Electronic Supporting Information

Defective Fe$^{3+}$ self-doped spinel ZnFe$_2$O$_4$ with oxygen vacancies for highly efficient electrochemical water splitting

Jianmin Wang$^1$, Yunan Wang$^{1*}$, Xinchao Xv$^1$, Yan Chen$^1$, Xi Yang$^1$, Jun Zhou$^1$, Song Li$^1$, Feng Cao$^1$, Gaowu Qin$^{1,2}$

$^1$Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Material Science and Engineering, Northeastern University, Shenyang 110819, China
$^2$Research Center for Metallic Wires, Northeastern University, Shenyang 110819, China

*caof@atm.neu.edu.cn
*qingw@smm.neu.edu.cn

‡ These authors contributed equally.

Experimental section

Preparation of samples

Pure ZnFe$_2$O$_4$ photoanodes were synthesized by a fast and effective spin-coating method. In a typical process, 1 mM of Zn(NO$_3$)$_2$ and 2 mM of Fe(NO$_3$)$_3$·9H$_2$O dissolved in a mixed solution containing ethanol and DI water. And then 1 g of PEG-400 was added into the solution with stirring for 30 min. To create films, the precursor solutions were spin coated onto FTO substrates with spun for 20 s at 3000 rpm. And the films were subsequently annealed in air at 600 °C for 2 h.

Fe$^{3+}$ self-doped ZnFe$_2$O$_4$ photoanodes with different doping concentrations were synthesized through constructing non-stoichiometric ZnFe$_2$O$_4$ and varying the ratio of Zn/Fe, and subsequent the same process with that of pure ZnFe$_2$O$_4$. Moreover, the samples with Zn/Fe=0.9/2.1, 0.93/2.07, 0.96/2.04 and 0.99/2.01 were successfully prepared and labeled as (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.1), (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.07), (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.04) and (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.01), respectively. Notably, (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.1) was taken as an example to exhibit the advantages of self-doping treatment for photoelectrochemical performances of materials. So, (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ mentioned in the paper without specific x value refers to (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$ (x=0.1).

ZnFe$_2$O$_4$ with oxygen vacancies were fabricated via subsequent hydrogen reduction treatment at 200 °C under a flow of 5% H$_2$ and 95% Ar for 30 min for initial
ZnFe$_2$O$_4$ or Fe$^{3+}$ self-doped ZnFe$_2$O$_4$, which were labeled as ZnFe$_2$O$_{4-y}$ and (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_{4-y}$, respectively. Moreover, to vary the concentrations of the oxygen vacancies, the hydrogen reduction treatment was also carried out for 10 min, 60 min and 120 min, respectively. Notably, ZnFe$_2$O$_{4-y}$-30 min and (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_{4-y}$-30 min were taken as examples to exhibit the advantages of oxygen vacancies for photoelectrochemical performances of materials. So, ZnFe$_2$O$_{4-y}$ and (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_{4-y}$ mentioned in the paper without specific hydrogen reduction treatment durations refer to ZnFe$_2$O$_{4-y}$-30 min and (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_{4}$-30 min.

**Characterizations**

The structures of the samples were measured by X-ray diffraction (XRD, Rigaku-D/max 2500V, Cu Kα radiation). The morphologies were observed by using field emission scanning electron microscopy (FE-SEM, JEOL JEM-7100F). The optical abilities were measured via UV visible spectrophotometer with an integrating sphere (PerkinElmer Lambda 750S) in the range of 400-800 nm. The composition and surface electronic state of elements were investigated by X-ray photoelectron spectroscopy (XPS).

**PEC performance measurements**

PEC properties were evaluated with a standard three electrodes system with Hg/HgO as the reference electrode, Pt mesh as counter electrode and the as-prepared photoanode as working electrode. A 1 M NaOH aqueous solution after saturated with nitrogen gas for 30 min was used as electrolytes. A 300W xenon lamp (Perfect Light, PLS-SXE300) with an AM1.5 filter was used to simulate the solar irradiation spectra, and the power was calibrated to 100 mW cm$^{-2}$. The applied voltage was swept in the range of 0.5-1.7 V vs. RHE with a scan rate of 10 mV s$^{-1}$. Mott-Schottky analysis was performed by sweeping the range of 0.4-1.0 V vs. RHE with an AC frequency of 10 kHz and an amplitude of 10 mV under dark condition. The electrochemical impedance spectroscopy (EIS) was measured at a DC potential of 1.23 V vs. RHE and in the AC potential frequency range of 100 kHz-100 mHz with an amplitude of 10 mV. O$_2$ evolution experiment was conducted at 1.23 V vs. RHE under AM1.5 illumination in 1 M NaOH. The amounts of evaluated O$_2$ were measured via Dissolved oxygen meters.
It is worthwhile to note that the electrolyte should be bubbled with highly pure N\textsubscript{2} for 30 min to remove the dissolved oxygen before the measurement, and the cell should be carefully sealed.

Fig. S1 XRD patterns of (a) obtained samples of ZnFe\textsubscript{2}O\textsubscript{4} with hydrogen reduction treatment for different durations, (b) ZnFe\textsubscript{2}O\textsubscript{4} with different Fe\textsuperscript{3+} self-doped concentrations and (c) obtained samples of ZnFe\textsubscript{2}O\textsubscript{4} with different Fe\textsuperscript{3+} self-doped concentrations and subsequent hydrogen reduction treatment for 30 min.

Fig. S2 SEM images of (a) ZnFe\textsubscript{2}O\textsubscript{4-y}–10 min, obtained samples of ZnFe\textsubscript{2}O\textsubscript{4} with hydrogen reduction treatment for 10 min, (b) (Zn\textsubscript{1-x}Fe\textsubscript{x})Fe\textsubscript{2}O\textsubscript{4}, Fe\textsuperscript{3+} self-doped ZnFe\textsubscript{2}O\textsubscript{4} through varying the ratio of Zn/Fe from 1/2 (x=0) to 0.93/2.07 (x=0.07), (c) (Zn\textsubscript{1-x}Fe\textsubscript{x})Fe\textsubscript{2}O\textsubscript{4}–30 min, obtained samples of (Zn\textsubscript{1-x}Fe\textsubscript{x})Fe\textsubscript{2}O\textsubscript{4} with hydrogen reduction treatment for 30 min.
\( x \text{Fe}_x \text{Fe}_2 \text{O}_{4-y} \) 30 min (\( x=0.07 \)) and (d) \( (\text{Zn}_{1-x} \text{Fe}_x) \text{Fe}_2 \text{O}_4 \) 60 min (\( x=0.04 \)).

Fig. S3 (a) Photocurrent density-potential curves of \( \text{ZnFe}_2 \text{O}_4 \) with different oxygen vacancy concentrations through varying the hydrogen reduction treatment durations. (b) Photocurrent density of \( \text{ZnFe}_2 \text{O}_4 \) with different \( \text{Fe}^{3+} \) self-doping concentrations. (c) Photocurrent density of \( \text{ZnFe}_2 \text{O}_4 \) with different \( \text{Fe}^{3+} \) self-doping concentrations and hydrogen reduction treatment for 30 min, respectively.

Fig. S4 Mott-Schottky plots of \( \text{ZnFe}_2 \text{O}_4 \) with different \( \text{Fe}^{3+} \) self-doping concentrations obtained at the frequency of 1 kHz and amplitude of 0.01 V under dark conditions.
Figure S5 The time course of O$_2$ evolution over the as-prepared (Zn$_{1-x}$Fe$_x$)$_2$O$_{4-y}$ (x=0.1).

Figure S6 (a) A zoom of traces of (Zn$_{1-x}$Fe$_x$)$_2$O$_4$ and (Zn$_{1-x}$Fe$_x$)$_2$O$_{4-y}$ in the Mott-Schottky plots. (b) The Mott-Schottky plots of Zn$_{1-x}$Fe$_x$Fe$_2$O$_4$ measured at different frequencies.