whole potential range. Notably, the potentials of maximum C_{bulk} value for p - n homojunctions (PN-10 and PN-10 with co-catalyst) are smaller than that of PN-10-O by 100–150 mV, indicating that the p - n homojunction can effectively separate the photo-generated electron and hole with a small bias. The surface-state capacitance (C_{ss}) of PN-10-O with surface composition of “ $\text{Sb}^{5+} + \text{Sb}^{3+}$ ” slightly increases compared to that of bare Fe_2O_3 , while C_{ss} of PN-10 significantly increases to ~2 times that of PN-10-O by surface composition of “ $\text{Sb}^{<3+} + \text{Sb}^{3+}$ ” (Fig. 4b). The higher C_{ss} comes from the contribution of the surface $\text{Sb}^{<3+}$ species, which helps to reduce charge recombination as mentioned above. The additional co-catalyst modification further enhances C_{ss} at potentials higher than water-oxidation (1.23 V_{RHE}), indicating a significant contribution of co-catalyst to OER.

Fig. 4c shows that trapping resistance (R_{trap}) values of PN-10-O, PN-10, and PN-10 with co-catalyst decrease greatly relative to that of bare Fe_2O_3 in the whole potential range of 0.8–1.5 V_{RHE} owing to the enhanced bulk separation efficiency by high valence doping effect. With the increase of potential, the charge transfer resistance (R_{ct}) of all Sb-doped photoanodes decreases

significantly owing to the enhanced surface conductivity. At potential of 0.9 V_{RHE} close to V_{on} , R_{ct} of PN-10-O is still much higher than that of bare Fe₂O₃, while R_{ct} of PN-10 and PN-10 with co-catalyst are comparable or even lower than that of bare Fe₂O₃. The huge different R_{ct} values near V_{on} of PN-10-O and PN-10 reflect the beneficial role of surface Sb^{<3+} species, which eventually enables higher J_{ph} .

Charge transfer through surface states is assumed as the predominant mechanism for surface charge transfer of OER⁵⁹. Thus, the proportion of charge transfer through surface states determines the rate of water oxidation on hematite photoanodes. Assuming that the rates of charge transfer and trapping are inversely proportional to their respective resistances, and the charge transfer efficiency (η_{ct}) can be estimated through the equation^{66,67}:

$$\eta_{ct} = \frac{k_{ct}}{k_{ct} + k_{trap}} = \frac{R_{trap}}{R_{ct} + R_{trap}} \quad (1)$$

where k_{ct} and k_{trap} are the rate constants of charge transfer and trapping, respectively. Fig. 4d shows the η_{ct} values at different potentials of 0.8–1.5 V_{RHE}. η_{ct} of PN-10-O keeps lower than that of bare Fe₂O₃ at potentials <1.15 V_{RHE} and becomes only a little better at higher potentials. Differently, at ~1.0 V_{RHE}, η_{ct} of PN-10 starts to exceed that of bare Fe₂O₃ and significantly increases up to ~80% at 1.23 V_{RHE}. The turning potential of 1.0 V_{RHE} is consistent with the potential at which J_{ph} of PN-10 exceeds that of bare Fe₂O₃. Therefore, these results indicate that high J_{ph} of PN-10 is generated by the contribution of surface Sb^{<3+} species instead of Sb³⁺ or Sb⁵⁺ ions. Further, co-catalyst modification enhances η_{ct} of PN-10 at all potentials.”

Refs:

59. Klahr, B., Gimenez, S., Fabregat-Santiago, F. et al. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with “Co-Pi”-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **134**, 16693–16700 (2012).

64. Wang, H. X., Wang, Y., Lin, Y. M. et al. Impact of NiCo₂O₄/SrTiO₃ *p-n* Heterojunctions on the Interface of Photoelectrochemical Water Oxidation. *ACS Appl. Mater. Interfaces* **15**, 28739–28746 (2023).

65. Ros, C., Andreu, T., David, J. et al. Degradation and regeneration mechanisms of NiO protective layers deposited by ALD on photoanodes. *J. Mater. Chem. A* **7**, 21892–21902 (2019).

66. Monllor-Satoca, D., Bärtsch, M., Fàbrega, C. et al. What do you do, titanium? Insight into the role of titanium oxide as a water oxidation promoter in hematite-based photoanodes. *Energy Environ. Sci.* **8**, 3242–3254 (2015).

67. Zhang, J. F., García-Rodríguez, R., Cameron, P. et al. Role of cobalt–iron (oxy)hydroxide (CoFeO_x) as oxygen evolution catalyst on hematite photoanodes. *Energy Environ. Sci.* **11**, 2972–2984 (2018).

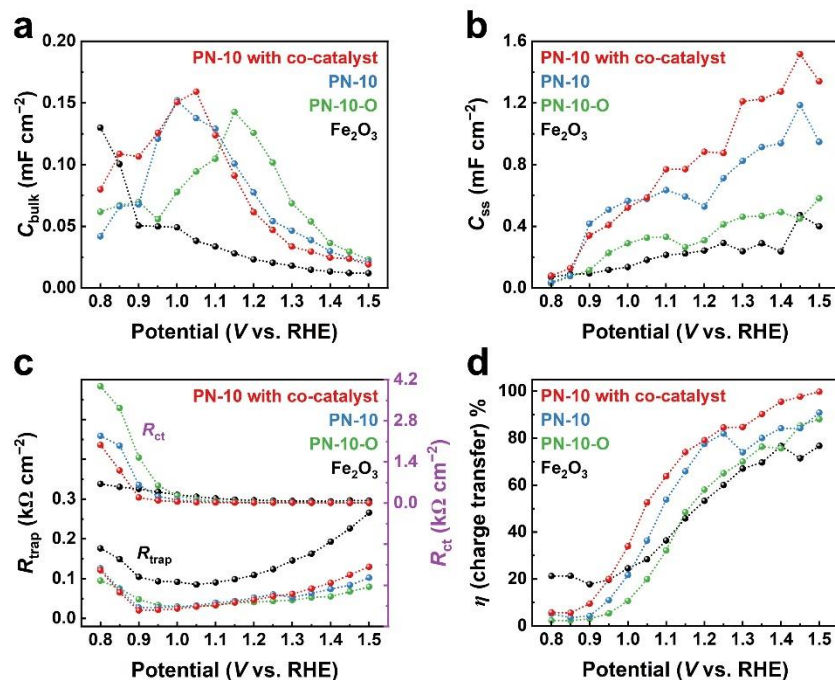


Fig. 4| PEIS of bare Fe₂O₃, PN-10-O, PN-10 and PN-10 with co-catalyst photoanodes. (a) Bulk capacitance, (b) surface-state capacitance, (c) trapping resistance, and (d) charge transfer efficiency.

We have revised the manuscript to incorporate these points and provide a more comprehensive discussion of the surface defects and their impact on performance.

Reviewer #4:

Comments to the Author: The authors have reported a parallel multi-stacked photoanodes of Sb doped hematite for PEC water oxidations. They proposed parallel-connected stack of six p - n homojunction hematite photoanodes records a near-theoretical J_{ph} of $\sim 10 \text{ mA cm}^{-2}$ at $1.23 V_{RHE}$ under standard PEC water splitting conditions, which sets a new benchmark of hematite photoanodes and promises its practical application for unbiased PEC water splitting. However, the manuscript needs further revisions to clarify the following points.

Response: We thank the reviewer's valuable comments that the parallel-connected stack of six p - n homojunction hematite photoanodes records a near-theoretical J_{ph} of $\sim 10 \text{ mA cm}^{-2}$ at $1.23 V_{RHE}$ under standard PEC water splitting conditions, which sets a new benchmark of hematite photoanodes and promises its practical application for unbiased PEC water splitting. All the comments from the reviewer help to improve the quality of this work. The point-by-point response to every comment follows below.

Comment 1: The band alignment of PN-10 homojunction of Fig. 2 shows that the energy gap between CBM of $Sb^{<3+}:Fe_2O_3$ and VBM of $Sb^{5+}:Fe_2O_3$ is only $\sim 0.7 \text{ eV}$. Thus, the nonadiabatic coupling CBM of $Sb^{<3+}:Fe_2O_3$ and VBM of $Sb^{5+}:Fe_2O_3$ is strong. In this case, the electrons in CBM of $Sb^{<3+}:Fe_2O_3$ can easily recombine with the holes in VBM of $Sb^{5+}:Fe_2O_3$, resulting in fast charge recombination and short charge carrier lifetime. Why does the Sb doping can promote charge separation in this situation?

Response 1: Thank the reviewer for this valuable comment. Based on the band arrangement determined by UPS and VBXPS, the small energy gap between CBM of $Sb^{<3+}:Fe_2O_3$ and VBM of $Sb^{5+}:Fe_2O_3$ tends to result in strong charge recombination, which would inhibit the PEC performance of the p - n homojunction photoanode. However, the p - n homojunction and some other benefits still cooperatively help to promote charge separation as following:

(1) Applied bias potential. PEC cells are quite different from photocatalysis systems, in which the applied bias potential could suppress the charge recombination effectively by extracting electrons to the current collector. On the other hand, the induced recombination of charges is also beneficial

to generate stronger oxidizing holes in VB and stronger reducing electrons in CB, thus partially compensating for the photocurrent loss.

(2) Ultrathin surface *p*-type layer. More importantly, the *p*-type $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ merely exists in the surface region with a small thickness of several nanometers, thus the charge recombination happens near to surface region as well. After co-catalyst modification, the photogenerated holes arriving at the surface can be quickly extracted and injected into OER, avoiding charge recombination. The diminished hole accumulation and recombination processes contribute to a significant J_{ph} increase from 3.33 to 4.21 mA cm^{-2} and better stability.

(3) *p*-*n* homojunction and gradient dopants. Additionally, the enhanced charge separation after Sb doping benefits from not only the formation of *p*-*n* homojunction but also the gradient doping of Sb^{5+} and Sn^{4+} . The better PEC performance of PN-10-O than that of bare Fe_2O_3 arises from the gradient doping of Sb^{5+} and Sn^{4+} , while further enhancement for PN-10 indicates that *p*-*n* homojunction indeed plays an important role in improving the PEC performance despite the partial charge recombination between CBM of $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ and VBM of $\text{Sb}^{5+}:\text{Fe}_2\text{O}_3$.

Relevant clarification has been added in the revised manuscript #.

(p. 21) With co-catalyst modification, however, the stability of *p*-*n* homojunction is greatly improved to ~96.9% due to the enhanced hole extraction and accelerated OER kinetics by the $\text{NiCoFe}(\text{OOH})_x$ co-catalyst, which protects the *p*-type $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ layer and stabilizes the surface structure as illustrated in Supplementary Fig. 29. Additionally, the small energy gap between conduction band minimum (CBM) of $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ and valence band maximum (VBM) of $\text{Sb}^{5+}:\text{Fe}_2\text{O}_3$ determined by UPS and VBXPS indicates that some charge carriers tend to recombine owing to the coupling of CBM of $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ and VBM of $\text{Sb}^{5+}:\text{Fe}_2\text{O}_3$. With co-catalyst loading, however, the photogenerated holes arriving at the surface $\text{Sb}^{<3+}:\text{Fe}_2\text{O}_3$ layer can be injected into OER immediately, thus preventing hole recombination with VBM electrons of $\text{Sb}^{5+}:\text{Fe}_2\text{O}_3$ and inactivation of the surface $\text{Sb}^{<3+}$ species. This will give rise to a remarkable J_{ph} increase with co-catalyst modification.

Comment 2: In page 17, the authors proposed that the fast OCP transient decay indicates a significant charge recombination when illumination is stopped, which implies on the other hand that the charge trapping is insignificant when illuminated. Please reveal in detail how does the charge trapping process occurs and provide the mechanism evidences?

Response 2: We thank the reviewer for this comment and clarification was made as follows:

It is generally recognized that when the system is displaced from a steady state under illumination at an open circuit, the evolution of free electron density is directly responsible for the OCP decay (*ChemPhysChem* 4, 859 – 864 (2003)), where the free electron density evolves from the initial steady state value (n) to the dark equilibrium concentration (n_0).

$$\text{OCP} = \frac{k_B T}{e} \ln\left(\frac{n}{n_0}\right) \quad (1)$$

The electron lifetime (τ_n) is derived from a general free electron recombination rate that counts also the contribution of trapping and de-trapping.

$$\tau_n = - \frac{k_B T}{e} \left(\frac{d\text{OCP}}{dt} \right)^{-1} \quad (2)$$

It must be realized that the measured lifetime τ_n does not in general correspond to the free carrier lifetime but consists of an average of characteristic times for survival of free and trapped electrons.

For PN-x photoanodes, the strong band bending in the semiconductor/electrolyte junction enables a large number of spatial charges in the depletion region, thus significant carrier recombination occurs at the transient when the illumination is removed. The fast decay kinetics at the transient indirectly reflects the insignificant charge trapping, indicative of the efficient carrier separation when illuminated.

When the photoanode is illuminated to a steady voltage, $d\text{OCP}/dt$ is equal to zero. The carrier lifetime changes exponentially over orders of magnitude when the steady state varies. As such, at the transient time from illumination to the dark, $d\text{OCP}/dt$ rapidly increases to a maximum at first, and then decreases gradually in a subsequent period. Correspondingly, the variable carrier lifetime rapidly decreases to a minimum and then increases gradually. The initial rapid lifetime attenuation well matches the carrier recombination process.

The excellent work by A. Zaban *et al.* has been cited in the revised manuscript to provide a better understanding of OCP measurements for readers #.

(p. 18) “The fast OCP transient decay indicates a significant charge recombination when illumination is stopped, which implies on the other hand that the charge trapping is insignificant when illuminated^{17,63}.”

Refs:

63. Zaban, A., Greenshtein, M., Bisquert, J. Determination of the electron lifetime in nanocrystalline dye solar cells by open-circuit voltage decay measurements. *ChemPhysChem* **4**, 859–864 (2003).

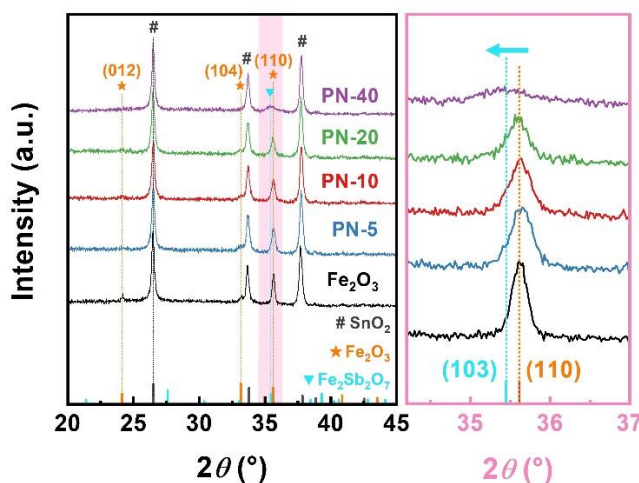
Comment 3: The XRD spectra of *p–n* homojunction hematite photoanodes in Supplementary Fig. 2 show that Sb doping can cause the formation of a new phase $\text{Fe}_2\text{Sb}_2\text{O}_7$. However, the peak of $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) only exists in PN-40, why this peak does not exist in PN-20? Whether the peak of $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) is corresponding to the peak of Fe_2O_3 (110)? In addition, why the authors choose the $\text{Fe}_2\text{Sb}_2\text{O}_7$ as the XRD standard card? The stoichiometric ratios of $\text{Fe}_x\text{Sb}_y\text{O}_z$ in PN-5, PN-10, PN-20, PN-40 are $\text{Fe}_2\text{Sb}_2\text{O}_7$?

Response 3: We thank the reviewer for these questions. The common $\text{Fe}_x\text{Sb}_y\text{O}_z$ compounds formed at high temperatures are mainly FeSbO_4 , FeSb_2O_6 (or $(\text{FeSbO}_4)(\text{Sb}_2\text{O}_4)_{1/2}$) and $\text{Fe}_2\text{Sb}_2\text{O}_7$. Note that Fe ions in these compounds are mainly in the form of Fe^{3+} , the valence state of Sb ions of FeSbO_4 , FeSb_2O_6 (or $(\text{FeSbO}_4)(\text{Sb}_2\text{O}_4)_{1/2}$) and $\text{Fe}_2\text{Sb}_2\text{O}_7$ successively decreases from the most stable +5 valence state (Sb^{5+} in FeSbO_4) to mixed valence states of +5, +3 and even lower ones (*Appl. Surf. Sci.* **252**, 7849–7855 (2006)). As claimed in the manuscript (Supplementary Fig. 8B and Supplementary Table 2), the compositions of Sb ions on the surface of PN-*x* are $\text{Sb}^{<3+}$ and Sb^{3+} , with the absence of Sb^{5+} , so the possible new phases formed on the surface are more inclined to be FeSb_2O_6 or $\text{Fe}_2\text{Sb}_2\text{O}_7$. The 2θ of (103) peaks of FeSb_2O_6 (JCPDS no. 07-0349) and $\text{Fe}_2\text{Sb}_2\text{O}_7$ (JCPDS no. 07-0065) are located at 35.02° and 35.45° , respectively. It should be noted that there is no separate peak of new phases observed in all XRD spectra of PN-*x* samples. In addition, the 2θ of $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) is very close to that of Fe_2O_3 (110) ($2\theta = 35.61^\circ$), hence the slight shift of Fe_2O_3 (110) peak to lower angles is most likely due to the formation of a small amount of $\text{Fe}_2\text{Sb}_2\text{O}_7$ instead of FeSb_2O_6 . Because of the subtle difference between $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) and Fe_2O_3 (110) and the low concentration of Sb used in this work, the Fe_2O_3 (110) peak is only gradually broadened

and shifted to a low angle by a small amount as the Sb concentration increases. It is also possible that a small amount of $\text{Fe}_2\text{Sb}_2\text{O}_7$ is produced at SbCl_3 concentrations less than 20 mM, but its (103) characteristic peak is masked by Fe_2O_3 (110). When the SbCl_3 concentration is significantly increased to 40 mM, the production of more $\text{Fe}_2\text{Sb}_2\text{O}_7$ species makes the clear shift of Fe_2O_3 (110) peak to a lower angle.

In all, the possible new $\text{Fe}_x\text{Sb}_y\text{O}_z$ phase is difficult to identify and the values of x , y , and z are also hard to determine. Based on the measurements and comprehensive comparisons, $\text{Fe}_2\text{Sb}_2\text{O}_7$ is the most likely phase to form on the surface and helps to better explain the behavior reflected by XRD. The relevant expressions have also been modified in the revised manuscript # (Supplementary Fig. 2).

(p. 7-8) “Moreover, the 2θ position shifts to lower angles when the concentration is high enough, which is related to the formation of a possible new phase $\text{Fe}_2\text{Sb}_2\text{O}_7$ by HMA. Among the common $\text{Fe}_x\text{Sb}_y\text{O}_z$ compounds (JCPDS no. 46-1387 for FeSbO_4 ; JCPDS no. 07-0349 for FeSb_2O_6 ; JCPDS no. 07-0065 for $\text{Fe}_2\text{Sb}_2\text{O}_7$), the $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) peak is the closest to the Fe_2O_3 (110) and is expected to induce such shift of the Fe_2O_3 (110) peak.”



Supplementary Fig. 2| XRD spectra of *p*–*n* homojunction hematite photoanodes with spin-coated SbCl_3 solutions of different concentrations. PN- x ($x = 5, 10, 20, 40$ mM) refers to the sample of Fe_2O_3 coated with different concentrations of SbCl_3 . The standard diffraction peak data of Fe_2O_3 (JCPDS no. 33-0664), SnO_2 (JCPDS no. 41-1445) and $\text{Fe}_2\text{Sb}_2\text{O}_7$ (JCPDS no. 07-0065) are depicted at the bottom. Note that the Fe ions in these compounds are mainly in the form of

Fe^{3+} , the valence state of Sb ions for FeSbO_4 (JCPDS no. 46-1387), FeSb_2O_6 (JCPDS no. 07-0349) and $\text{Fe}_2\text{Sb}_2\text{O}_7$ successively decreases from the most stable +5 valence (Sb^{5+} in FeSbO_4) to a mixed valence state of +5, +3 and even lower ones¹. As shown in Supplementary Fig. 8B and Supplementary Table 2, the compositions of Sb ions on the surface of PN-*x* are $\text{Sb}^{<3+}$ and Sb^{3+} , with the absence of Sb^{5+} , so the possible new phases formed on the surface are more inclined to be determined as FeSb_2O_6 or $\text{Fe}_2\text{Sb}_2\text{O}_7$. On the other hand, the 2θ of $\text{Fe}_2\text{Sb}_2\text{O}_7$ (103) is the closest to that of Fe_2O_3 (110) ($2\theta = 35.61^\circ$) compared to that of FeSb_2O_6 , hence the slight shift of Fe_2O_3 (110) peak to lower angles is most likely due to the formation of a small amount of $\text{Fe}_2\text{Sb}_2\text{O}_7$ instead of FeSb_2O_6 .

Refs:

1. Huang, Y., Ruiz, P. The nature of antimony-enriched surface layer of Fe–Sb mixed oxides. *Appl. Surf. Sci.* **252**, 7849–7855 (2006).

Comment 4: Under normal circumstances, the calcination temperature from $\beta\text{-FeOOH}$ to $\alpha\text{-Fe}_2\text{O}_3$ is 500 or 550°C, why 400°C is chosen in this paper?

Response 4: Thanks for the reviewer's comment. In our work, we have converted the yellow $\beta\text{-FeOOH}$ nanorods film into red Fe_2O_3 nanorods film under 400 °C in order to avoid significant chemical reactions between SbCl_3 and $\beta\text{-FeOOH}$ when applying spin-coating. Consequently, a uniform SbOCl layer as a dopant source could be obtained on the surface of nanorods. The transformation of $\beta\text{-FeOOH}$ to Fe_2O_3 could eliminate the dehydration process and pore generation during the phase transition from Fe_2O_3 to $\alpha\text{-Fe}_2\text{O}_3$ by HMA, thereby avoiding an uncontrollable effect on the doping behavior of Sb. Our previous experiments have also demonstrated that FeOOH/SbOCl cannot give an excellent PEC performance comparable to that of PN-10 upon HMA. Here, annealing at 400 °C for 1 h is just a pre-treatment, and high crystalline *p-n* homojunction hematite nanorods should be achieved by HMA.

Comment 5: In page 7 of Supplementary, please check whether the “(O_C, 532.5–533.1 eV)” is correct.

Response 5: We thank the reviewer for this comment and have carefully checked the fitted peak positions of the chemisorbed oxygen (O_C) and corrected the figures in the revised manuscript. Fig. 2b, c and Supplementary Fig. 8A, C have also been optimized to visualize the BE positions of oxygen compositions. In our work, the binding energies of O_C peaks extracted from the O 1s spectra of all samples were in the range of 532.2 to 533.1 eV, which are consistent with those obtained on hematite photoanodes in the previous reports (*Adv. Mater.* **28**, 6405–6410 (2016); *Adv. Energy Mater.*, 2401298 (2024)).

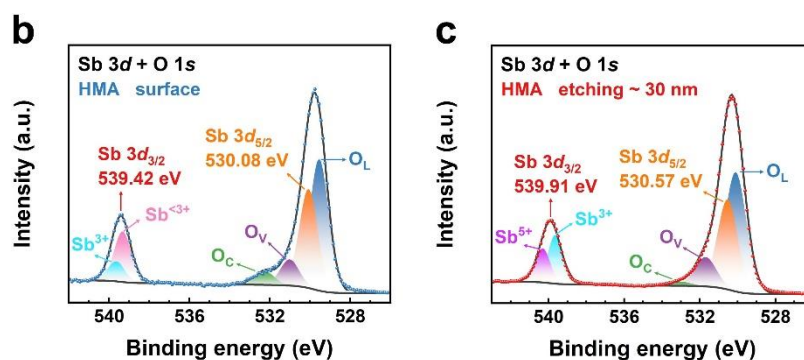
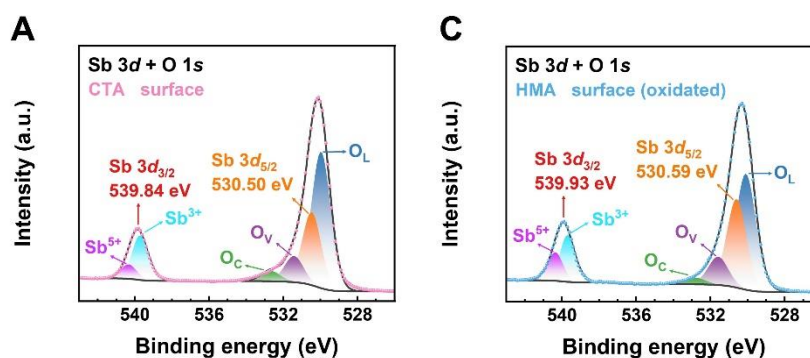


Fig. 2b and c| Sb 3d + O 1s XPS of PN-10 on the surface (b) and at etching depth of ~30 nm (c).



Supplementary Fig. 8A and C| Surface Sb 3d + O 1s XPS spectra of Sb:Fe₂O₃-CTA (A) and PN-10-O (C).

Response Letter

Reviewer #4:

Comments to the Author: *This paper is probably publishable, but should be reviewed again in revised form before it is accepted. The authors proposed that the photogenerated holes can be quickly extracted by co-catalyst, is there any experimental evidence for that? In addition, photogenic holes participate in OER reaction very slowly. How does it inhibit charge recombination?*

Response: Thank the reviewer for this additional comment. In the revised manuscript, we have employed comprehensive measurements to provide more experimental evidence for the suppressed surface charge recombination and the accelerated OER kinetics. Besides the evaluations already available in the manuscript, we added calculations of surface hole losses at varying applied potentials to directly reflect the role of surface species such as $\text{Sb}^{<3+}$ and $\text{NiCoFe}(\text{OOH})_x$ co-catalyst on photogenerated holes. As shown in Supplementary Fig. 21, the amount of hole loss due to surface recombination is calculated from anodic “spikes” according to the method in Li’s work (*ACS Catal.* **11**, 12736–12744 (2021)). After loading $\text{NiCoFe}(\text{OOH})_x$ co-catalyst, the significantly increased hole accumulation on the surface at a potential close to V_{on} suggests the strengthened hole extraction. In contrast, the reduced hole loss at higher potentials signifies the inhibited charge recombination and accelerated OER. The chronoamperometry measurements under chopped illumination have been added in the revised manuscript # (Supplementary Fig. 21).

The amount of hole loss at different applied potentials can be calculated by chronoamperometry measurement under chopped illumination⁵⁸ (Supplementary Fig. 21). In Supplementary Fig. 21F, the hole loss amount of PN-10-O is smaller than that of bare Fe_2O_3 owing to the enhanced conductivity on the surface after Sb doping, while PN-10 with surficial $\text{Sb}^{<3+}$ species further reduces the hole loss of recombination especially at potentials $<1.3 V_{\text{RHE}}$, which is indicative of more effective hole injection to OER, thus generating a higher steady J_{ph} (4.21 mA cm^{-2}) at $1.23 V_{\text{RHE}}$. The $\text{NiCoFe}(\text{OOH})_x$ co-catalyst serves as an OER booster to increase the hole injection efficiency significantly. As shown in Fig. 3a, $\text{NiCoFe}(\text{OOH})_x$ has no significant effect on the improvement of V_{on} . However, the amount of hole accumulation on the surface after

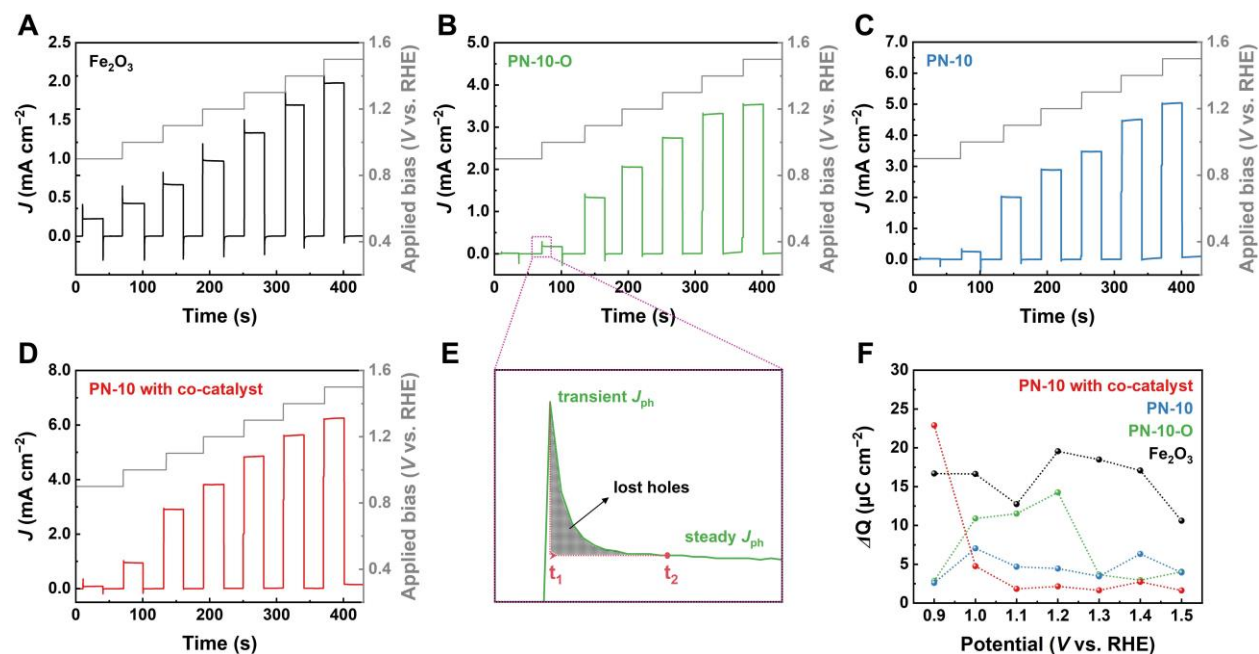
NiCoFe(OOH)_x loading on PN-10 at a potential close to V_{on} (0.9 V_{RHE}) is remarkably increased (Supplementary Fig. 21F), which implies the possible function of hole extraction of NiCoFe(OOH)_x co-catalyst. When the applied potential increases, the hole loss of PN-10 with co-catalyst becomes much smaller than those of bare Fe₂O₃, PN-10-O, and PN-10 photoanodes, indicating its efficient hole injection and accelerated OER. It was previously reported that the metal oxide/(oxy)hydroxide could have beneficial roles in both hole collection and oxygen-evolution catalysis at the same time^{59,60}.

Refs:

58. Wang, P. P., Fu, P., Ma, J. P. et al. Ultrathin Cobalt Oxide Interlayer Facilitated Hole Storage for Sustained Water Oxidation over Composited Tantalum Nitride Photoanodes. *ACS Catal.* **11**, 12736–12744 (2021).

59. Nellist, M. R., Laskowski, F. A. L., Qiu, J. et al. Potential-sensing electrochemical atomic force microscopy for in operando analysis of water-splitting catalysts and interfaces. *Nat. Energy* **3**, 46–52 (2018).

60. Laskowski, F. A. L., Nellist, M. R., Qiu, J. et al. Metal Oxide/(oxy)hydroxide Overlayers as Hole Collectors and Oxygen-Evolution Catalysts on Water-Splitting Photoanodes. *J. Am. Chem. Soc.* **141**, 1394–1405 (2019).



Supplementary Fig. 21| Chopped illumination chronoamperometry measurements of bare Fe_2O_3 (A), PN-10-O (B), PN-10 (C) and PN-10 with co-catalyst (D) from 0.9 to 1.5 V_{RHE} at an interval of 0.1 V_{RHE} . The shadow area between t_1 and t_2 in (E) corresponds to the amount of charges for the anodic transients. The amount of hole loss at the surface of photoanodes (Q_h) from transient state to steady state can be calculated by integrating the immediate photocurrent density I ($I = \text{transient } J_{\text{ph}} - \text{steady } J_{\text{ph}}$) as a function of time.

$$Q_h = \int_{t_1}^{t_2} I dt \quad (3)$$

Additionally, more experimental results on photogenerated holes are also summarized here, including surface charge separation efficiency (Fig. 3e), OCP-derived carrier lifetime (Fig. 3f), PEIS analysis (Fig. 4), and the effect of co-catalyst.

As shown in Fig. 3e, with co-catalyst modification, the surface charge separation efficiency (η_{surface}) is significantly increased in the whole potential range from 0.9 to 1.4 V_{RHE} owing to more efficient hole extraction and utilization, reaching ~80% at 1.23 V_{RHE} and ~90% at 1.4 V_{RHE} . More detailed evaluations of η_{surface} for the other photoanodes can be found in the manuscript.

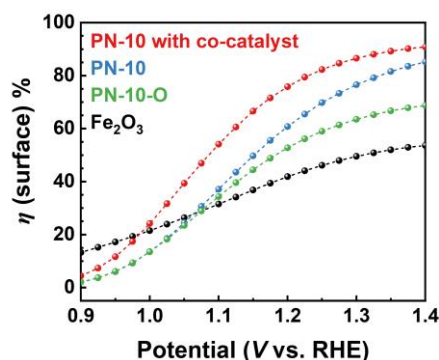


Fig. 3e| Surface charge separation efficiencies measured in 1 M NaOH solution with the addition of 0.5 M Na_2SO_3 as a hole scavenger.

The strong band bending in the semiconductor/electrolyte junction enables a large number of spatial charges in the depletion region, thus significant carrier recombination occurs at the transient when the illumination is removed. The fast decay kinetics at the transient indirectly reflects the insignificant charge trapping, indicative of the efficient carrier separation when illuminated. As shown in Fig. 3f, with the formation of *p-n* homojunction, PN-10 significantly reduces carrier lifetime at the transient to 1.3 s, while co-catalyst further lowers it by an order of magnitude to about 245 ms, indicating that the charge accumulated in the depletion layer is well extracted and injected into the OER.

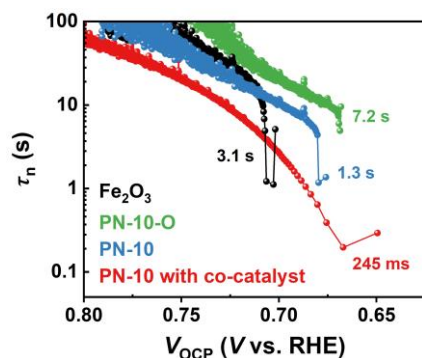


Fig. 3f] OCP-derived carrier lifetimes of different photoanodes.

In Fig. 4b, the surface-state capacitance (C_{ss}) of PN-10 with the surface composition of “ $Sb^{<3+} + Sb^{3+}$ ” increases to ~ 2 times that of bare Fe_2O_3 and PN-10-O, while the additional co-catalyst modification further enhances C_{ss} , remarkably, especially at potentials higher than water-oxidation potential ($1.23 V_{RHE}$), indicating a significant contribution of co-catalyst to OER.

Charge transfer through surface states is assumed as the predominant mechanism for surface charge transfer of OER. Thus, the proportion of charge transfer through surface states determines the rate of water oxidation on hematite photoanodes. As shown in Fig. 4d, co-catalyst modification enhances charge transfer efficiency (η_{ct}) of PN-10 at all potentials, which exceeds 80% at $1.23 V_{RHE}$ of water oxidation. More detailed evaluations of the charge transfer characteristics for the other photoanodes can be found in the manuscript.

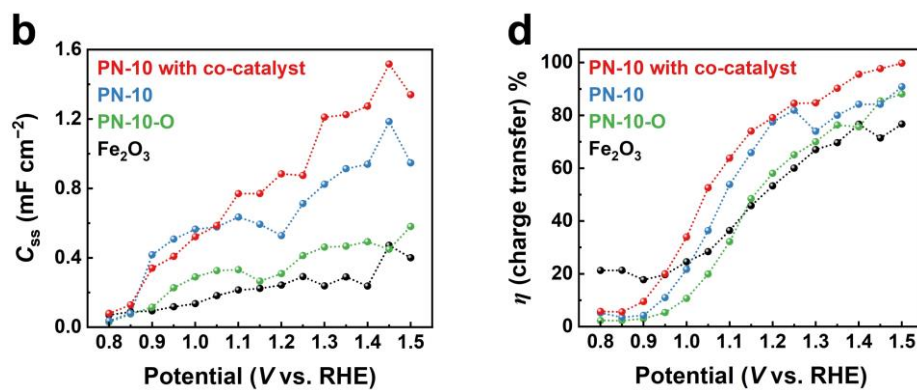


Fig. 4| PEIS of bare Fe_2O_3 , PN-10-O, PN-10 and PN-10 with co-catalyst photoanodes. (b) surface-state capacitance, (d) charge transfer efficiency.