

Supporting Information

One Dimensional Hematite Photoanodes with Spatially Separated Pt and FeOOH Nanolayers for Efficient Solar Water Splitting

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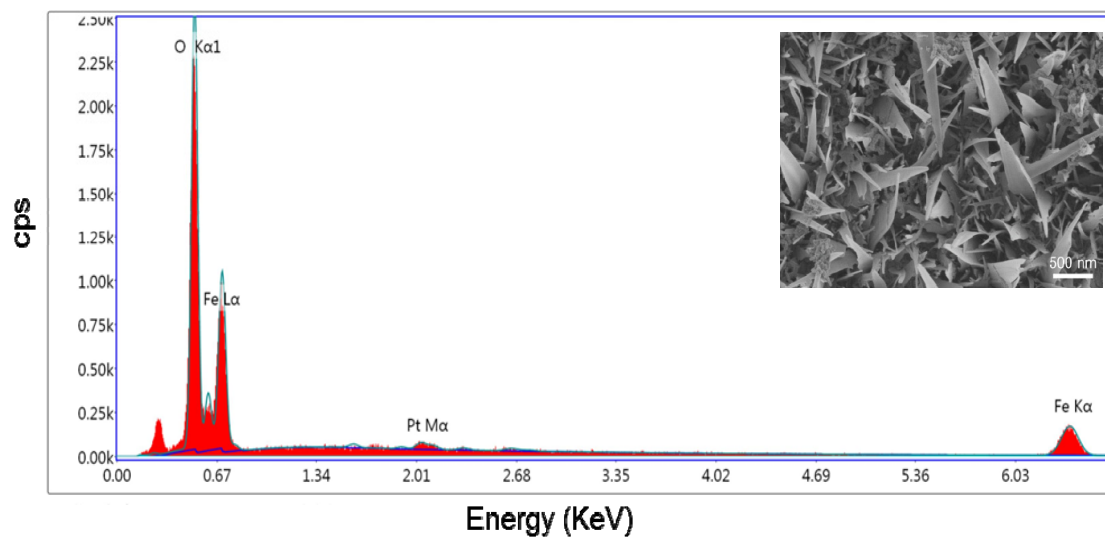


Figure S1 SEM-EDS scanning of FeOOH/ α -Fe₂O₃ NFs/Pt sample.

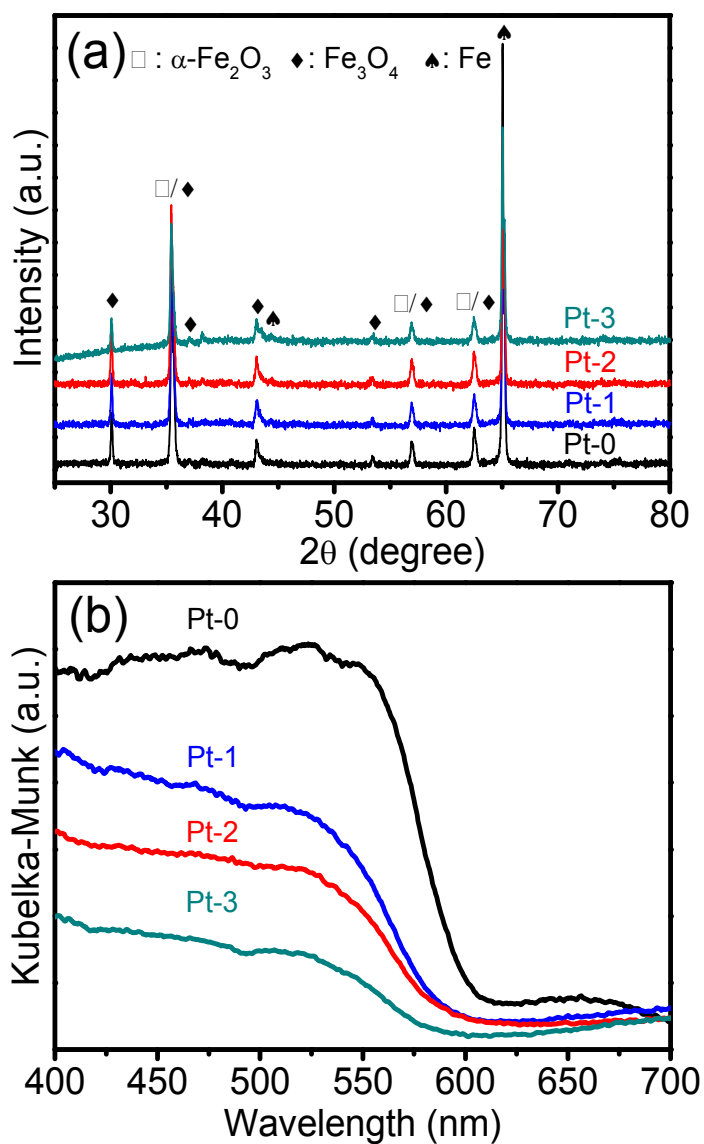


Figure S2 (a) XRD patterns and (b) UV-vis diffuse reflectance spectra of FeOOH/ α -Fe₂O₃ NFs/Pt-x photoanodes in 5 mM H₂PtCl₆ aqueous solutions for various times. Pt-0: reference NFs, Pt-1: 2 h; Pt-2: 6 h; Pt-3: 10 h.

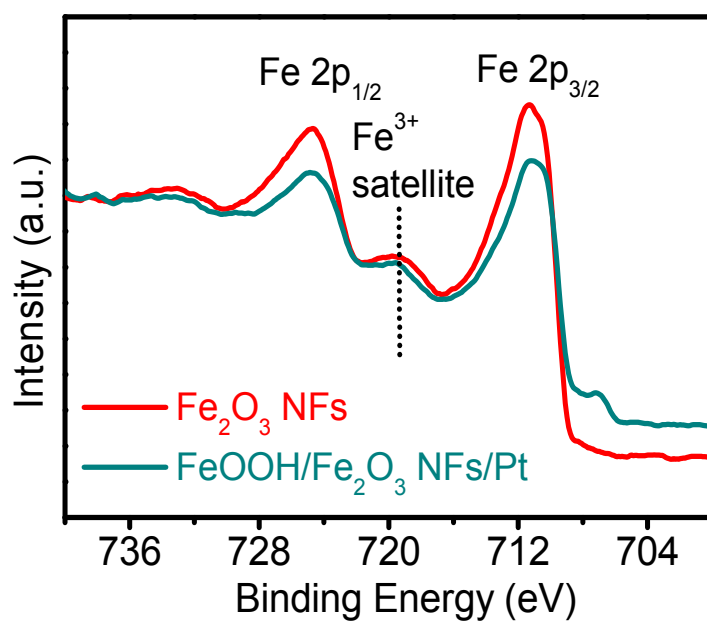


Figure S3 XPS high resolution Fe 2p spectra of $\alpha\text{-Fe}_2\text{O}_3$ NFs and FeOOH/ $\alpha\text{-Fe}_2\text{O}_3$ NFs/Pt samples.

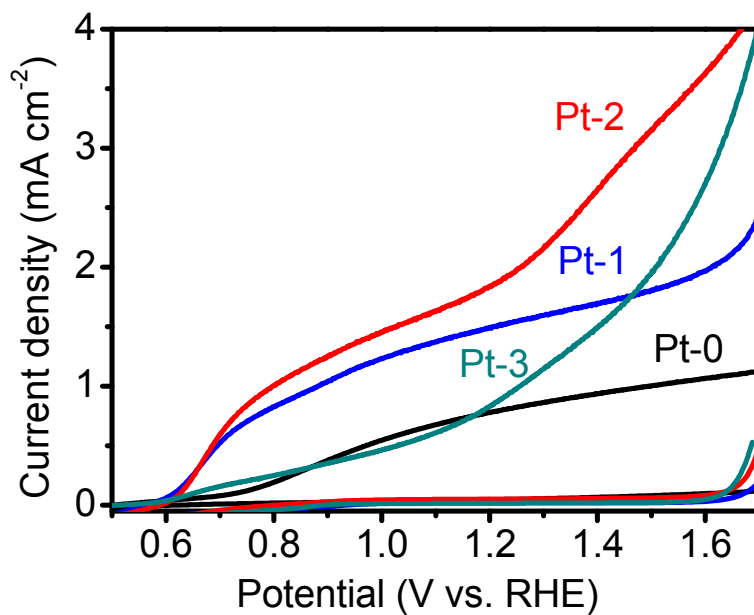


Figure S4 J - V curves of FeOOH/ $\alpha\text{-Fe}_2\text{O}_3$ NFs/Pt- x photoanodes in 5 mM H_2PtCl_6 aqueous solutions for various times. Pt-0: reference NFs, Pt-1: 2 h; Pt-2: 6 h; Pt-3: 10 h.

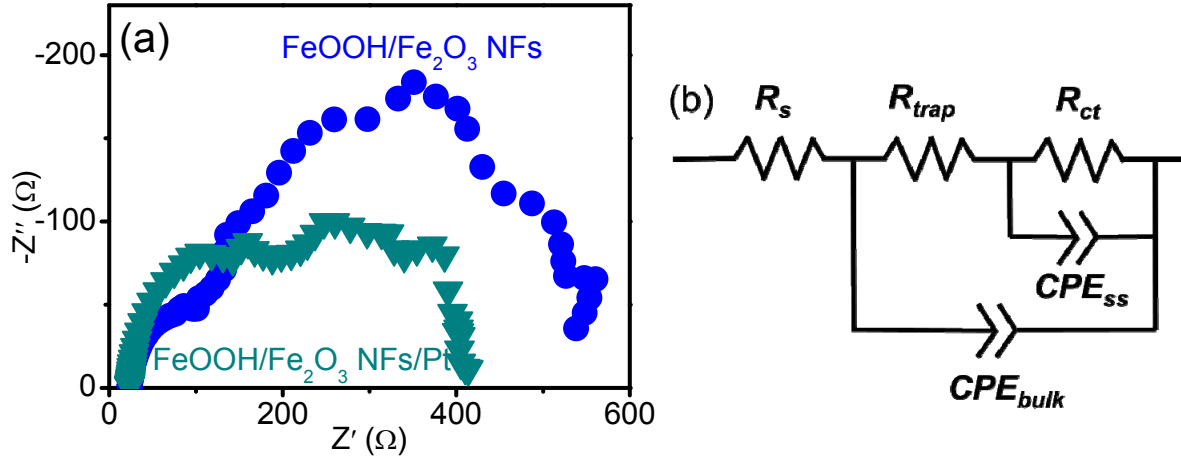


Figure S5 (a) Electrochemical impedance spectroscopy (EIS) of FeOOH/ α -Fe₂O₃ NFs and FeOOH/ α -Fe₂O₃ NFs/Pt photoanodes. The EIS measurements were carried out in 1 M KOH at 1.23 V_{RHE} under AM 1.5G (100 mW cm⁻²) illumination; (b) equivalent circuit model for the photoanodes of EIS as shown in Figure 3d. The α -Fe₂O₃ NFs samples were immersed in 5 mM H₂PtCl₆ and 5 mM FeCl₃ solutions for 6 h for FeOOH/ α -Fe₂O₃ NFs/Pt and FeOOH/ α -Fe₂O₃ NFs, respectively.

Table S1 EIS fitting results of R_{trap} and R_{ct} for α -Fe₂O₃ NFs, Pt/ α -Fe₂O₃ NFs, FeOOH/ α -Fe₂O₃ NFs, and FeOOH/ α -Fe₂O₃ NFs/Pt photoanodes as shown in Figure 3d.

| Sample | α -Fe ₂ O ₃ NFs | Pt/ α -Fe ₂ O ₃ NFs | FeOOH/ α -Fe ₂ O ₃ NFs | FeOOH/ α -Fe ₂ O ₃ NFs/Pt |
|-------------------------|---|--|--|--|
| R_{trap} (Ω) | 1372 | 1993 | 373 | 294 |
| R_{ct} (Ω) | 4820 | 6025 | 656 | 403 |

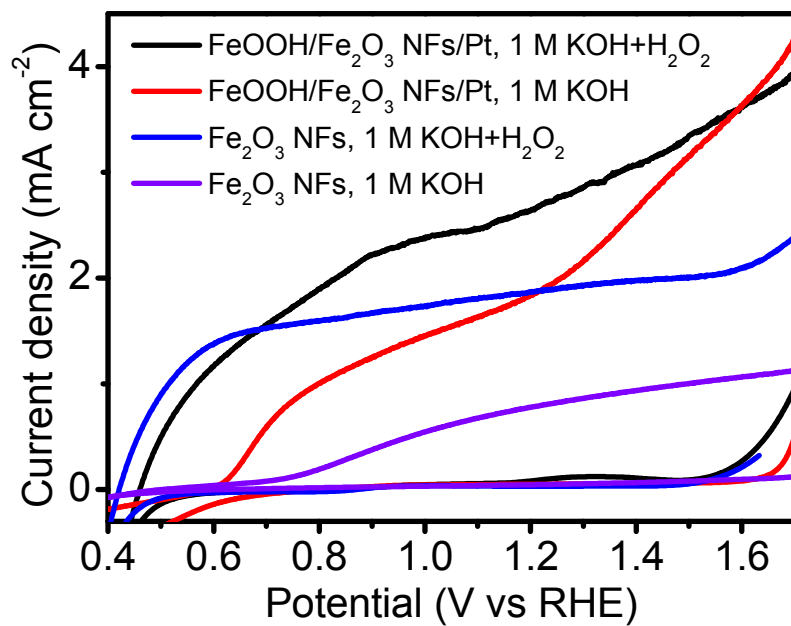


Figure S6 *J-V* curves for α -Fe₂O₃ NFs and FeOOH/ α -Fe₂O₃ NFs/Pt photoanodes in 1 M KOH containing H₂O₂ under AM 1.5G illumination.

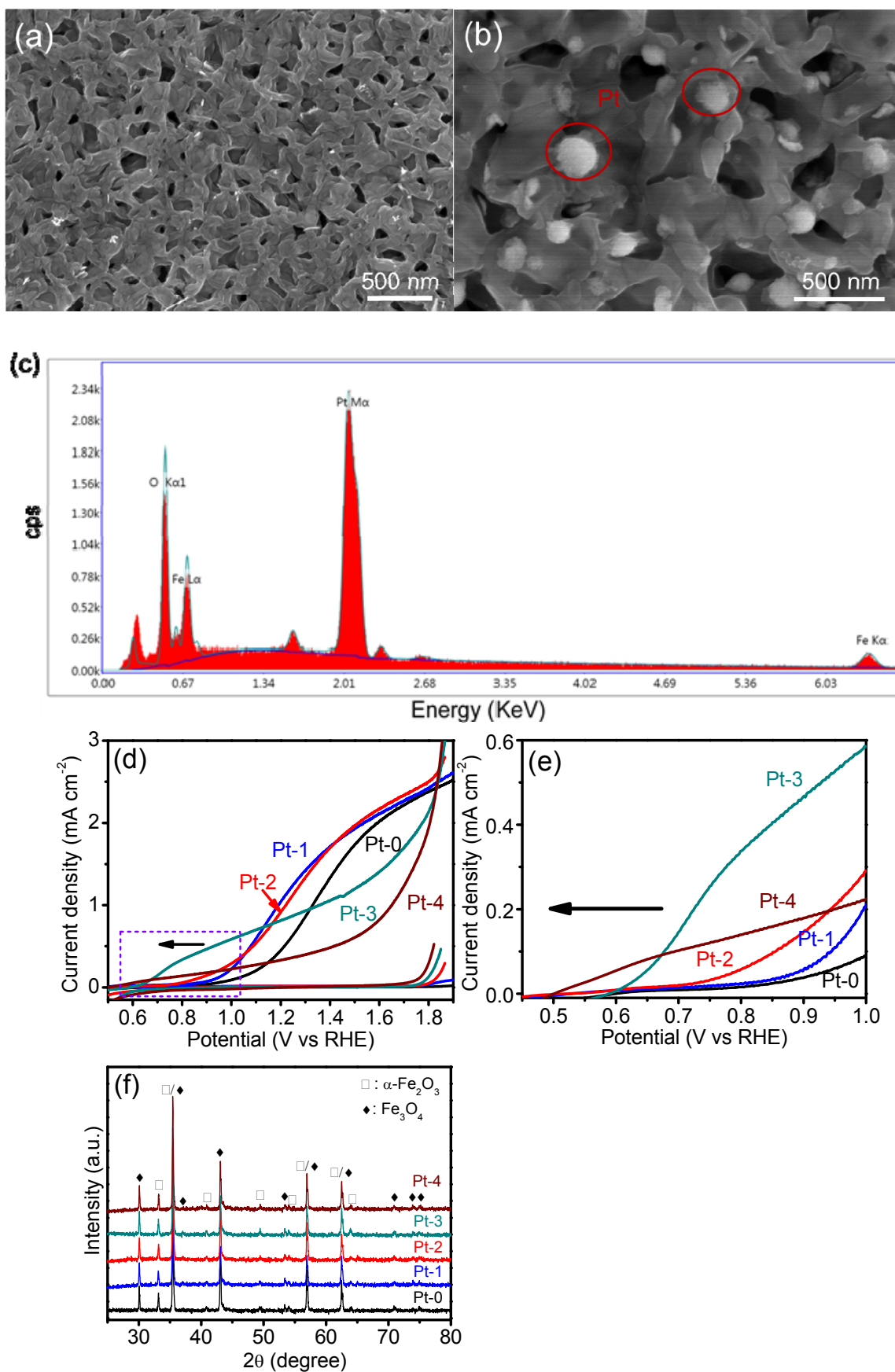


Figure S7 (a,b) SEM images of (a) α -Fe₂O₃ NCs and (b) FeOOH/ α -Fe₂O₃ NCs/Pt samples; (c) SEM-EDS scanning of FeOOH/ α -Fe₂O₃ NCs/Pt sample; (d) J - V curves of FeOOH/ α -Fe₂O₃

NCs/Pt-x photoanodes in H_2PtCl_6 aqueous solutions for various times; (e) J - V curves in the range of $0.45 V_{\text{RHE}}$ to $1.0 V_{\text{RHE}}$; (f) XRD patterns of corresponding samples. Pt-0: reference NCs, Pt-1: 2 h; Pt-2: 4 h; Pt-3: 8 h; Pt-4: 14 h. The solar water splitting experiments were carried out in 1 M KOH electrolytes under AM 1.5G (100 mW cm^{-2}) illumination.

A top nanocoral (NC) structure is formed on the hematite as the annealing temperature up to 600°C (Figure S7a), while the larger particles around 50-200 nm are found on the top of NCs after decoration with FeOOH and Pt NPs (Figure S7b).

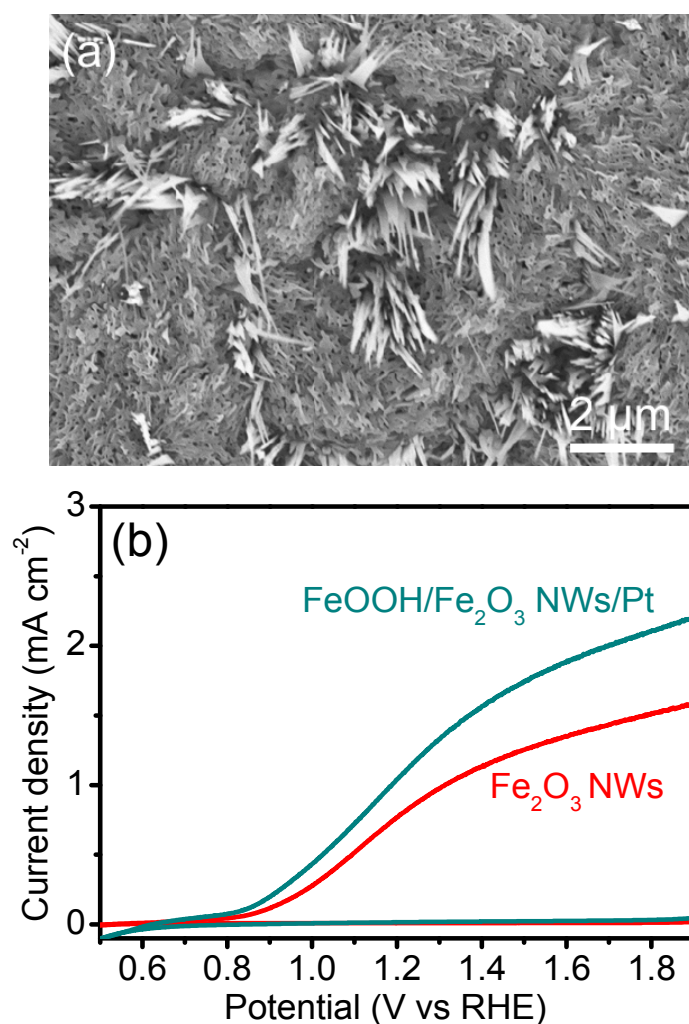


Figure S8 (a) SEM image and (b) J - V curves of FeOOH/ α -Fe₂O₃ NWs/Pt-x photoanodes in H_2PtCl_6 aqueous solutions for 6 h. The solar water splitting experiments were carried out in 1 M KOH electrolytes under AM 1.5G (100 mW cm^{-2}) illumination.

We further increased the annealing temperature to 800 °C, and found that a nanoworm (NW) structure with a thickness of 2-3 μm is obtained on the iron substrate (Figure S8a). In Figure S8b, the pristine $\alpha\text{-Fe}_2\text{O}_3$ NWs photoanode shows an onset potential of 0.8 V_{RHE} , and a photocurrent of 0.8 mA cm^{-2} at 1.23 V_{RHE} . After the treatment in H_2PtCl_6 solution, the photocurrent between 0.8 and 1.8 V_{RHE} is enhanced compared to the as-grown NWs photoanode, - the photocurrent densities of 1.1 mA cm^{-2} and 1.9 mA cm^{-2} are obtained at 1.23 V_{RHE} and 1.60 V_{RHE} , respectively.

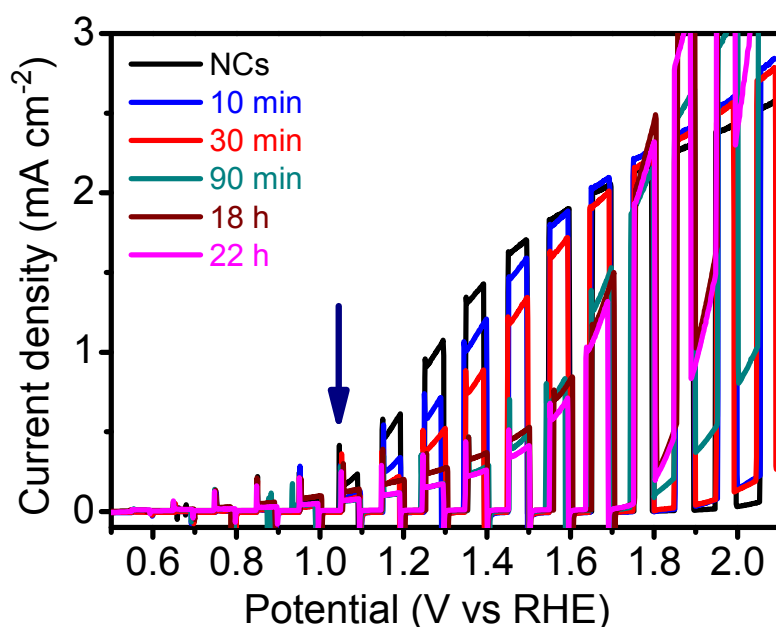


Figure S9 J - V curves of $\text{FeOOH}/\alpha\text{-Fe}_2\text{O}_3$ NCs in 5 mM FeCl_3 aqueous solutions for various times.

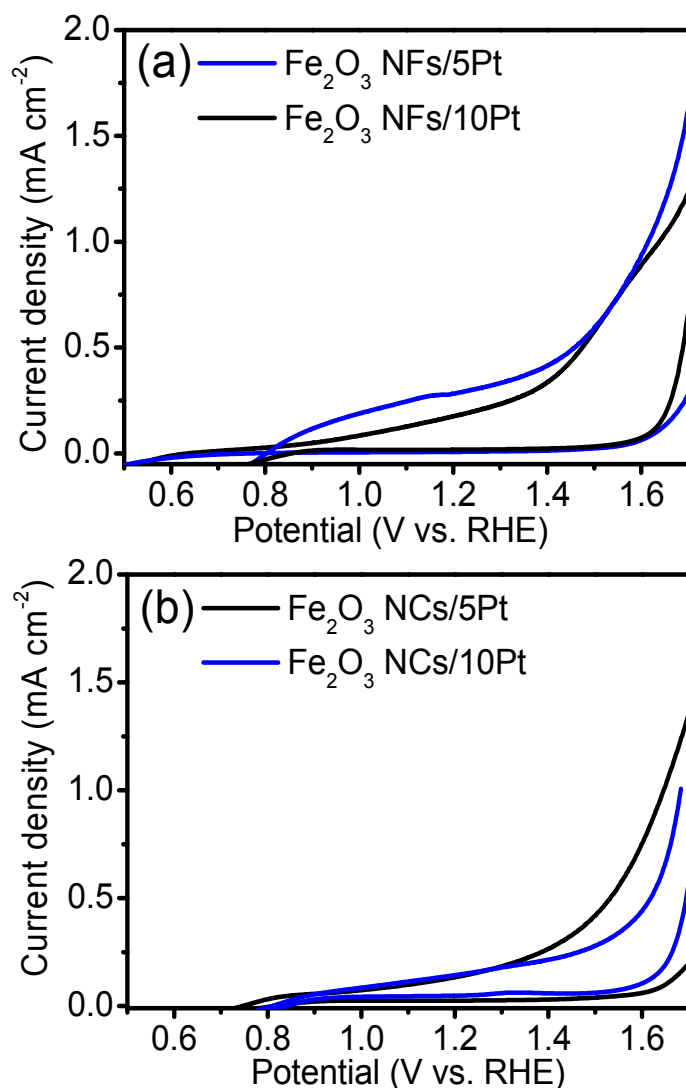


Figure S10 J - V curves of (a) Pt/ α - Fe_2O_3 NFs and (b) Pt/ α - Fe_2O_3 NCs photoanodes. The α - Fe_2O_3 samples were sputtered for 5 sec and 10 sec Pt nanoparticles, respectively.

The Pt nanoparticles deposited on the hematite NFs and NCs were carried out, and the J - V curves were shown in Figure S10. After sputtering Pt nanoparticles on the hematite, both of NFs and NCs photoanodes show a decay in the photocurrent compared to the pristine ones. Moreover, with increasing sputtering time of Pt nanoparticles, they show a decreased photoresponse, indicating that Pt NPs on the top surface could not promote the efficient electron-hole separation and transport for water oxidation.

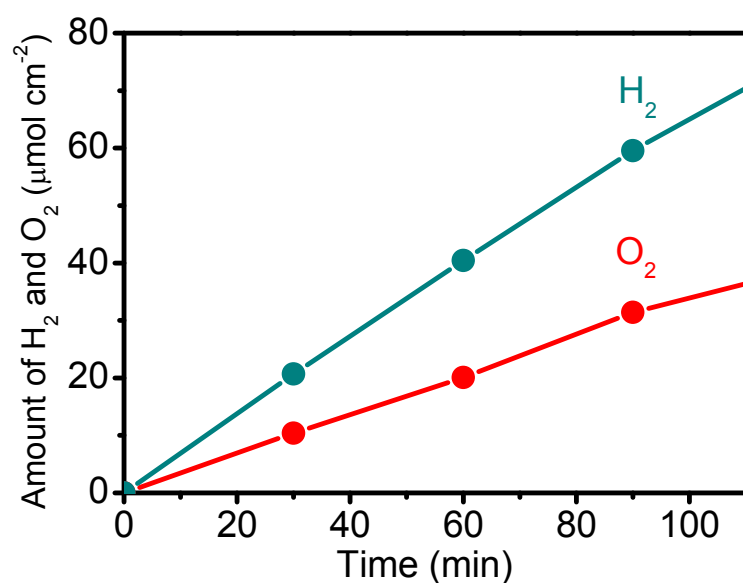


Figure S11 Time dependence of H₂ and O₂ gases from FeOOH/ α -Fe₂O₃ NFs/Pt sample at 1.6 V_{RHE} in 1 M KOH under AM 1.5G illumination (100 mW cm⁻²).

The hydrogen and oxygen evolution was tested by gas chromatography during the stability measurement (at 1.6 V_{RHE}) as shown in Fig. S11, and the stoichiometric ratio of H₂ and O₂ is almost kept at 2:1.

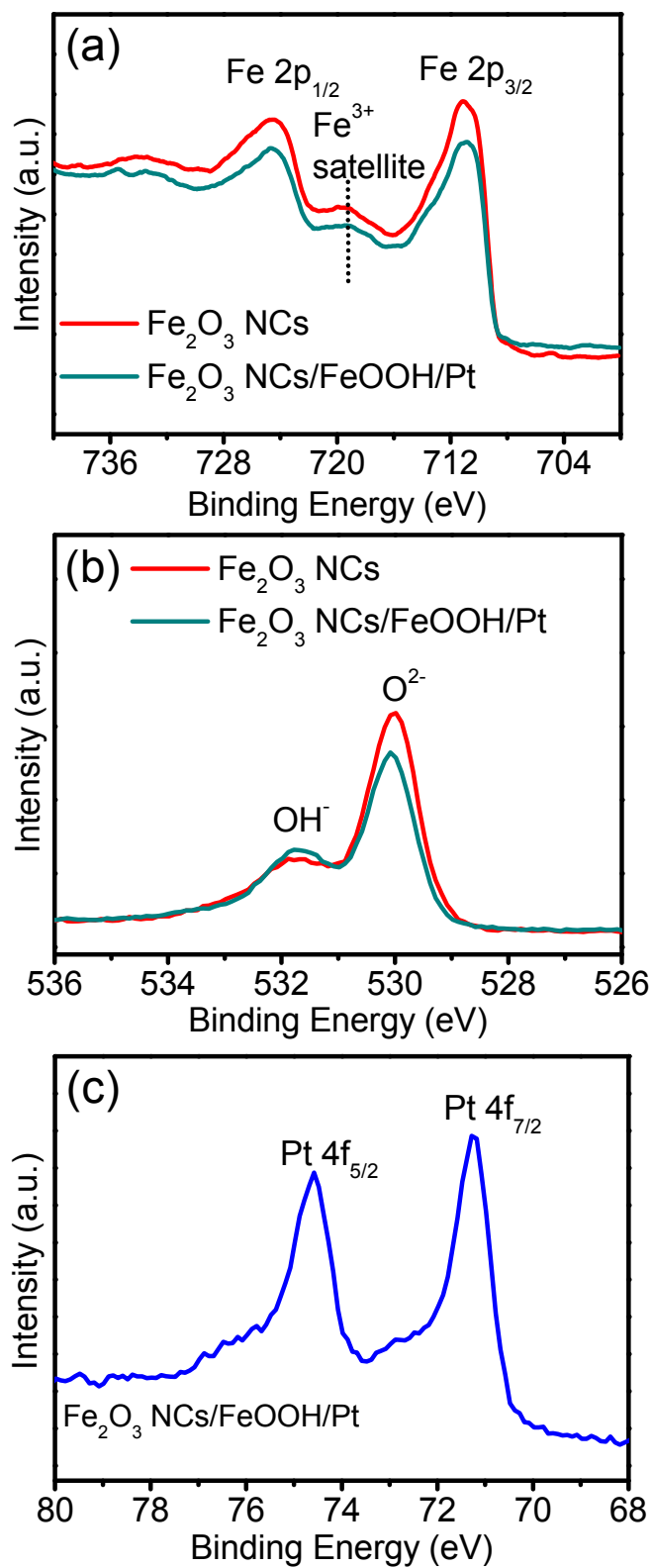


Figure S12 High resolution (a) Fe 2p, (b) O 1s, and (c) Pt 4f spectra of α -Fe₂O₃ NCs and α -Fe₂O₃ NCs/FeOOH/Pt samples. The α -Fe₂O₃ NFs were immersed in a 5 mM H₂PtCl₆ solution for 2 h.

For the α -Fe₂O₃ NCs/FeOOH/Pt sample, it shows the Fe 2p spectra (Fig. S12a) at 724.7 eV (Fe 2p_{1/2}) and 710.9 eV (Fe 2p_{3/2}) with a shake-up satellite line at 719.2 eV, which are characteristic for Fe³⁺ in α -Fe₂O₃ NCs and α -Fe₂O₃ NCs/FeOOH/Pt samples. Moreover, the α -Fe₂O₃ NCs/FeOOH/Pt sample has a relatively higher intensity of OH peak than that for the pristine NCs (Fig. S12b). The α -Fe₂O₃ NCs/FeOOH/Pt sample in the Pt 4p region (Fig. S12c) shows two major peaks at 74.6 eV (Pt 4f_{5/2}) and 71.2 eV (Pt 4f_{7/2}), which can be assigned to metal Pt. These results confirm the formation of FeOOH and Pt on the α -Fe₂O₃ NCs.

Table S2 Summary of recent key advances in hematite-based photoanodes for PEC water splitting under AM 1.5G illumination (100 mW cm⁻²)

| Photoanodes | Photocurrent density at 1.23 V _{RHE} | Onset potential | Electrolyte |
|--|---|----------------------------|----------------|
| Fe ₂ O ₃ on FTO ¹ | 1.98~3.3 mA cm ⁻² | 0.9 V _{RHE} | 1 M NaOH |
| Co-Pi/Pt doped Fe ₂ O ₃ on FTO ² | 4.32 mA cm ⁻² | 0.6 V _{RHE} | 1 M NaOH |
| Ultrathin FeOOH modified Fe ₂ O ₃ NRs on FTO ³ | 1.21 mA cm ⁻² | 0.65 V _{RHE} | 1 M NaOH |
| C/Co ₃ O ₄ -Fe ₂ O ₃ NRs on FTO ⁴ | 1.48 mA cm ⁻² | ~0.8 V _{RHE} | 1 M NaOH |
| Mesoporous single crystalline Fe ₂ O ₃ on FTO ⁵ | 0.61 mA cm ⁻² | 0.95~1.0 V _{RHE} | 1 M NaOH |
| Gradient P doped Fe ₂ O ₃ nanobundles on FTO ⁶ | ~1.48 mA cm ⁻² | 0.8 V _{RHE} | 1 M KOH |
| ZrO ₂ induced Fe ₂ O ₃ nanotubes on FTO ⁷ | ~1.5 mA cm ⁻² | 0.8 V _{RHE} | 1 M KOH |
| FeOOH/Fe₂O₃/Pt on iron substrate in this work | 2.0 mA cm⁻² | 0.6 V_{RHE} | 1 M KOH |

Here it should be mentioned that for the hematite-based nanostructures grown on FTO, it need a higher temperature (higher than 750 °C) to activate and leads to Sn diffusion from FTO substrates to the hematite photoanodes (Sn doping). However, in our work, we have gone to the efforts to greatly reduce the surface and interface recombination by coupling electron and hole transfer layers-spatial separated FeOOH and Pt on one dimensional hematite photoanodes without additional doping, leading to a lower onset potential and a higher photoresponse.

References

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