

Electronic Supplementary Information (ESI)

A facile spray pyrolysis method to prepare Ti-doped ZnFe_2O_4 for boosting photoelectrochemical water splitting

Yongsheng Guo,^a Ningsi Zhang,^a Xin Wang,^a Qinfeng Qian,^a Shiyong Zhang,^c Zhaosheng Li^{*a} and Zhigang Zou^{ab}

^a Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, Nanjing University, 22 Hankou Road, Nanjing, 210093, People's Republic of China;

^b Jiangsu Key Laboratory for Nano Technology, Department of Physics, Nanjing University, 22 Hankou Road, Nanjing, 210093, People's Republic of China;

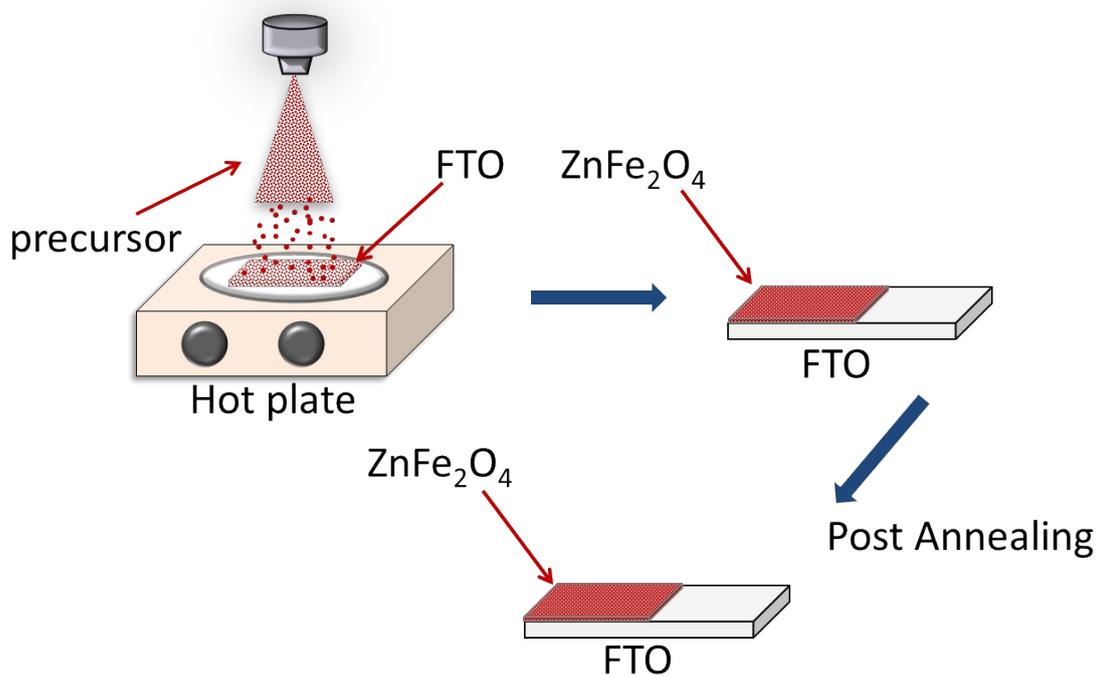
^c Hunan Key Laboratory of Applied Environmental Photocatalysis, Changsha University, Changsha, People's Republic of China.

*Corresponding author:

Prof. Z. Li

E-mail: zsli@nju.edu.cn

Fax: +86-25- 83686304(800)



Scheme S1 Schematic illustration of the ZnFe₂O₄ photoanodes preparation procedure. When the temperature of the hot palte was 400 °C, the films were coated on FTO by spray pyrolysis.

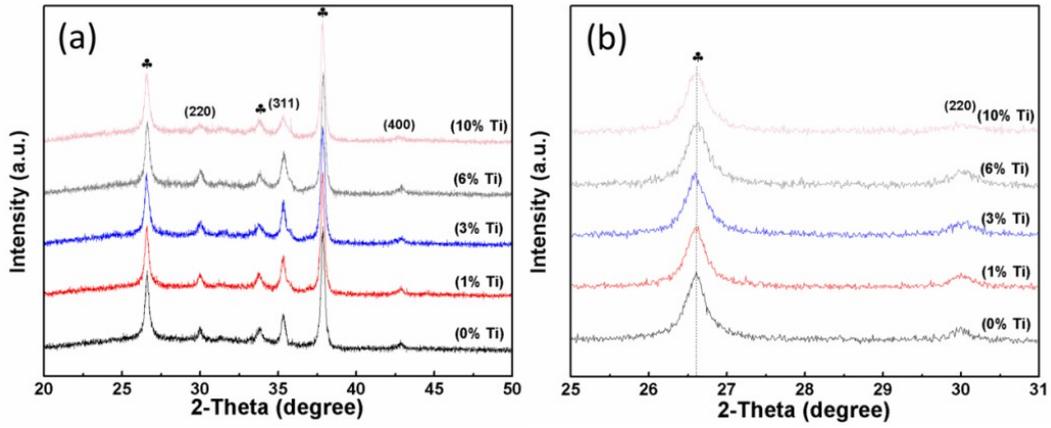


Fig. S1 XRD patterns of ZnFe_2O_4 with different Ti doping concentrations. (\clubsuit = peaks from FTO). The peaks in Fig. S1 (a) at $2\theta = 30^\circ$, 35.2° and 42.8° represent (2 2 0), (3 1 1) and (4 0 0) crystal planes of the cubic spinel ZnFe_2O_4 . (b) Magnified view from 25° to 31° . (ZnFe_2O_4 : PDF#22-1012, SnO_2 : PDF#46-1088)

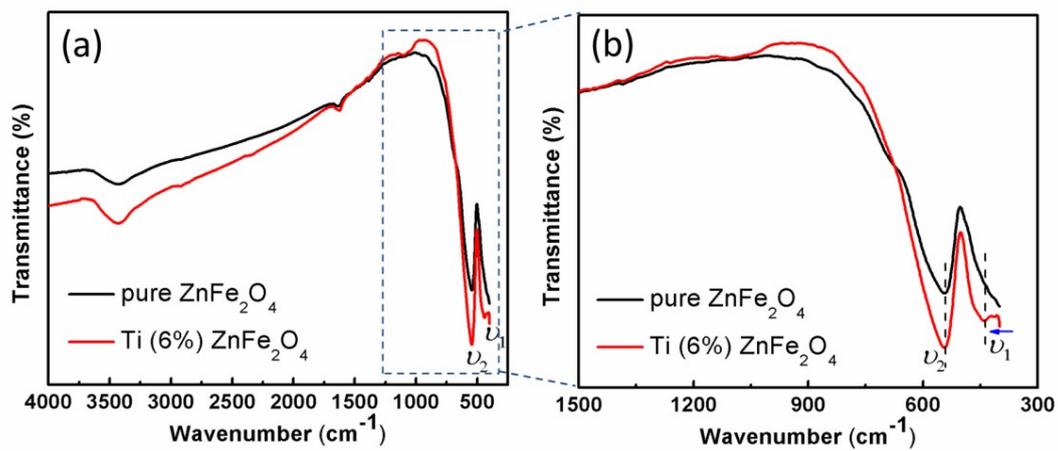


Fig. S2 FTIR spectra of pure and 6% Ti-doped ZnFe_2O_4 samples: (a) wavenumbers from 4000 to 400 cm^{-1} , (b) Magnified view from 1500 to 400 cm^{-1} .

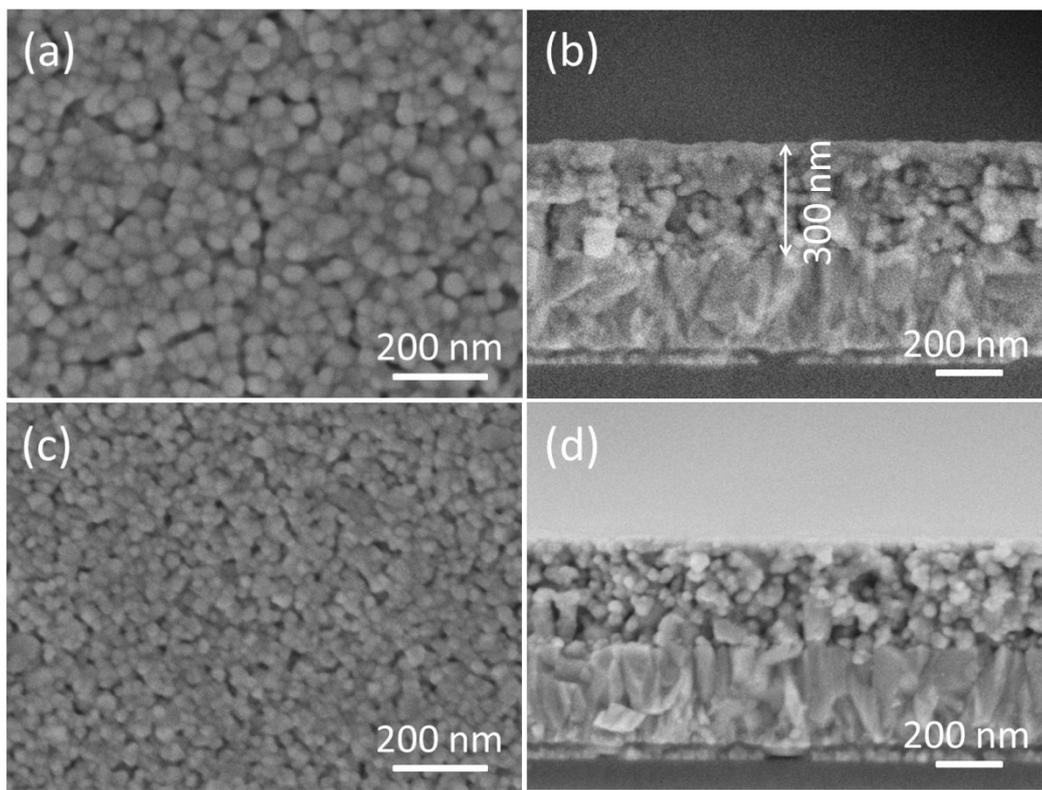


Fig. S3 SEM images for the (a) top view of pure ZnFe₂O₄. (b) cross section view of pure ZnFe₂O₄. (c) top view of 6% Ti-doped ZnFe₂O₄. (d) cross section view of 6% Ti-doped ZnFe₂O₄.

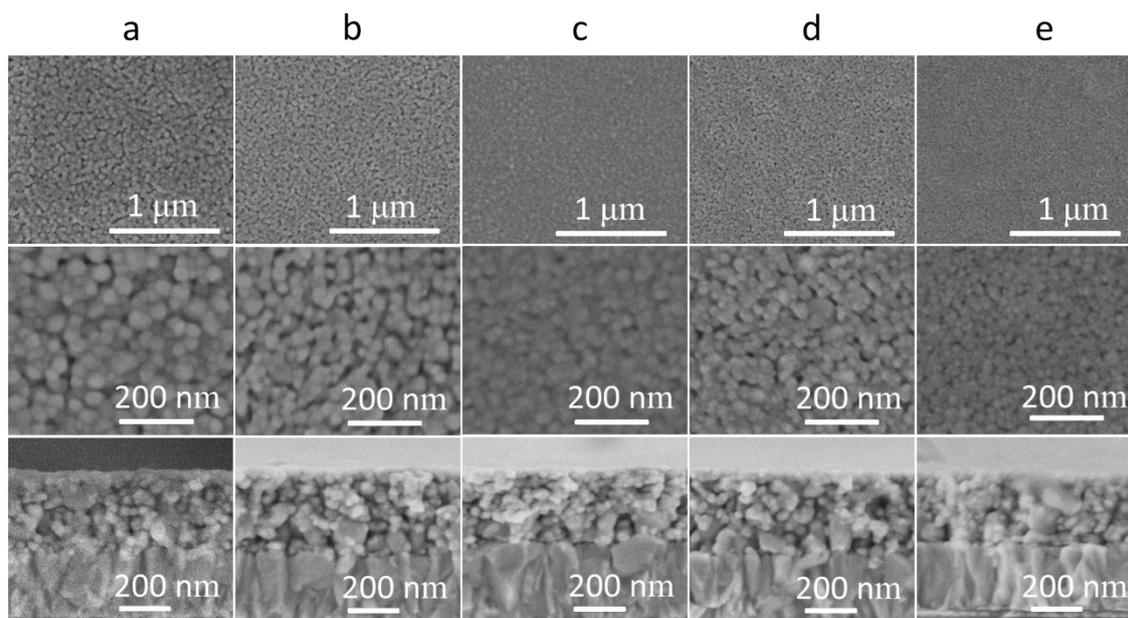


Fig. S4 Top view and cross section view SEM images of ZnFe₂O₄ with different Ti doping concentrations. (a = 0%, b = 1%, c = 3%, d = 6%, e = 10%).

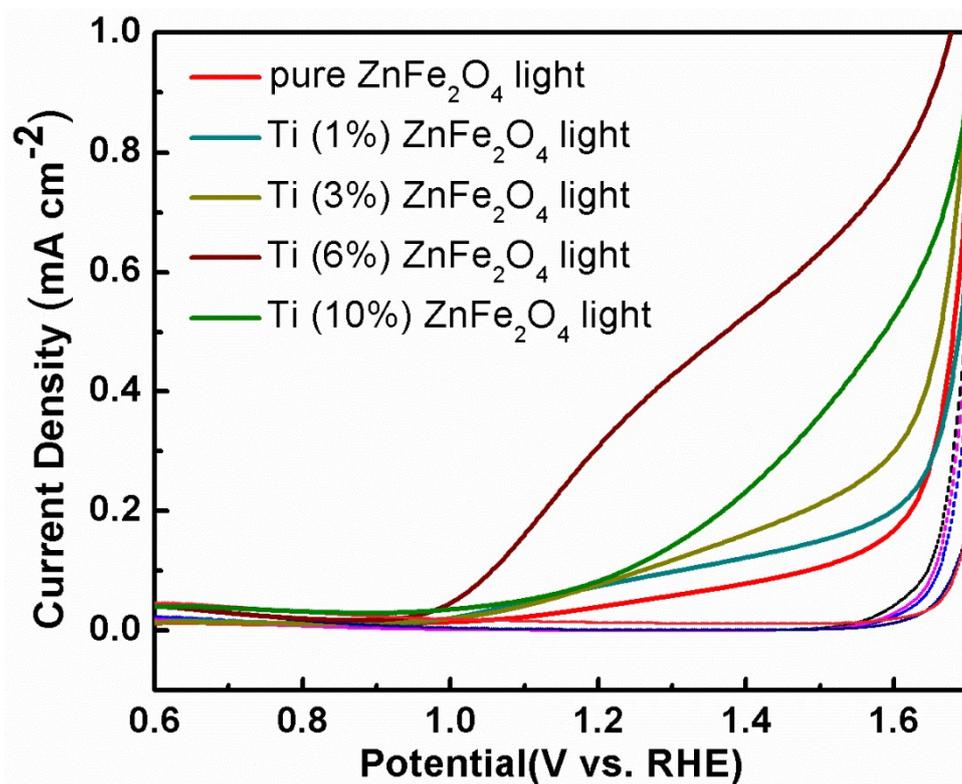


Fig. S5 Current-Potential curves of ZnFe₂O₄ photoanodes with different Ti doping concentrations measured in 1 M NaOH aqueous solution under AM 1.5 G illumination (100 mW cm⁻²).

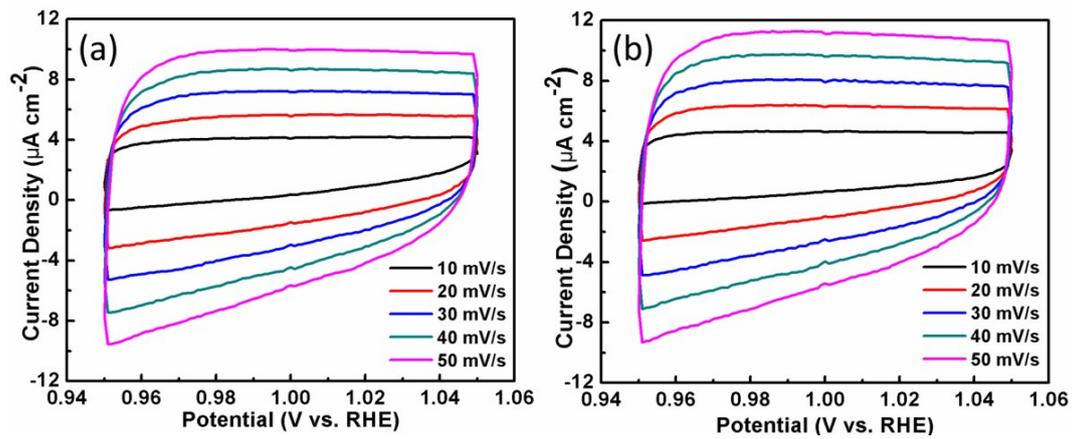


Fig. S6 Cyclic voltammetry with different scan rates of (a) pure ZnFe_2O_4 photoanode and (b) 6% Ti-doped ZnFe_2O_4 photoanode.

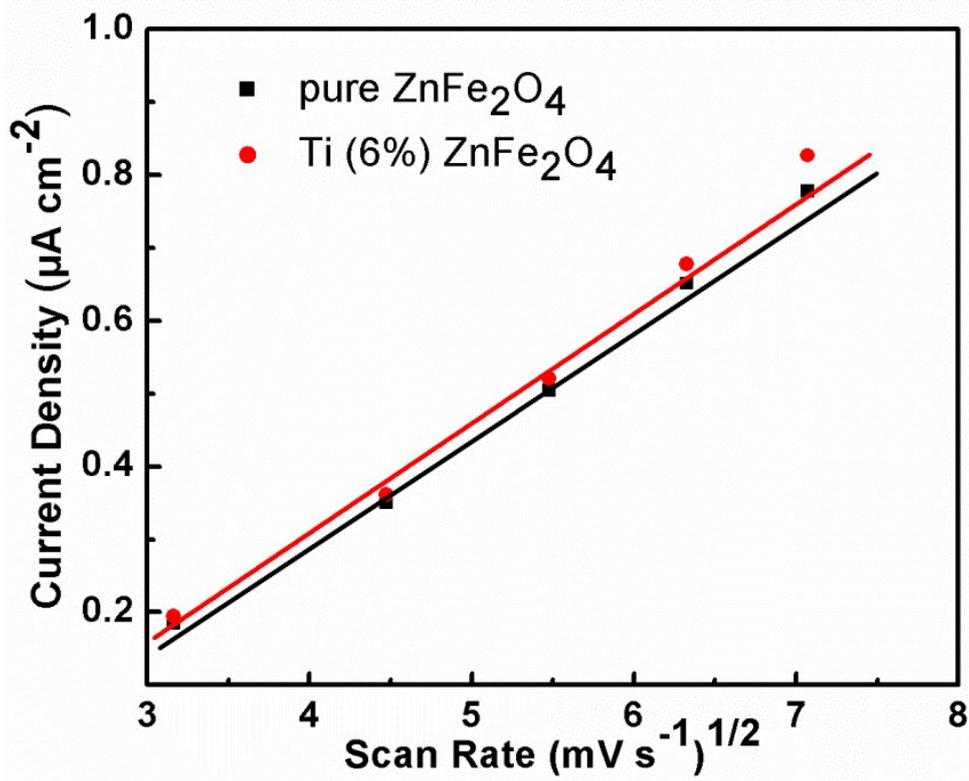


Fig. S7 The Randles-Sevcik plot of $I-v^{1/2}$.

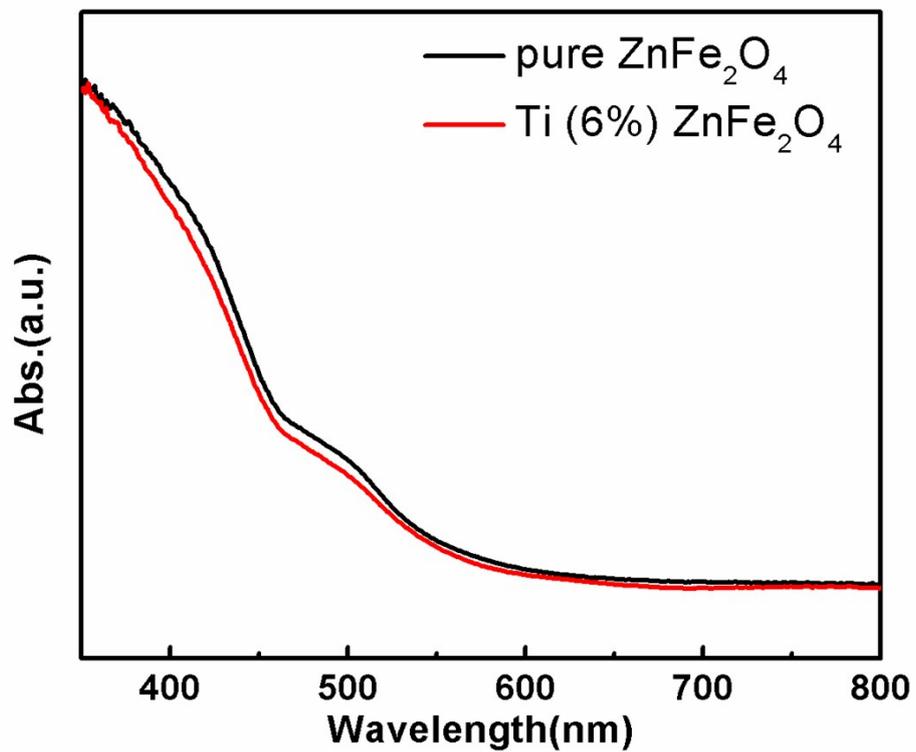


Fig. S8 UV-vis spectrum of pure ZnFe₂O₄ and 6% Ti-doped ZnFe₂O₄ photoanodes.

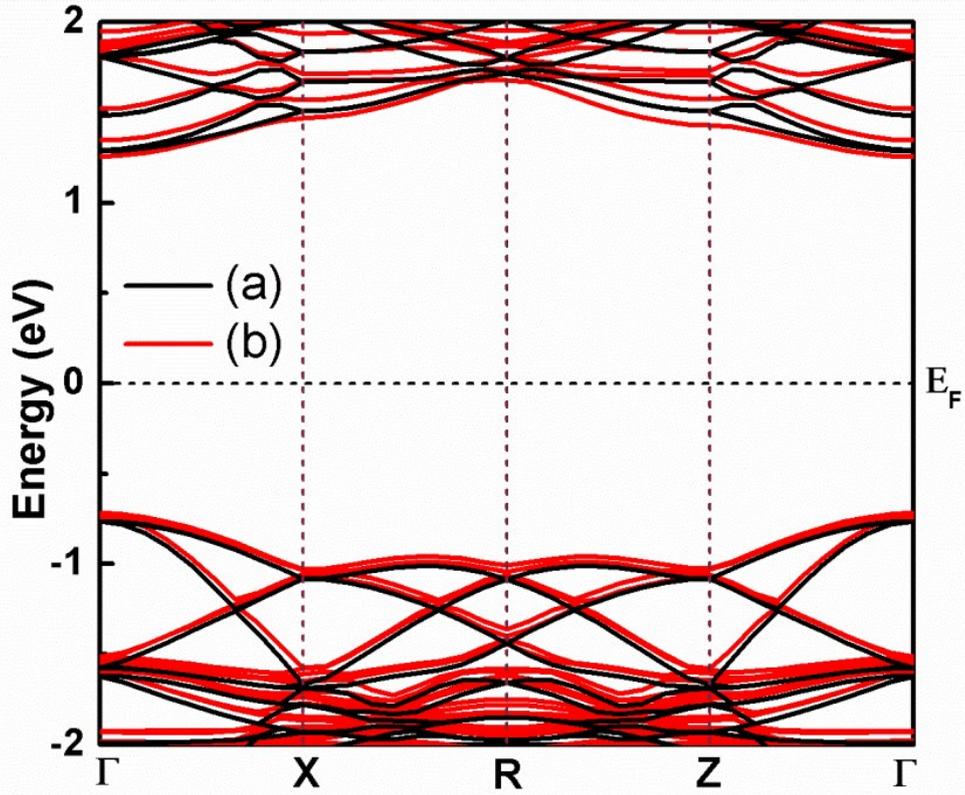


Fig. S9 Band structure of ZnFe₂O₄: (a) pure ZnFe₂O₄, (b) 6% Ti-doped ZnFe₂O₄.

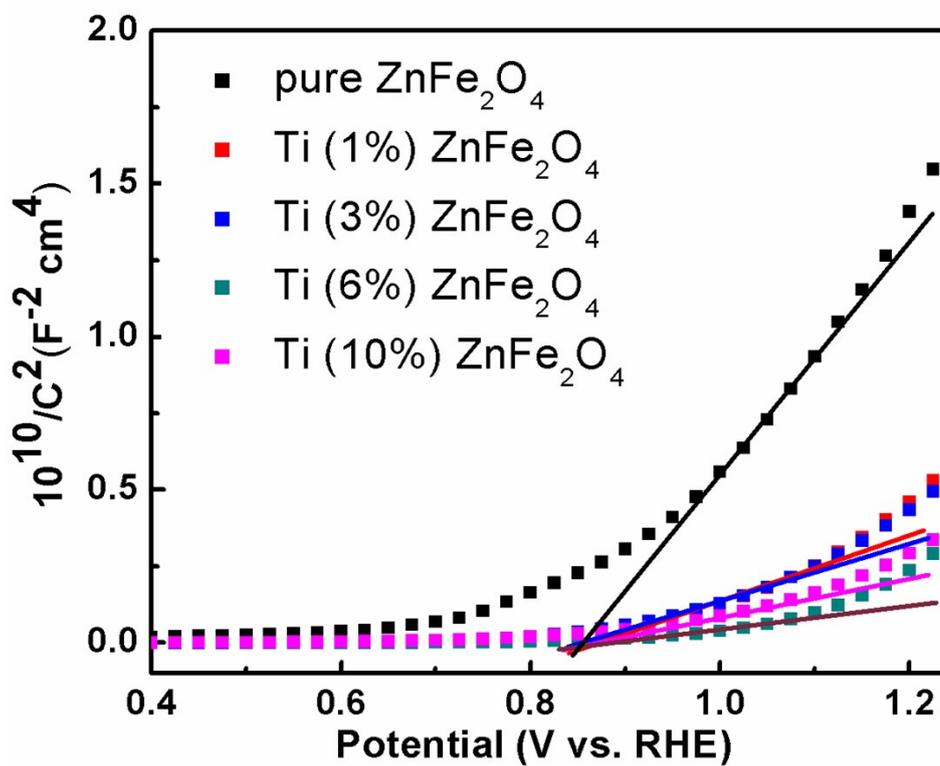


Fig. S10 Mott-Schottky plots of pure ZnFe₂O₄ and Ti-doped ZnFe₂O₄ photoanodes in 1 M NaOH, the ac amplitude is 5 mV and the frequency is 1000 Hz.

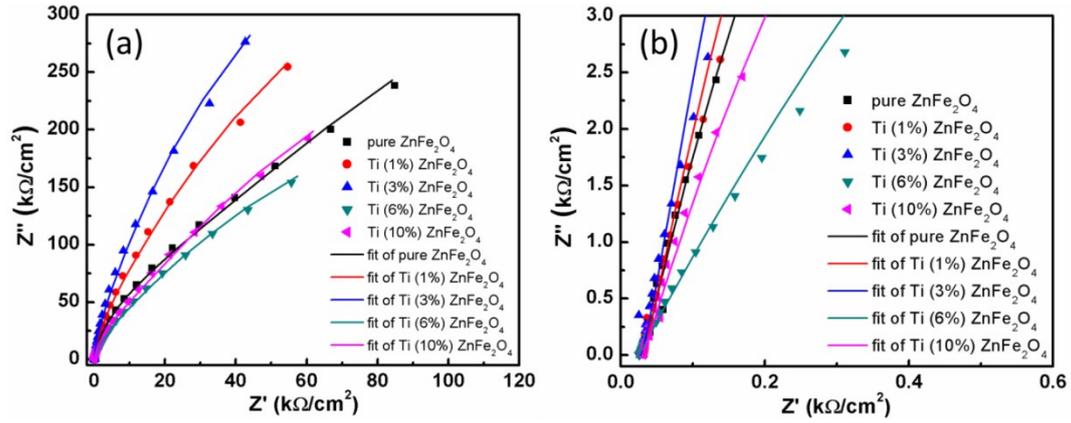


Fig. S11 (a) The Nyquist plots of pure ZnFe_2O_4 and Ti-doped ZnFe_2O_4 from the raw data and fitting data. (b) the magnified plot in the high frequency.

Table S1 Fitting data of the two-RC equivalent circuit.

| Samples | Pure | 1% Ti-doped | 3% Ti-doped | 6% Ti-doped | 10% Ti-doped |
|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| R_s (Ω) | 31.64 | 31.3 | 27.4 | 25.23 | 30.12 |
| R_1 (Ω) | 1.25×10^6 | 1.58×10^6 | 1.98×10^6 | 7.46×10^5 | 9.02×10^5 |
| CPE_1 (F) | 6.89×10^{-6} | 6.26×10^{-6} | 5.81×10^{-6} | 9.36×10^{-6} | 8.22×10^{-6} |
| R_2 (Ω) | 54585 | 23414 | 21674 | 16035 | 31318 |
| CPE_2 (F) | 1.32×10^{-5} | 2.85×10^{-5} | 3.16×10^{-5} | 3.35×10^{-5} | 1.79×10^{-5} |

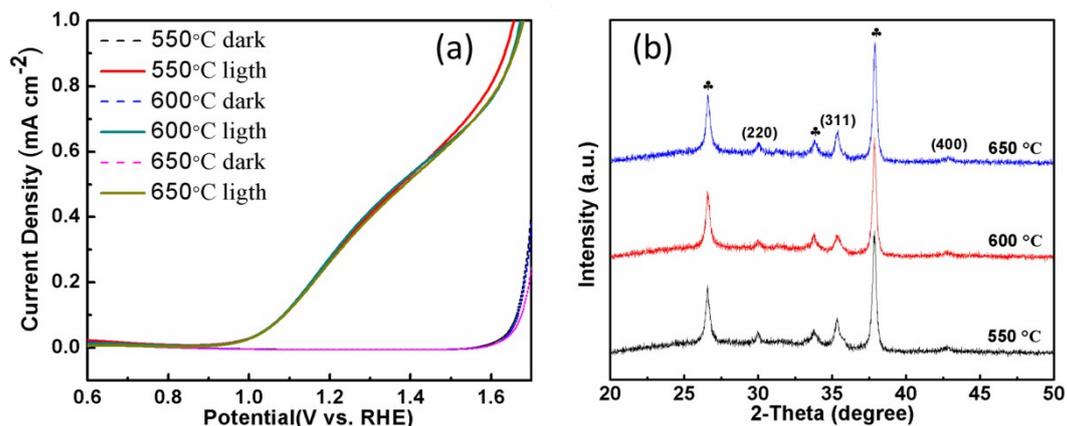


Fig. S12 Current-Potential curves (a) and XRD patterns (b) of 6% Ti-doped ZnFe₂O₄ calcined at different temperatures.

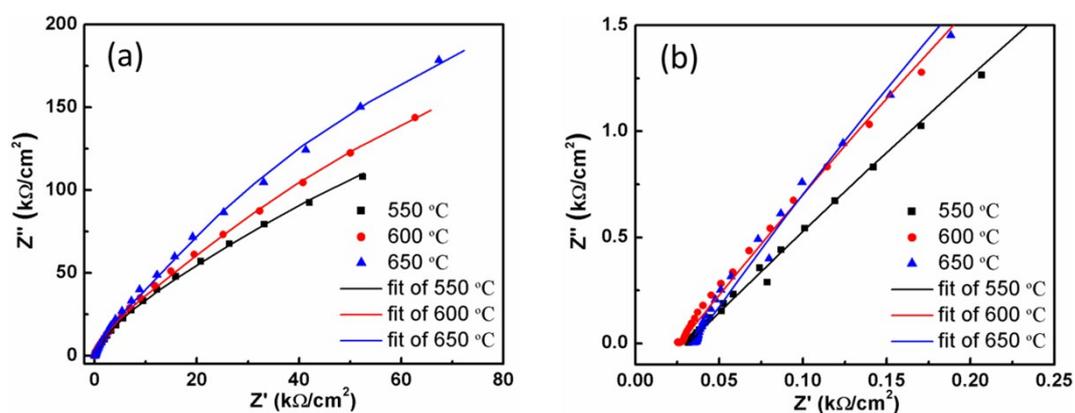


Fig. S13 (a) The Nyquist plots of 6% Ti-doped ZnFe₂O₄ calcined at different temperatures from the raw date and fitting data. (b) Magnified plot in the high frequency.

Table S2 Fitting data of the two-RC equivalent circuit.

| Samples | 550 °C | 600 °C | 650 °C |
|--------------------|-----------------------|-----------------------|-----------------------|
| R _s (Ω) | 31.58 | 26.3 | 34.49 |
| R ₁ (Ω) | 5.15×10 ⁵ | 5.8×10 ⁵ | 7.75×10 ⁵ |
| CPE1(F) | 1.36×10 ⁻⁵ | 1.01×10 ⁻⁵ | 7.71×10 ⁻⁶ |
| R ₂ (Ω) | 23421 | 23174 | 12048 |
| CPE2(F) | 2.89×10 ⁻⁵ | 2.07×10 ⁻⁵ | 2.44×10 ⁻⁵ |

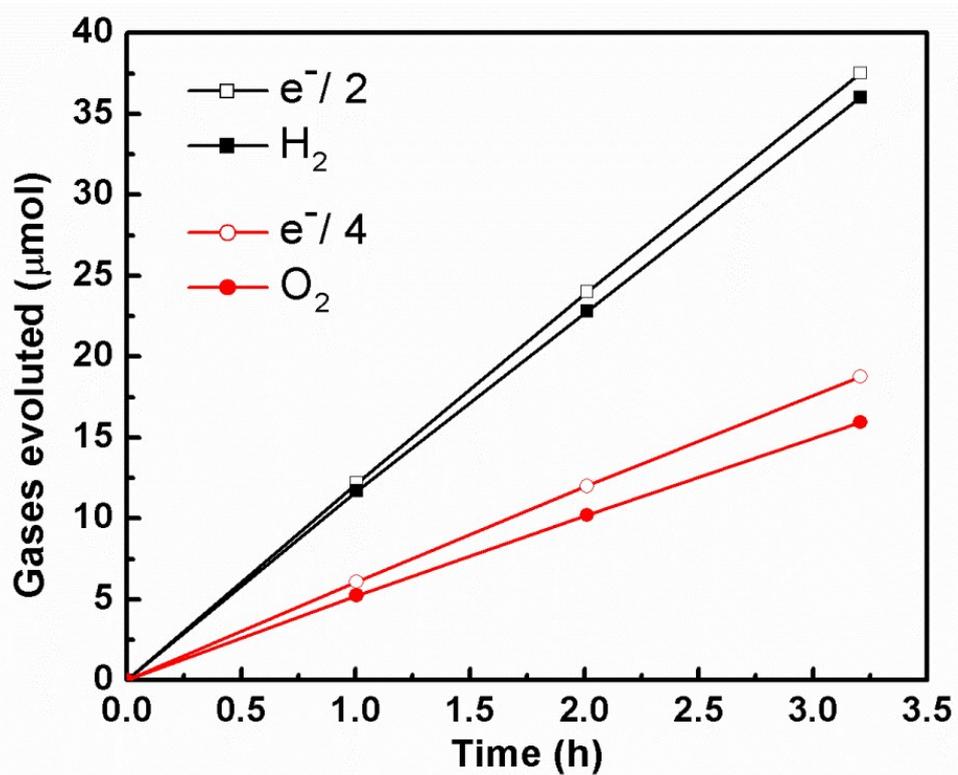


Fig. S14 The Faradaic Efficiency of 6% Ti-doped ZnFe₂O₄ measured at 1.23 V vs. RHE under AM 1.5 G illumination (100 mW cm⁻²).