

## Supporting information

### Nanostructured ZnO/ZnFe<sub>2</sub>O<sub>4</sub> Heterojunction for Visible Light Photoelectrochemical Oxidation of Water

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## Experimental

ZnO nanorods were prepared as follows: Precursor solution was prepared by dissolving 3.78 g zinc nitrate ( $\text{Zn}(\text{NO}_3)_2$ ) and 2.8 g hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ) in 100 mL DI water. The substrates deposited with zinc oxide seed layer were put in a 100 mL bottle containing 80 mL precursor solutions. The reaction was conducted at 95 °C for 3 h. After growth, the substrates were washed with deionized water several times and allowed to dry in air. The ZnO nanorods arrays were obtained after annealing the sample at 350 °C for 1 h to remove the organic residue.

ZnO seed layer on FTO were grown as following method: 0.5g zinc acetate and 0.25g poly(vinyl alcohol) powders were dissolved into 3 mL deionized water, followed by a vigorous magnetic stirring for 1 h at 60 °C to get zinc oxide colloid. The as-prepared zinc oxide colloid solution was then spin-coated on the pretreated FTO glass substrates and the samples were then annealed at 500 °C for 1 h.

Synthesis of  $\text{ZnFe}_2\text{O}_4$  nanoparticles and surface modification were conducted according to the method reported earlier.<sup>1,2</sup> Deposition solution was prepared by dissolving 2 mg  $\text{ZnFe}_2\text{O}_4$  particles in 5 mL DI water.

The morphology and size of ZnO nanorods and ZnO/ $\text{ZnFe}_2\text{O}_4$  film were characterized by using a field-emission scanning electron microscope (Zeiss ULTRA Plus) operated at an accelerating voltage of 5 kV. X-ray diffraction patterns (XRD) were recorded on a PANalytical X'Pert PRO instrument using Cu K $\alpha$  radiation (40 kV,  $\lambda = 1.5406 \text{ \AA}$ ) between 20° to 70° at a scanning rate of 0.067°/s. UV-visible diffusion reflectance spectra were measured on a UV-2550 (Shimadzu) spectrometer by using  $\text{BaSO}_4$  as the reference. Photoelectrochemical measurements were made using a three-electrode configuration with the ZnO or ZnO/ $\text{ZnFe}_2\text{O}_4$  film as the working photoelectrode, saturated calomel electrode (SCE) as the reference electrode, and platinum foil as the counter electrode in 0.1 M  $\text{Na}_2\text{SO}_4$ . Sunlight was simulated with a 300 W xenon lamp and an AM1.5G filter (HSX-F300, Beijing NBeT Technology Co., Ltd), coupled with a 420 nm UV filter. The light intensity was set using a calibrated crystalline silicon solar cell. Photocurrent response and electrochemical impedance spectroscopy (EIS) were recorded using a CHI-660D potentiostat. The superimposed alternating current (AC) signal was maintained at 5 mV, while the frequency was scanned between 100 kHz and 0.05 Hz at potentials of 0.8 V versus SCE under illumination by visible light in an electrolyte of 0.1 M  $\text{Na}_2\text{SO}_4$ , with Pt as the counter electrode. STEM-EDX mapping techniques were measured using an FEI Tecnai TF20 microscope operated at 200 kV.

## References:

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