Electronic Supplementary Information

Microwave-assisted fabrication of porous hematite photoanodes for solar water splitting

Yidong Hou*, Chong Zheng, Zezhou Zhu and Xinchen Wang

1. Experimental

1.1 Preparation of the hematite films

The fluorine-doped tin oxide (FTO) coated glass (10 mm×40 mm) was cleaned with acetone, ethanol and deionized, respectively. The hematite films were prepared through two steps according to the reported. Firstly, FeOOH film was grown on FTO by hydrothermal method. Typically, an aqueous solution (10 mL) was adjusted to pH = 1.5 by concentrated hydrochloric acid, which containing 0.15 M FeCl₃, 0.2 M NaF and 0.3 mM TiOCl₂ then was sealed in a 30 mL Teflon liner. The liners were put into a self-sealing autoclave and heated at 100 °C for 10 h. After the reaction, yellow β -FeOOH films deposited on the FTO glass were obtained and the films were rinsed with deionzed water. For microwave assisted annealing, 2.0 g of graphite powder as an effective microwave absorber was placed in a porcelain boat and the yellow β -FeOOH thin film was slightly buried on the flat surface of the graphite to expose only the surface of the thin film. A household microwave oven of 500 W was employed and the annealing was performed for 18 min. The obtained α -Fe₂O₃ was denoted as "Fe₂O₃-MA". For comparison, the yellow β -FeOOH film was converted into α -Fe₂O₃ by conventional annealing in a muffle furnace at 600 °C for 2h. The obtained α - Fe_2O_3 was denoted as " Fe_2O_3 -CA", and its crystal phase and morphology were characterized and the results are shown in Fig. S11.

1.2 Characterization of the samples

X-ray diffraction (XRD) data were collected using a Bruker D8 Advance X-ray diffractometer (Cu K1 irradiation, λ =1.5406Å). The scanning electron microscope (SEM) was collected on a Hitachi New Generation SU8010 field emission scanning electron microscope. Transmission electron microscopy (TEM), energy dispersive X-ray (EDX) spectrum, and the corresponding elemental mapping of the samples were obtained on a FEI Tencai 20 microscope equipped with an EDX spectrometer. UV-Vis diffuse reflectance spectra were collected using a Varian Cary 500 UV-Vis-NIR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific ESCA Lab250 spectrometer which consists of a monochromatic Al K α as the X-ray source. All the binding energies were calibrated by the C1s peak at 284.6 eV. Raman scattering measurements were performed with a multichannel modular triple Raman system (Renishaw Co.) using a confocal microscope with a 532 nm excitation laser.

1.3 PEC performance measurements and electrochemical analysis

The water oxidation photocurrents over hematite films were performed using a Zennium electrochemical workstation with three-electrode configuration. The three electrodes were the working electrode (the hematite film), a platinum-mesh as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode. The hematite photoanode was prepared by sealing a part of the hematite-covered FTO

electrode with scotch tape except for the 1.0 cm² unsealed area left for photoexcitation experiments. Experiments were performed in 1.0 M NaOH aqueous solutions (pH=13.6). A xenon lamp (500 W) was used as the illumination source and illuminated the photoanode with a light cable. The irradiance intensity at the working electrode was measured as ~ 80 mW cm⁻² by a spectroradiometer (International Light Technologies Model RPS-900R). Current measurements were performed in the dark and under light by using linear sweep voltammetry at a scan rate of 20 mV s⁻¹. The potentials obtained *vs.* Ag/AgCl were converted to the reversible hydrogen electrode (RHE) scale according to the Nernst equation ($E_{RHE}=E^{\theta}_{Ag/AgCl}+0.059$ pH+ $E_{Ag/AgCl}$, E_{RHE} is the converted potential *vs.* RHE, $E^{\theta}_{Ag/AgCl}=0.1976$ V at 25 °C and $E_{Ag/AgCl}$ is the experimentally measured potential *vs.* Ag/AgCl reference electrode).

1.4 Hydrogen and oxygen measurements

The photocurrent *vs.* time profile was recorded at a constant potential of 1.23 *vs.* RHE in a standard three-electrode configuration using an H-type glass cell with working electrode and counter-electrode compartments separated by a glass frit. Before the reactions, both the working electrode compartment and the counter electrode part were flushed with Ar, and the cell was closed off. The produced O_2 was detected by a QxySense System with a sensor placed in the headspace of the reaction cell of oxygen evolution part. H₂ quantification was carried out using a gas chromatograph equipped with a thermal conductivity detector.



Fig. S1 (a) SEM and (b) XRD pattern of the obtained β -FeOOH film



Fig. S2 Digital photo of β -FeOOH films (a) before and (b) after microwave-assisted annealing.



Fig. S3 (a)Ti2p and (b) Sn3d XPS spectra of Fe_2O_3 -MA film.



Fig. S4 EDX spectrum Fe₂O₃-MA and its elemental mapping of the selected region.



Fig. S5 Irradiance spectrum of the simulated solar source with Xenon lamp.



Fig. S6 XRD patterns of the α -Fe₂O₃ films obtained from microwave-assisted annealing of β -FeOOH films with different time.



Fig. S7 SEM images of α -Fe₂O₃ films obtained from microwave-assisted annealing of β -FeOOH films with different time.



Fig. S8 Optical absorption spectrum of Fe₂O₃-MA-18min.



Fig. S9 (a) Soar photocurrent spectrum of the optimum Fe_2O_3 -MA electrode at 1.23 V *vs.* RHE obtained by multiplication of its IPCE spectrum with photoflux spectrum of global sunlight (100 mW/m², AM 1.5G); (b) The integrated photocurrent under global sunlight between 300 nm and a given wavelength (integral of curve a).



Fig. S10 Nyquist plots for the electrodes measured at 1.23 V vs. RHE under light illumination.



Fig. S11 XRD, SEM and TEM of Fe_2O_3 -CA film.