Electronic Supporting Information

Defective Fe³⁺ self-doped spinel ZnFe₂O₄ with oxygen vacancies for highly efficient electrochemical water splitting

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Experimental section

Preparation of samples

Pure $ZnFe_2O_4$ 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 $Fe(NO_3)_3 \cdot 9H_2O$ 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 $ZnFe_2O_4$ photoanodes with different doping concentrations were synthesized through constructing non-stoichiometric $ZnFe_2O_4$ and varying the ratio of Zn/Fe, and subsequent the same process with that of pure $ZnFe_2O_4$. 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 $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.1), $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.07), $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.04) and $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.01), respectively. Notably, $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.1) was taken as an example to exhibit the advantages of self-doping treatment for photoelectrochemical performances of materials. So, $(Zn_{1-x}Fe_x)Fe_2O_4$ mentioned in the paper without specific x value refers to $(Zn_{1-x}Fe_x)Fe_2O_4$ (x=0.1).

$ZnFe_2O_4$ 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

$ZnFe_2O_4$ or Fe^{3+} self-doped $ZnFe_2O_4$, which were labeled as $ZnFe_2O_{4-y}$ and $(Zn_{1-x}Fe_x)Fe_2O_{4-y}$, 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, $ZnFe_2O_{4-y}$-30 min and $(Zn_{1-x}Fe_x)Fe_2O_{4-y}$-30 min were taken as examples to exhibit the advantages of oxygen vacancies for photoelectrochemical performances of materials. So, $ZnFe_2O_{4-y}$ and $(Zn_{1-x}Fe_x)Fe_2O_{4-y}$ mentioned in the paper without specific hydrogen reduction treatment durations refer to $ZnFe_2O_{4-y}$-30 min and $(Zn_{1-x}Fe_x)Fe_2O_4$-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_2 for 30 min to remove the dissolved oxygen before the measurement, and the cell should be carefully sealed.
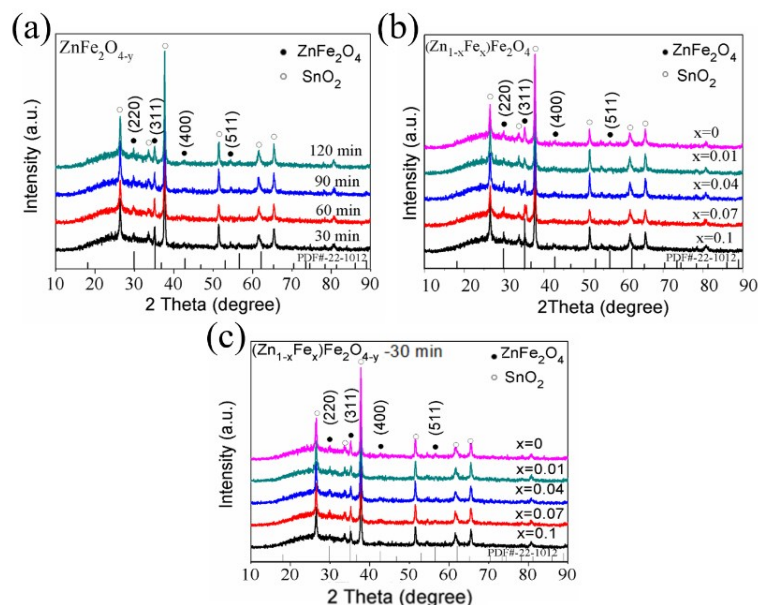

Fig. S1 XRD patterns of (a) obtained samples of $ZnFe_2O_4$ with hydrogen reduction treatment for different durations, (b) $ZnFe_2O_4$ with different Fe^{3+} self-doped concentrations and (c) obtained samples of $ZnFe_2O_4$ with different Fe^{3+} self-doped concentrations and subsequent hydrogen reduction treatment for 30 min.
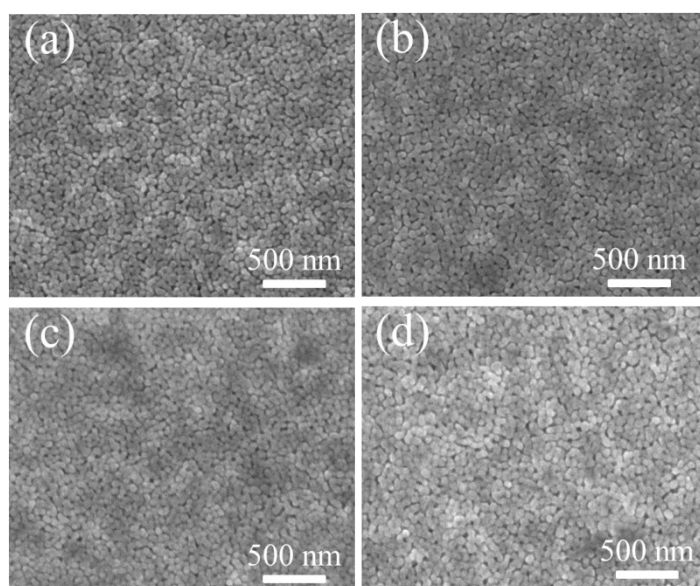
Fig. S2 SEM images of (a) $ZnFe_2O_{4-y}$-10 min, obtained samples of $ZnFe_2O_4$ with hydrogen reduction treatment for 10 min, (b) $(Zn_{1-x}Fe_x)Fe_2O_4$, Fe^{3+} self-doped $ZnFe_2O_4$ through varying the ratio of Zn/Fe from 1/2 (x=0) to 0.93/2.07 (x=0.07), (c) $(Zn_{1-}$

$_x$Fe$_x$)Fe$_2$O$_{4-y}$-30 min (x=0.07) and (d) (Zn$_{1-x}$Fe$_x$)Fe$_2$O$_4$-60 min (x=0.04).
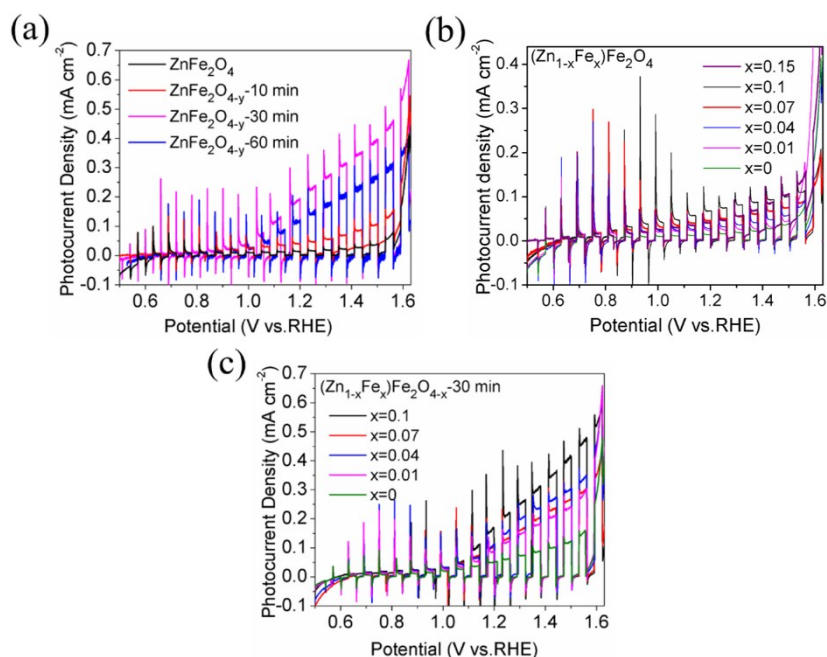

Fig. S3 (a) Photocurrent density-potential curves of ZnFe$_2$O$_4$ with different oxygen vacancy concentrations through varying the hydrogen reduction treatment durations. (b) Photocurrent density of ZnFe$_2$O$_4$ with different Fe^{3+} self-doping concentrations. (c) Photocurrent density of ZnFe$_2$O$_4$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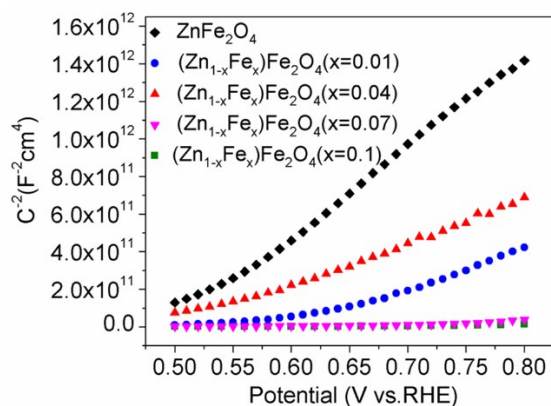

Fig. S4 Mott-Schottky plots of ZnFe$_2$O$_4$ with different Fe^{3+} self-doping concentrations obtained at the frequency of 1 kHz and amplitude of 0.01 V under dark conditions.
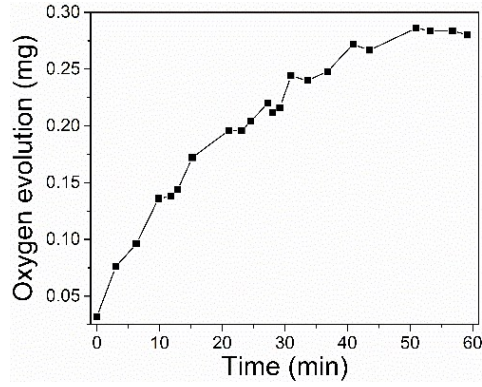
Figure S5 The time course of O_2 evolution over the as-prepared $(Zn_{1-x}Fe_x)Fe_2O_{4-y}$ (x=0.1).
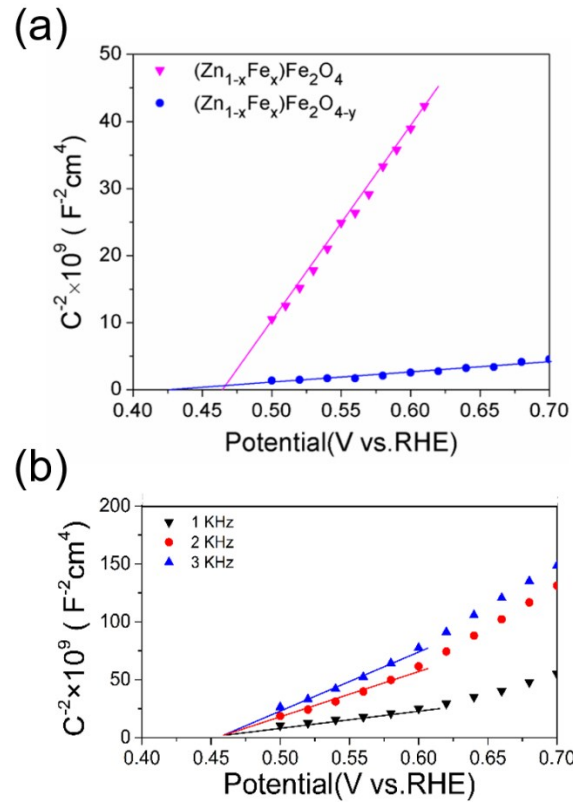

Figure S6 (a) A zoom of traces of $(Zn_{1-x}Fe_x)Fe_2O_4$ and $(Zn_{1-x}Fe_x)Fe_2O_{4-y}$ in the Mott-Schottky plots. (b) The Mott-Schottky plots of $Zn_{1-x}Fe_xFe_2O_4$ measured at different frequencies.