

Facile fire treatment of nanostructured hematite with enhanced photoelectrochemical water splitting performance

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Experimental details:

Material preparation

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Acros, 99+%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Aladdin, 99%), $\text{SnCl}_4 \cdot 9\text{H}_2\text{O}$ (Sinopharm, 99%), NaNO_3 (Sinopharm, 99%), Citric acid (Alfa Aesar, 99+%), Ethylene glycol and Ethanol (Fluka, 99.8%) were used in the synthesis.

In a typical experiment, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.00 mmol, 0.808 g), citric acid (5.00 mmol, 1.05 g) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.1 mmol, 35.0 mg) were mixed in 10 mL of ethanol. After stirring for at least 2 h, ethylene glycol (10.0 mmol, 0.5 mL) was added to the mixture, which was stirred for another 2 h. The resulting solution was spin coated onto a clean fluorine-doped tin oxide (FTO) glass substrate at 2000 rpm for 1 min. The resulting films were dried on a hot plate at 100 °C for 10 min, and then annealed in air at 450 °C in muffle furnace for 60 min to remove the traces of organic material, followed by annealing at 800 °C (ramp rate: 15 °C·min⁻¹) for additional 20 min.

Hematite nanowires were prepared on a fluorine-doped tin oxide (FTO) glass substrate by a previously reported method.¹ A Teflon-lined stainless steel autoclave was filled with 20 ml aqueous solution containing 0.1 M of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 0.1 M sodium nitrate (NaNO_3). The solution pH was adjusted to 1.4 by HCl. A pre-cleaned piece of FTO glass substrate was put into the autoclave. The autoclave was heated at 95 °C for 6 h and allowed to cool down at ambient conditions. A uniform layer of iron oxyhydroxide ($\alpha\text{-FeOOH}$) film (yellow in color) was formed on the FTO substrate. The $\alpha\text{-FeOOH}$ film was washed with deionized (DI) water to remove residual salt. To introduce Sn-doping into the nanowires, we intentionally added 1-2 drops of tin (IV) chloride (SnCl_4) ethanol solution (2 mg/ml) onto the $\alpha\text{-FeOOH}$ film, and then sintered in air at 550 °C for 30 min, followed by annealing at 800 °C for additional 20 min.

The hematite thin films and the hematite nanowires on FTO were burned with a cigarette lighter, and keep moving for 30 s to prevent local overheating. Afterwards, the hematite thin films were allowed to cool down at ambient conditions and washed with deionized (DI) water to remove residuals.

Co-Pi was coated on the surface of the hematite thin films by photoassisted electrodeposition using a three electrode cell consisting of an Ag/AgCl (KCl sat.) reference electrode, a platinum plate as counter electrode, and photoanodes as working electrode. Electrolyte used was a 0.5 mM $\text{Co}(\text{NO}_3)_2$ solution (Alfa Aesar, puratronic, 99.999%) in 0.1 M potassium phosphate buffer (Acros Organics, monobasic, 99+ %, ACS reagent) titrated to pH 7 with 1 M NaOH (Reactolab SA, pur past.). The catalyst was deposited potentiostatically with an applied potential of +0.3 V vs. Ag/AgCl (KCl sat.) under illumination for 4 min.

Characterization

UV-Vis total reflectance spectra of hematite thin films were recorded with a UV-VIS-NIR Lambda 750S (PerkinElmer) spectrophotometer, equipped with an integrating sphere. The surface morphologies were observed with a Hitachi S-4800 field-emission scanning electron microscope (SEM). Transmission electron microscope (TEM) analysis was carried out on a JEOL JEM-2100F instrument. The oxidation states were analyzed with an X-ray photoelectron spectroscopy (XPS, Perkinelmer, PHI1600 ESCA). The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference. The Photoluminescence (PL) spectra and Raman spectra were obtained with a Renishaw inVia Reflex Raman microscope and spectrometer. Monochromatic illumination for IPCE measurement was provided by a 150 W Xe Tunable PowerArc Illuminator (Changzhou Hongming Instrument Technology Co., Ltd.) and the

number of photons at each wavelength was measured with a photodiode power sensor (Changzhou Hongming Instrument Technology Co., Ltd.).

. Photoelectrochemical response measurements were carried out using a three-electrode setup, with a platinum counter-electrode and a Ag/AgCl/KCl(sat.) reference electrode ($E = 0.210$ V vs NHE). All the potentials in this work are converted using the reversible hydrogen electrode (RHE) as the reference electrode, according to the following equation::

$$E(RHE) = E(Ag/AgCl) + 0.197 + 0.059 \times pH \quad (1)$$

The surface area of the film in contact with the electrolyte (1.0 M NaOH) was 1.0 cm². The electrochemical behaviour was monitored with an IVIUM compactstat, while the light was provided by a 300 W Xenon-arc lamp, calibrated to provide 1 sun (100 mW·cm⁻²) of AM 1.5 illumination to the sample. The measurement of H₂ and O₂ was carried out by connecting the photoelectrochemical cell to a sealed system to circulate the gas toward the gas chromatograph (GC, Perkinelmer Clarus 500, TCD detector, carrier gas (Ar) flow rate = 36 mL/min; oven temperature = 50 °C; detector temperature = 120 °C) for the analysis. The sealed system was previously vacuumed to evacuate the air and the dissolved oxygen.

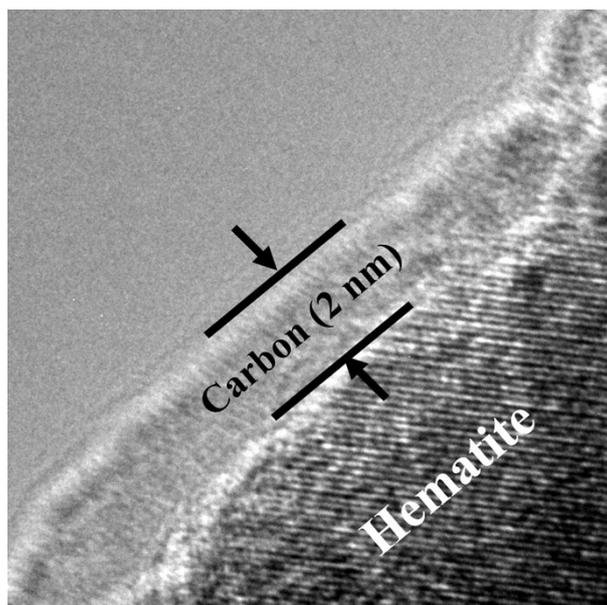


Figure S1. The interfacial TEM image of the hematite photoanode after the butane fire treatment.

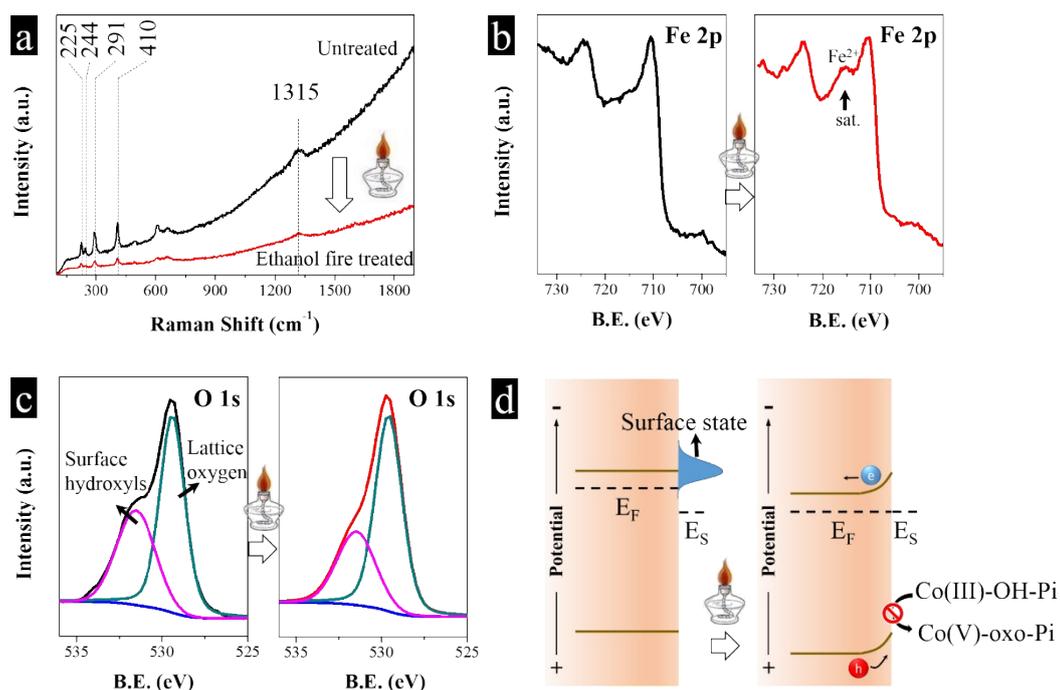


Figure S2. (a) Raman spectra of the hematite thin films before and after the ethanol fire treatment; (b) Fe 2p and (c) O 1s X-ray photoelectron spectra (XPS) of the hematite thin films before and after the ethanol fire treatment; (d) Simplified band diagram of the hematite before and after the ethanol fire treatment.

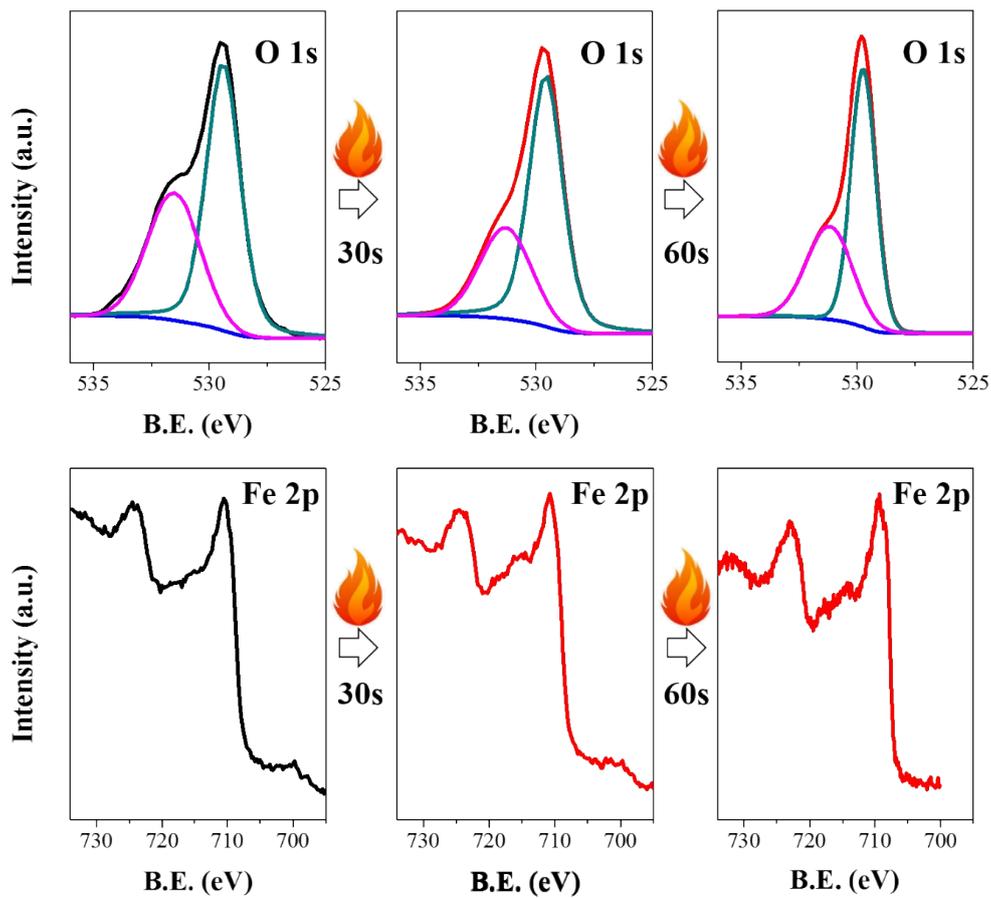


Figure S3. O 1s and Fe 2p X-ray photoelectron spectra (XPS) of the hematite thin films after 0, 30 and 60 s butane fire treatment, respectively.

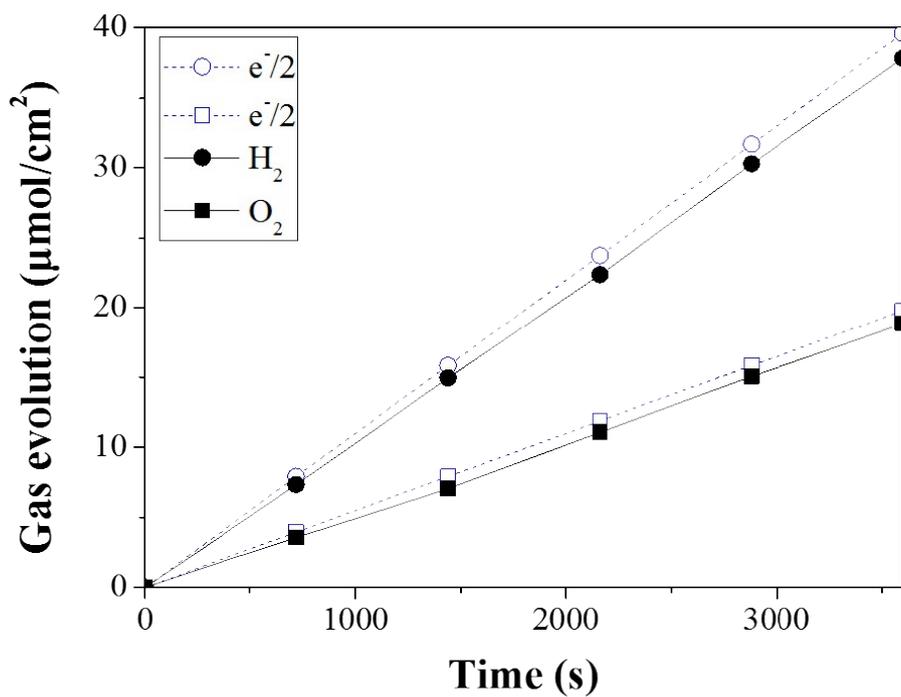


Figure S4. Gas evolution from the butane fire treated hematite photoanode (decorated with Co-Pi cocatalyst), which is compared with the evolution of H₂ (e⁻/2) and O₂ (e⁻/4) expected from the photocurrent. The measurement was performed at constant potential 1.23 V vs. RHE.

References

- 1 Y. Yang, M. Forster, Y. Ling, G. Wang, T. Zhai, Y. Tong, A. J. Cowan and Y. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 3403.