Electronic Supplementary Information (ESI)

Highly-oriented $Fe_2O_3/ZnFe_2O_4$ nanocolumnar heterojunction with improved charge separation for photoelectrochemical water oxidation

Zhibin Luo, Chengcheng Li, Dong Zhang, Tuo Wang* and Jinlong Gong*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University; Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, China

*Corresponding Authors:

Prof. T. Wang E-mail: wangtuo@tju.edu.cn Fax: +86-22-87401818

Prof. J. Gong E-mail: jlgong@tju.edu.cn Fax: +86-22-87401818

Experimental Section

1. Reactive ballistic deposition of bare Fe₂O₃

A homemade reactive ballistic deposition (RBD) system was used to prepare the porous hematite thin films. The base pressure of the high vacuum chamber of RBD system is around 5×10^{-8} mbar. Oxygen as reactive gas was induced to backfill the vacuum chamber to about 1×10^{-6} mbar using a leak valve. A homemade e-beam evaporator was used to evaporate an iron rod in a minimum purity of 99.95%. And the iron rod was mounted on the top of the e-beam evaporator directly near the tungsten filament. The Fe evaporation was conducted in the O₂ ambient at about 1×10^{-6} mbar. Fluorine-doped tin oxide (FTO) coated glasses were used as the substrates. The sample holder could rotate in full 360 degrees, making it possible to have arbitrary deposition angles. The distance between the evaporation source and the substrate was approximately 4 inches.

The sample holder was fixed at an angle of 75° respected to the substrate normal. The deposition angle was determined by taking the balance between the PEC performance and porosity of the bare Fe₂O₃. A quartz crystal microbalance (QCM) was used to monitor the deposition rates to estimate the thickness of the deposited films. In our preparation, we fixed a deposition rate of about 2 nm per minute, and the deposition time was set 100 minutes to have a thickness of 200 nm.

2. Atomic layer deposition of zinc oxide coatings

Thin layers of zinc oxide (ZnO) were deposited on the surface of the porous hematite thin films via a homebuilt thermal atomic layer deposition (ALD) system at 200 °C. Diethyl zinc (DEZ) and deionized water at room temperature were used as the precursors. The dosing and the purging lengths for DEZ and deionized water were both 0.05 s and 10 s, respectively. A silicon wafer was used as a monitor sample to determine the growth rate of the ZnO. Spectroscopic ellipsometry measurement shows a ZnO growth rate of 0.1 nm per cycle at 200 °C. And 60 cycles ALD could form a thickness of about 6 nm ZnO layer.

3. Formation of Fe₂O₃/ZnFe₂O₄ heterojunction

 $ZnFe_2O_4$ was obtained via a solid state reaction at the Fe_2O_3/ZnO interface at a high temperature of 500 °C by annealing. The annealing condition of 500 °C for 3 hours were essential for the formation of $ZnFe_2O_4$ with expected crystalline, and further annealing could not result in an improvement of

crystalline. Finally, the samples were soaked in 1 M KOH solution for more than 10 h to ensure that there was no excess ZnO remaining.

4. Structural characterization

The crystal structure of the samples were investigated by an X-ray diffractometer (type D/MAX 2500) equipped with a nickel-filtered Cu K α radiation (λ =1.5416 Å) at 40 kV and 140 mA. The XRD spectra were collected at a scanning speed of 0.02° per step over a 2 θ range from 25° to 40°. The morphology and nanostructure of the samples were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S-4800, 5kV) and transmission electron microscopy (TEM, JEM 2100 F, 200 kV). Optical reflectance and transmittance properties of the samples were recorded on a Shimadzu UV-2550 spectrophotometer.

5. Photoelectrochemical (PEC) tests

The PEC performance of the samples were evaluated using a three-electrode system, where the samples, a saturated Ag/AgCl electrode and a platinum foil (2 cm \times 2 cm area) were used as the working electrode, reference electrode and counter electrode, respectively. The electrolyte was a 1.0 M KOH aqueous solution. The current-voltage (I-V) characteristics of the electrode were investigated with an electrochemical workstation (IVIUM CompactStat.e20250) at a scan rate of 50 mV per second. The samples was sealed using black tapes with an exposure area of 1 cm². A 300 W xenon lamp (Beijing Perfectlight Technology Co. Lt; LS-SXE300CUV) equipped with an AM 1.5G filter was used as the light source. The power intensity of the simulated sunlight was calibrated to 100 mW cm⁻². Prior to I-V tests, nitrogen purging of more than half an hour was conducted to remove the dissolved oxygen in the electrolyte.

The measured potential with respect to Ag/AgCl reference electrodes could be converted to reversible hydrogen electrode (RHE) following:¹

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \, pH + E^{0}_{Ag/AgCl} \tag{1}$$

where E_{RHE} is the converted potential vs. RHE, $E_{Ag/AgCl}$ is the applied potential against Ag/AgCl reference electrode, and $E^{0}_{Ag/AgCl} = 0.197$ V at 25 °C.

The incident photon-to-electron conversion efficiency (IPCE) was obtained using a quantum efficiency/IPCE system (Zolix Solar Cell Scan, 100) under monochromatic light. The IPCE spectra were measured at a constant potential (1.23 V vs. RHE), at the wavelength from 350 nm to 700 nm.

The IPCE is calculated from the current density recorded at different wavelengths using the following formula:²

$$IPCE = 1240 j / (P_{light} \times \lambda)$$
⁽²⁾

where *j* is the measured current density (mA cm⁻²), P_{light} is the calibrated and monochromated illumination power (mW cm⁻²), and λ is the wavelength (nm) of the incident light at the measured photocurrent and illumination intensity.

The photoluminescence (PL) spectra were recorded using HORIBA Jobin Yvon spectrofluorometer with a Xe lamp as a light source with an excitation wavelength of 320 nm.

I-V curves under chopped illumination were conducted at a bias of 1.23 V vs. RHE at 10 mV s⁻¹ under 420 nm illumination, using the IPCE system for precise control of chopping time intervals.

6. Schematic illustration of the synthesis procedure of Fe₂O₃/ZnFe₂O₄ heterojunction

Highly-oriented Fe₂O₃/ZnFe₂O₄ nanocolumnar arrays photoanode was fabricated employing RBD and ALD techniques. A brief schematic illustration of the sample preparation procedure is shown in **Scheme S1**. The thin film of Fe₂O₃ nanocolumnar arrays was fabricated by evaporating metallic Fe metal in a high vacuum chamber with oxygen as the reactive gas (**Scheme S1a**), followed by depositing the ZnO overlayer using ALD (**Scheme S1b**). ZnFe₂O₄ was obtained via a solid state reaction at a high temperature of 500 °C in air. In the annealing process, Fe₂O₃ reacted with ZnO stoichiometrically to form ZnFe₂O₄ during the solid state reaction (**Scheme S1c**). After annealing, the as prepared sample was soaked in 1 M KOH aqueous solution to remove unreacted ZnO (**Scheme S1d**), ensuring that no excess ZnO remained over the Fe₂O₃/ZnFe₂O₄ photoelectrode. In the remainder of this paper, we denote the prepared heterojunction photoanode as Fe₂O₃/ZnFe₂O₄(*x* nm), where *x* indicates the thickness of ZnFe₂O₄ overlayer.



Scheme S1 Schematic illustration of the synthesis procedure of $Fe_2O_3/ZnFe_2O_4$ heterojunction photoanode. (a) RBD of Fe_2O_3 nanocolumnar arrays on FTO substrate; (b) ALD of ZnO over Fe_2O_3 nanocolumnar array thin film; (c) Solid state reaction between Fe_2O_3 and ZnO that forms $ZnFe_2O_4$ overlayer; (d) The removal of excess ZnO through KOH etching.



Fig. S1 XRD of bare Fe_2O_3 and $Fe_2O_3/ZnFe_2O_4$ heterojunction photoanodes with increasing $ZnFe_2O_4$ to Fe_2O_3 ratios.



Fig. S2 SEM images for the (a) bare Fe_2O_3 , (b) $Fe_2O_3/ZnFe_2O_4(6 \text{ nm})$, (c) $Fe_2O_3/ZnFe_2O_4(12 \text{ nm})$ and (d) $Fe_2O_3/ZnFe_2O_4(18 \text{ nm})$ thin films.



Fig. S3 UV-vis spectra of bare Fe_2O_3 and $Fe_2O_3/ZnFe_2O_4$ heterojunction photoanodes (Absorptance = 1 – Reflectance – Transmittance).



Fig. S4 IPCE for bare Fe_2O_3 and $Fe_2O_3/ZnFe_2O_4$ heterojunction photoanodes in the region of 350 to 700 nm at a potential of 1.23 V vs. RHE.

References

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