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Electronic Supplementary Information(EIS)

A novel wide-spectrum response hexagonal $YFeO_3$ photoanode for solar water splitting

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Experimental

1. Preparation of $YFeO_3$ powder

$YFeO_3$ nanoparticles were prepared by a citric acid assisted sol-gel process. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3•9H_2O$ 98.5% China National Pharmaceutical Group Corporation), yttrium nitrate hexahydrate ($Y(NO_3)_3•6H_2O$ 99.9% Aladdin) and citrate ($C_6H_8O_7$ 99.5% Aladdin) with a 1:1:4 molar ratio were added into 120 mL deionized water under vigorous stirring. The citrate was used as complexing agent to not only chelate metal ions, but also prevent aggregation and hydrolyzation. Subsequently, the solution was kept at 75 °C for 4 h to make sure that metal ions can be fully chelated and then heated up to 120 °C to speed up the evaporation process under vigorous stirring until there was no water left. Put the sol in the 120 °C oven for another 12 h to fully dehydrate and puff. The porous crumb gel was obtained after dehydrating and puffing. The gel was calcined at 450 °C for 3 h to obtain a dark brown fluffy power product, which was used as the precursor of $YFeO_3$. The precursor calcined at various temperatures (700 °C and 800 °C) for 3 h in air. After nature cooling, the products were obtained.

2. Preparation of $YFeO_3$ nanoparticle photoelectrodes

The fluorine-doped tin oxide (FTO) coated glass (1 cm×2 cm) was cleaned using successive ultrasonication with deionized water, sodium hydroxide, hydrochloric acid, acetone and ethanol for 30 min, respectively. The $YFeO_3$ nanoparticle-assembled films were prepared by electrophoretic deposition. $YFeO_3$ (40 mg) and I_2 (10 mg) were added into 50 mL acetone via ultrasonic concussion for 30 min. The DC power was used as the external power supply. The voltage is 15 V. The deposition time is 5 min. The thickness of the films can be controlled by altering deposition time, such as 1 min, 2 min, 3 min and 5 min, etc. After drying in air, the films were dropped with 10 mM $TiCl_4$ methanol solution then dried again in air. Subsequently, the films were calcined at 300 °C for 3 min. This procedure was repeated for four to six times. Finally, the post treated films were heated at 650 °C for 1 h and then 700 °C for 10 min in air.

3. Characterization of the samples

The crystal structure of these as-prepared samples were determined by powder X-ray diffraction (XRD, Rigaku Ultima III, Cu K_{α} radiation) at 40 kV and 40 mA. The XRD spectra were collected at a scanning speed of 0.02° per step over a 2θ range from 10° to 80°. The morphologies of the samples were examined with a scanning electron microscope (SEM; ZEISS ULTRA 55 with an accelerating voltage of 3 kV) and a transmission electron microscope (TEM, JEOL JEM-200CX). Optical reflectance and transmittance properties of the samples were measured with a Shimadzu UV-2550 spectrophotomerer. The Mott-Schottky curves were measured using an electrochemical analyzer (CHI-760E, Shanghai Chenhua, China) in a three-electrode system. The electrolyte was 1 M NaOH aqueous solution (pH = 13.6). The ac amplitude was 5 mV and the frequency was 500 Hz.

4. Photoelectrochemical (PEC) performance measurements

The photoelectrochemical (PEC) performance of the films were tested in a three-electrode system using an electrochemical analyzer (CHI-660D, Shanghai Chenhua, China). The electrolyte was 1 M NaOH aqueous solution (pH = 13.6). The $YFeO_3$ nanoparticle-assembled photoanode was used as a working electrode. A Pt wire and a saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. The films area exposed to the light was 1 cm^2. The light source was AM 1.5 G simulated sunlight. The light intensity was 100 mW cm^{-2}. The photocurrent of the samples was measured under the back-side illumination. Linear sweep voltammetry (LSV) was performed with a scan rate of 30 mV s^{-1}.

All the potentials described in this study refer to the reversible hydrogen electrode (RHE) potential, which was calculated following the formula[1]:

$$E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.059\mathrm{pH} + E^{0}_{\mathrm{SCE}}$$

where E_{RHE} is the converted potentials vs. RHE, E_{SCE} is the saturated calomel electrode potential, E^{0}_{SCE} is the potential of SCE and is 0.242 V at 25 °C, and pH is the pH value of electrolyte.

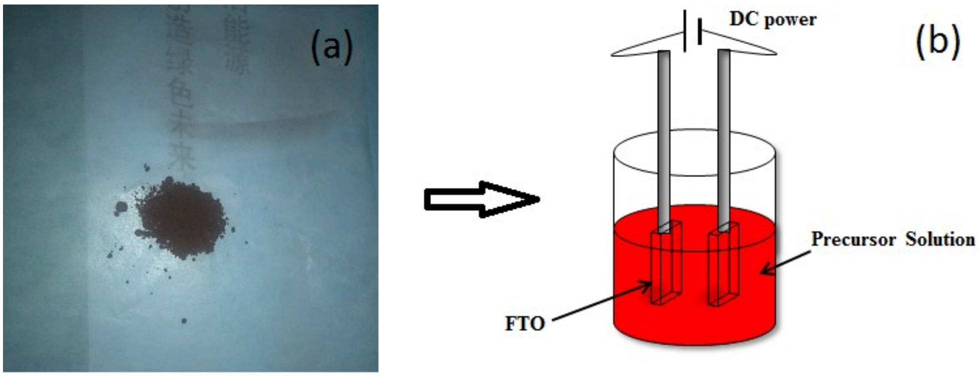
The incident photo-to-electron conversion efficiency (IPCE) was obtained using the same three-electrode setup and 1 M NaOH aqueous solution (pH = 13.6) under the illumination of monochromatic light. The IPCE spectra was measured at a constant potential (1.6 V vs. RHE), at the wavelength from 350 nm to 589 nm. The IPCE was calculated from the current density recorded at different wavelength using the following formula[2]:

$$\mathrm{IPCE}\ (\lambda) = 1240\, j\, /(P_{\mathrm{light}} \times \lambda)$$

where j is the measured current density (mA cm^{-2}), P_{light} is the incident light intensity (mW cm^{-2}) for each wavelength, and λ is the wavelength (nm) of the incident light at the measured photocurrent and illumination intensity. Xe lamp (Ushio) is used as the light source. The monochromatic light is obtained by Xe lamp passed through a monochromator from 350 nm to 589 nm. The power of single wavelength is measured by light intensity meter (840-C, Newport, USA).

I-t curve was recorded at a constant potential of 1.23 V vs. RHE in a standard three-electrode system with a sample interval of 0.1 s under the illumination of AM 1.5 G simulated sunlight.

5. A brief schematic illustration of the photoelectrode preparation procedure



Scheme S1 Schematic illustration of the photoelectrode preparation procedure of $YFeO_3$ nanoparticle-assembled photoanode. (a) $YFeO_3$ precursor powder; (b) The experimental apparatus of electrophoretic deposition for preparing photoelectrodes.

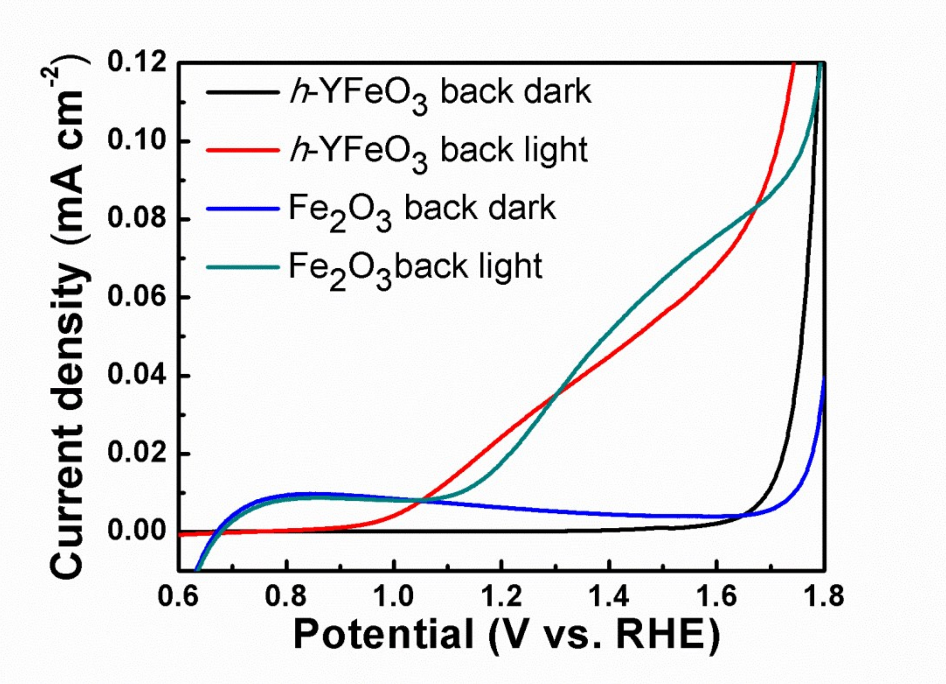


Fig. S1 Current-potential curves of *h*-YFeO$_3$ and hematite nanoparticle-assembled photoanodes measured in 1 M NaOH aqueous solution under AM 1.5 G illumination (100 mW cm^{-2}).

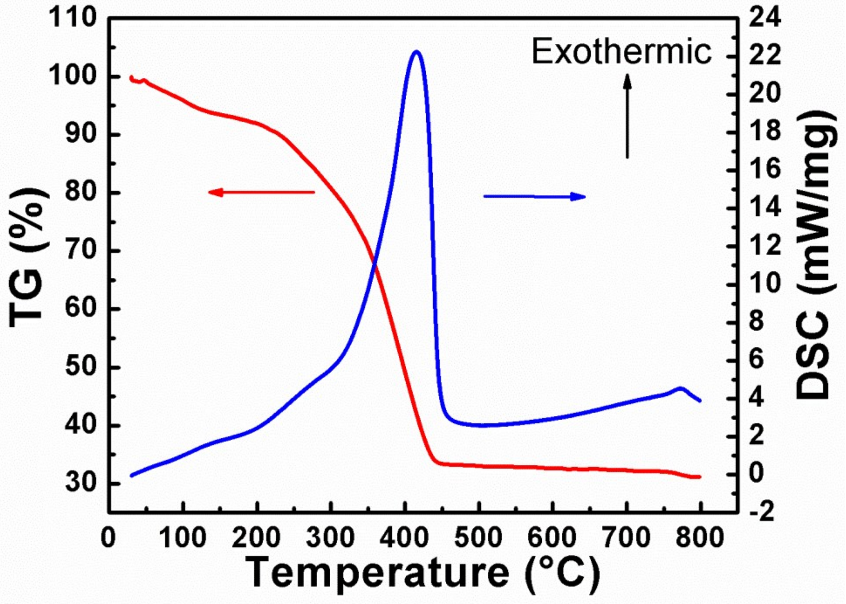


Fig. S2 TG-DSC of sol-gel YFeO$_3$

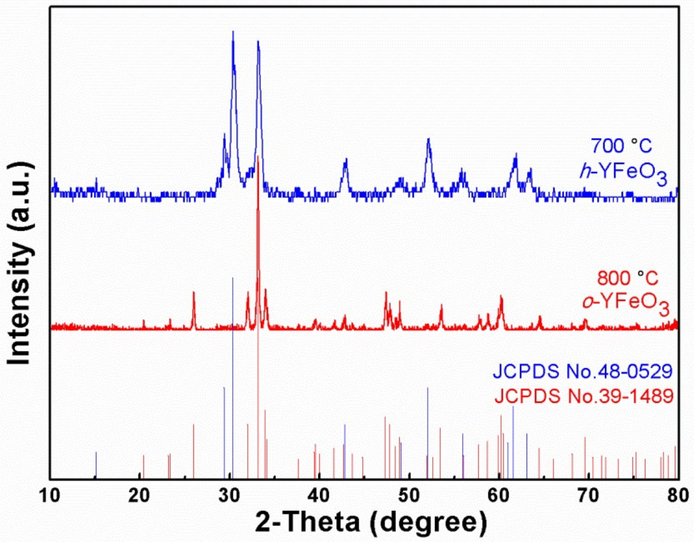


Fig. S3 XRD patterns of $YFeO_3$ nanoparticles obtained at different calcination temperatures: *h*-$YFeO_3$ (JCPDS card No. 48-0529) and *o*-$YFeO_3$ (JCPDS card No. 39-1489).

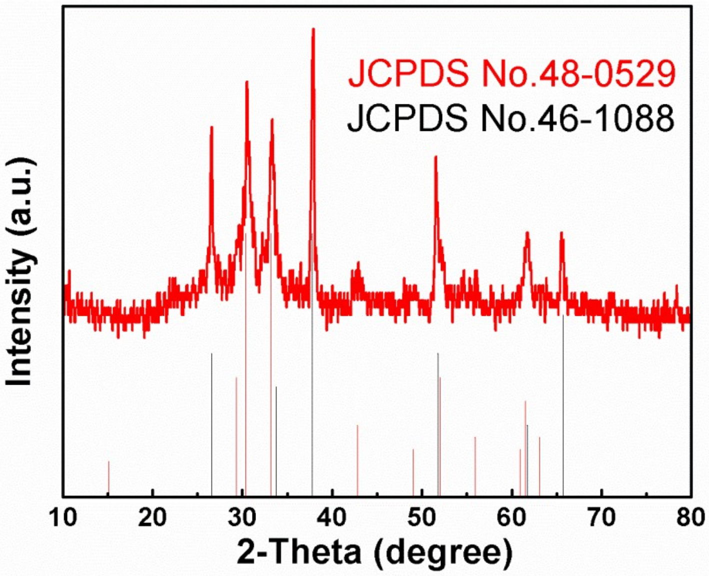


Fig. S4 XRD pattern of *h*-$YFeO_3$ nanoparticle-assembled films annealed at 650 ^{o}C for 1 h and then 700 ^{o}C for 10 min.

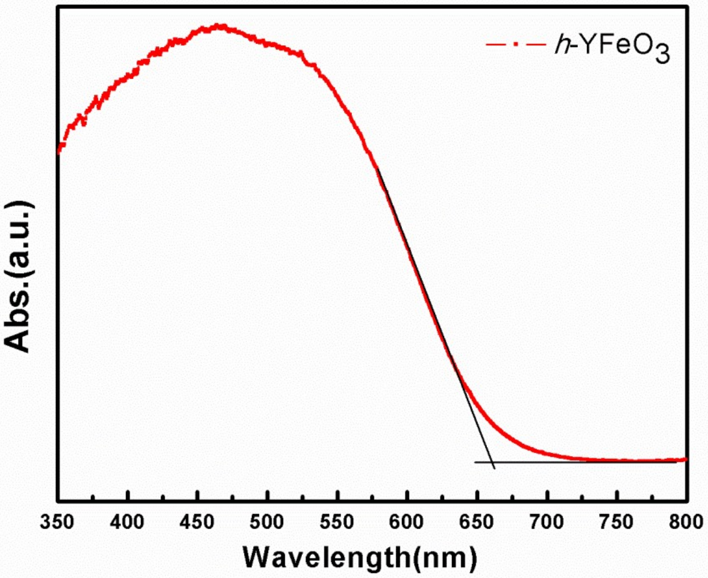


Fig. S5 UV-vis absorption spectra obtained for the *h*-$YFeO_3$ powder.

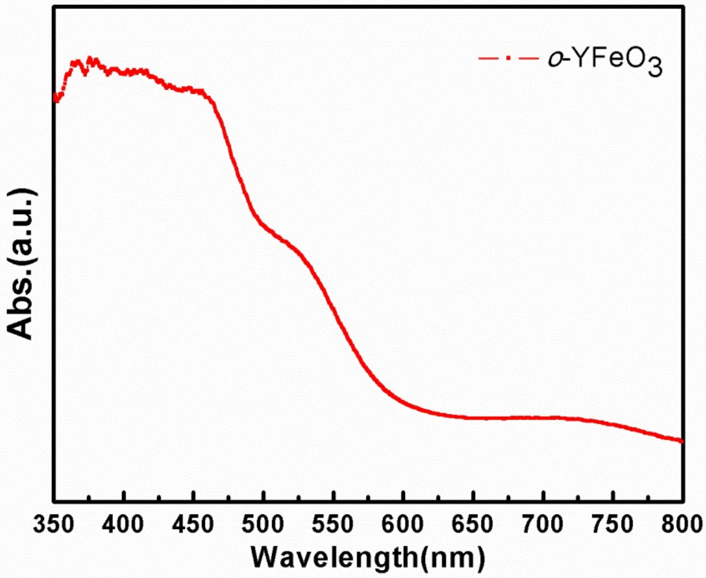


Fig. S6 UV-vis absorption spectra obtained for the *o*-$YFeO_3$ powder.

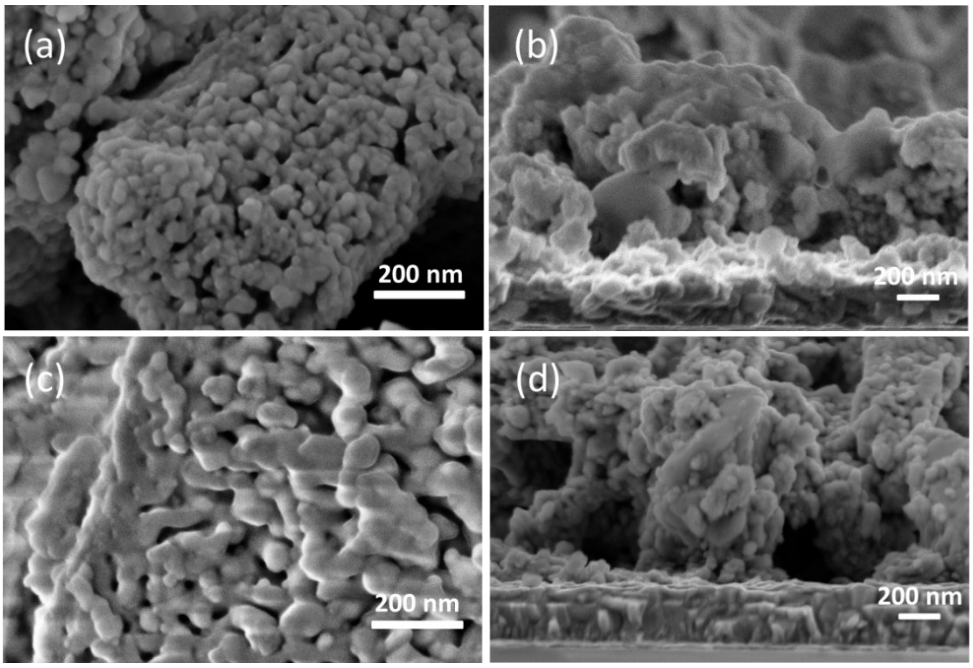


Fig. S7 SEM images for the nanoparticle-assembled films. (a) top view of *h*-$YFeO_3$ photoelectrode; (b) cross section of *h*-$YFeO_3$ photoelectrode; (c) top view of *o*-$YFeO_3$ photoelectrode and (d) cross section of *o*-$YFeO_3$ photoelectrode.

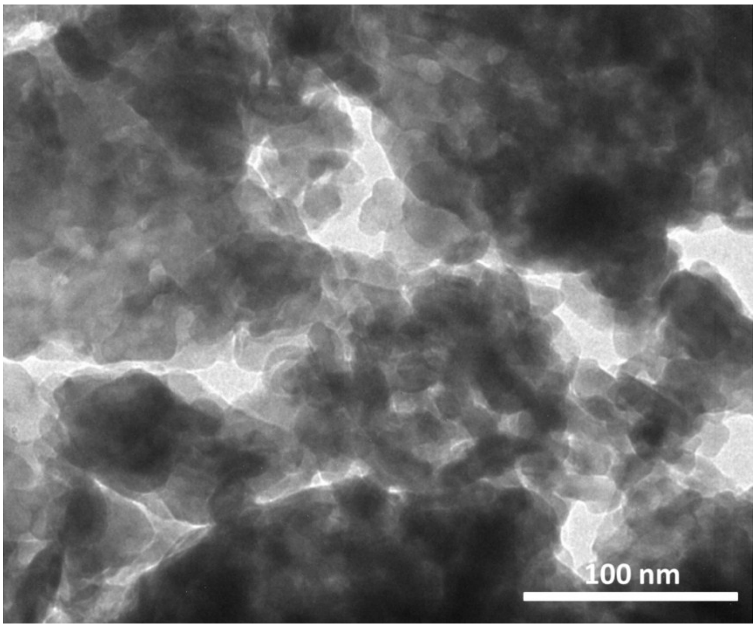
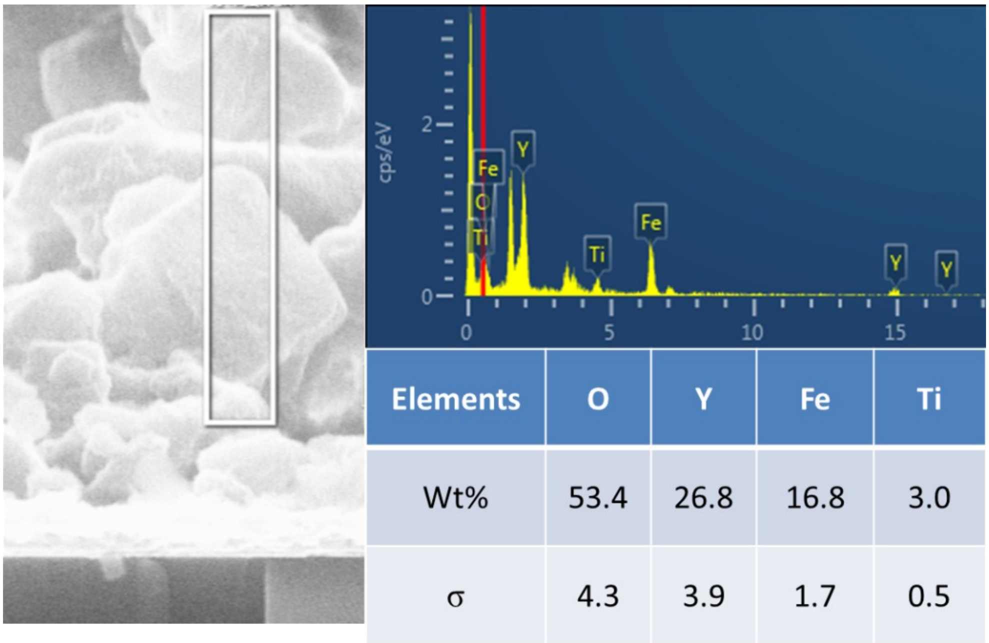


Fig. S8 TEM image of *h*-$YFeO_3$ nanoparticles.



Elements	O	Y	Fe	Ti
Wt%	53.4	26.8	16.8	3.0
σ	4.3	3.9	1.7	0.5

Fig. S9 EDS spectrum of the cross-section view of *h*-$YFeO_3$ nanoparticle-assembled film.

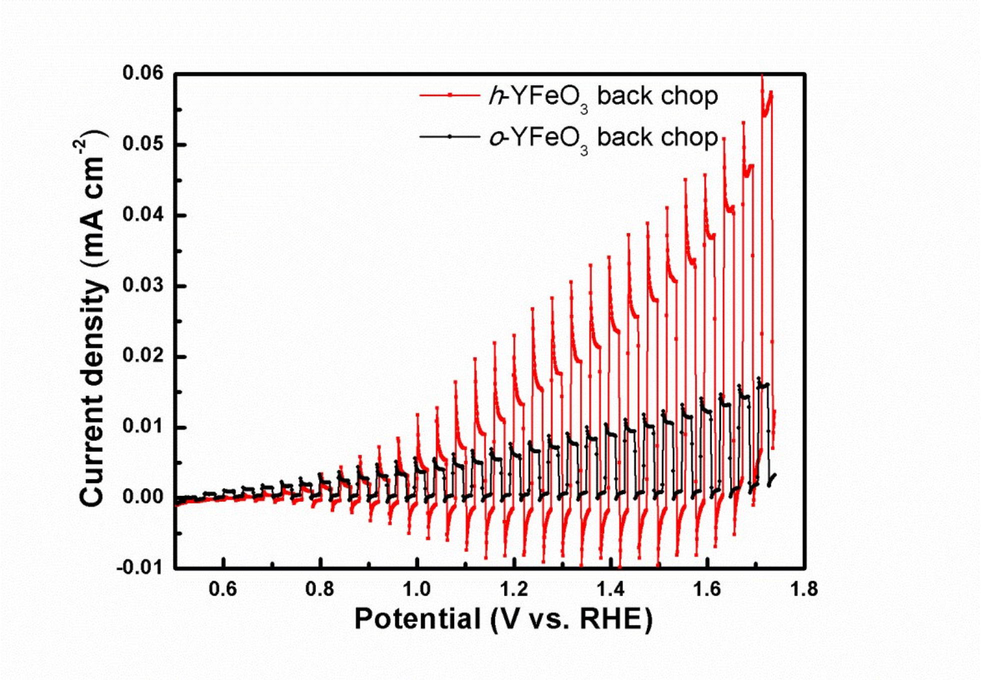


Fig. S10 Linear sweep voltammograms for the *h*-$YFeO_3$ and *o*-$YFeO_3$ nanoparticle-assembled films under chopped light with a scan rate of 30 mV s^{-1} in 1 M NaOH aqueous solution (pH = 13.6).

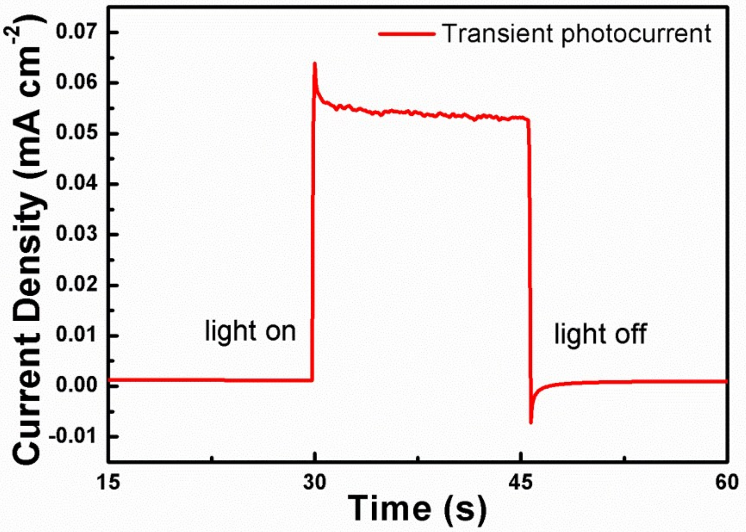


Fig. S11 Transient photocurrent curve of *h*-YFeO$_3$ nanoparticle-assembled film at the potential of 1.6 V vs. RHE.

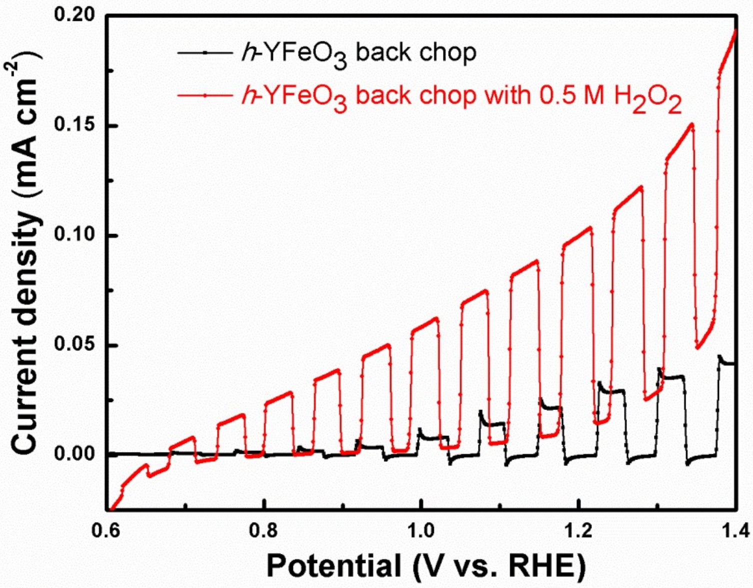


Fig. S12 Linear sweep voltammograms of *h*-YFeO$_3$ nanoparticle-assembled films under chopped light with a scan rate of 30 mV s^{-1} in 1 M NaOH with 0.5 M H$_2$O$_2$ aqueous solution (pH = 13.6).

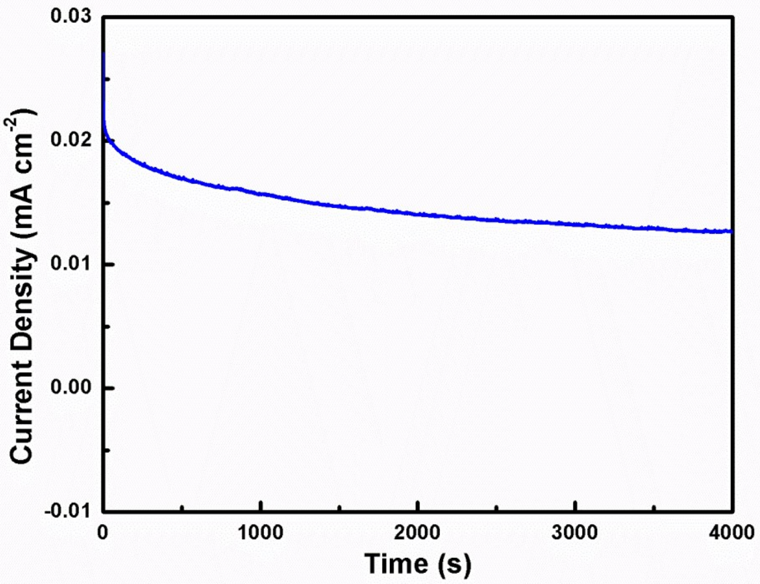


Fig. S13 Photocurrent-time curve of *h*-$YFeO_3$ nanoparticle-assembled film measured at a potential of 1.23 V vs. RHE.

References

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2 A. Wolcott, W. A. Smith, T. R. Kuykendall, Y. Zhao and J. Z. Zhang, *Adv. Funct. Mater.*, 2009, **19**, 1849.