Supporting Information of the MS of '*$ZnFe_2O_4$-ZnO nanorod array p-n junction composite and its photoelectrochemical performance*'

Experimental

$ZnFe_2O_4$-ZnO NRA composite photoelectrode fabrication – A fluorine-doped tin oxide (FTO) glass (13 × 10 mm) was first ultrasonically cleaned with acetone of analytical grade for 5 min, rinsed with deionized water, and then dried with a clean, dry airflow. One longitudinal edge of the conductive side was then carefully covered with insulating tape, with the exposed effective area of the FTO glass measuring 1 cm^2. A ZnO seed layer was deposited on the surface of the cleaned FTO glass using sol-gel method. ZnO NRA was formed on the ZnO seed layer through hydrothermal reaction by exposing the ZnO seed layer in 0.025 M $C_4H_6O_4Zn \cdot 2H_2O$ and $C_6H_{12}N_4$ for 4 h. And then, the ZnO NRA was heated to 500 °C for 1 h at a heating rate of 5 $°C \cdot min^{-1}$ to increase its crystallinity. After that, $ZnFe_2O_4$ was loaded on the surface of ZnO NRA using chemical bath deposition method. First, A mixed solution with 0.14 M $Zn(NO_3)_2 \cdot 6H_2O$ and 0.28 M $FeSO_4 \cdot 7H_2O$ was made under condition of ice bath. The pH value of the mixed solution was adjusted to 4.5 using 0.075 M $Na_2C_2O_4$. After 10 min of stirring, the prepared ZnO NRA was immersed into the mixed solution for 2 min. Followed by rinsing with deionized water, the prepared ZnO NRA was then dried using dry pure airflow. After repeating two times, the color of the ZnO NRA gradually changed to greenblack. After that, the prepared ZnO NRA was then heated to 500 °C for 2 h at a heating rate of 5 $°C \cdot min^{-1}$. Finally, the color of the ZnO NRA changed to jacinth. A copper wire was connected to the conductive side of the FTO glass using conductive silver tape. Uncoated parts of the conductive side of the FTO glass were isolated with parafilm after the conductive silver tape had dried.

Characterizations of $ZnFe_2O_4$-ZnO NRA – The morphologies of the ZnO NRA and $ZnFe_2O_4$-ZnO NRA composite photoelectrodes were observed using a scanning electron microscope (SEM) (JSM-6700F; JEOL, Tokyo, Japan) and high-resolution transmission electron microscope (HRTEM). The crystalline structures of the photoelectrodes were identified by X-ray diffraction (XRD) (D/MAX-2500/PC; Rigaku Co., Tokyo, Japan). The analysis of the chemical composition of the photoelectrodes was performed using Raman spectroscopy (LabRAM HR UV-NIR; HORIBA Jobin Yvon, France). The optical absorption properties of the photoelectrodes were investigated using a UV/Vis diffuse reflectance spectrophotometer (U-41000; HITACHI, Tokyo, Japan). The luminous intensities of the photoelectrodes were studied using photoluminescence spectroscopy (PLS) (PL, Fluoro Max-4, HORIBA Jobin Yvon, France).

Photoelectrochemical measurements – Photo-induced volt-ampere characteristic curve (i-V curve) and photo-induced current density (i-t curve) of the ZnO NRA and $ZnFe_2O_4$-ZnO NRA composite photoelectrodes were measured using CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The three-electrode system was employed to do the measurements. The photoelectrodes were used as working electrode. The Ag/AgCl electrode was acted as reference electrode and the platinum electrode was used as counter electrode. The electrolyte is 0.25 M Na_2S + 0.35 M Na_2SO_3. The i-V curves were measured from -1.0 V to 0.8 V with a scan rate of 0.02 $V \cdot s^{-1}$. The i-t curves were measured at a bias potential of 0.5 V. Cyclic voltammetry (CV) curves of the ZnO NRA and $ZnFe_2O_4$-ZnO NRA composite photoelectrodes in 0.5 $mol \cdot L^{-1}$ Na_2SO_4 under dark condition were measured at the potential range of -1.2 to 1 V with the scanning rate of 50 mV s-1. The white light source was a 300 W Xe arc lamp (PLS-SXE300, Beijing Changtuo Co. Ltd., Beijing, China). A 420-nm cutoff filter was use to remove light with wavelengths less than 420 nm and ultimately generate visible light.

The formation mechanism of $ZnFe_2O_4$-ZnO NRA composite

$Zn(NO_3)_2 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ in oxalic acid solution can slowly hydrolyze to form amorphous $ZnFe_2O_4$ nanoparticles. Subsequently, these amorphous $ZnFe_2O_4$ nanoparticles can gradually form a loose nano fibrous micelle [1]. If the ZnO NRA is immersed into the $ZnFe_2O_4$ precursor electrolyte, these loose nano fibrous micelle can be adsorbed on the surface of ZnO NRA. These loose nano-fibers become close, dense and shrink in the subsequent annealing process at 500 ^oC. Nanorods tilt in different degrees and a three-dimensional network nanometer structure is formed due to the existence of the internal stress.

Supporting figures

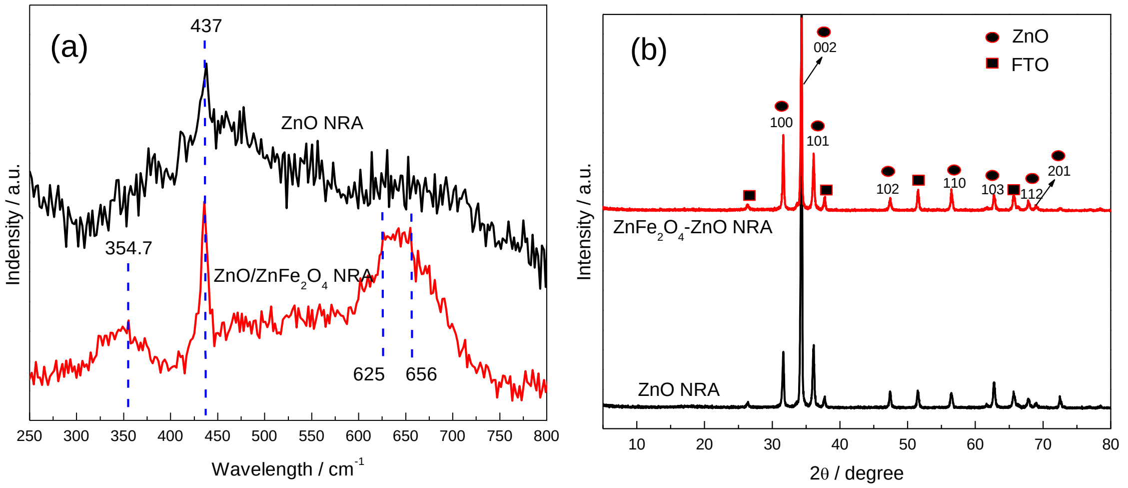


Figure S1. The Raman spectra (a) and XRD patterns (b) of ZnO NRA and $ZnFe_2O_4$-ZnO NRA composite photoelectrodes.

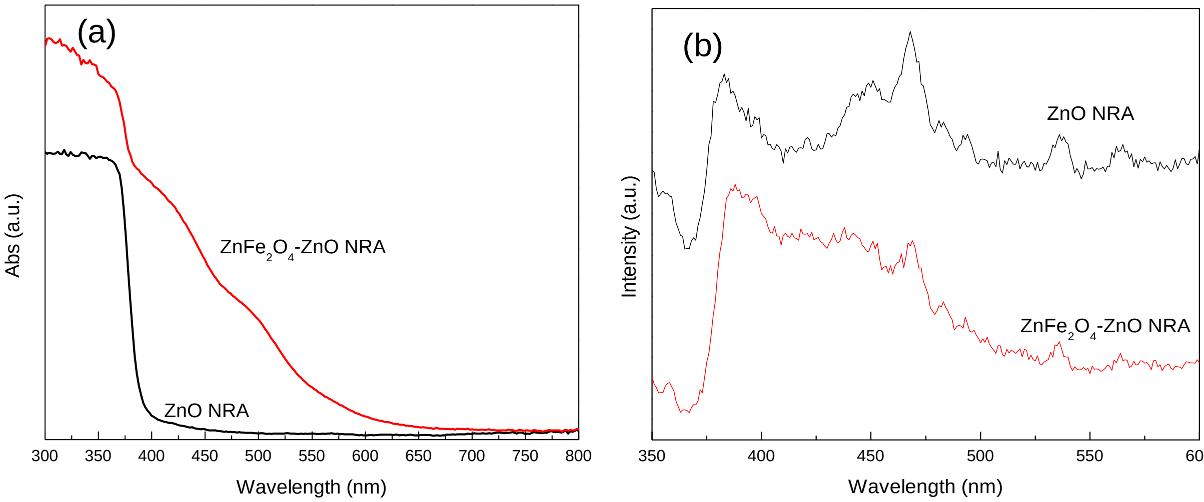


Figure S2. UV/Vis diffuse reflection spectra (a) and photoluminescence spectra (b) of ZnO NRA and $ZnFe_2O_4$-ZnO NRA composite photoelectrodes.

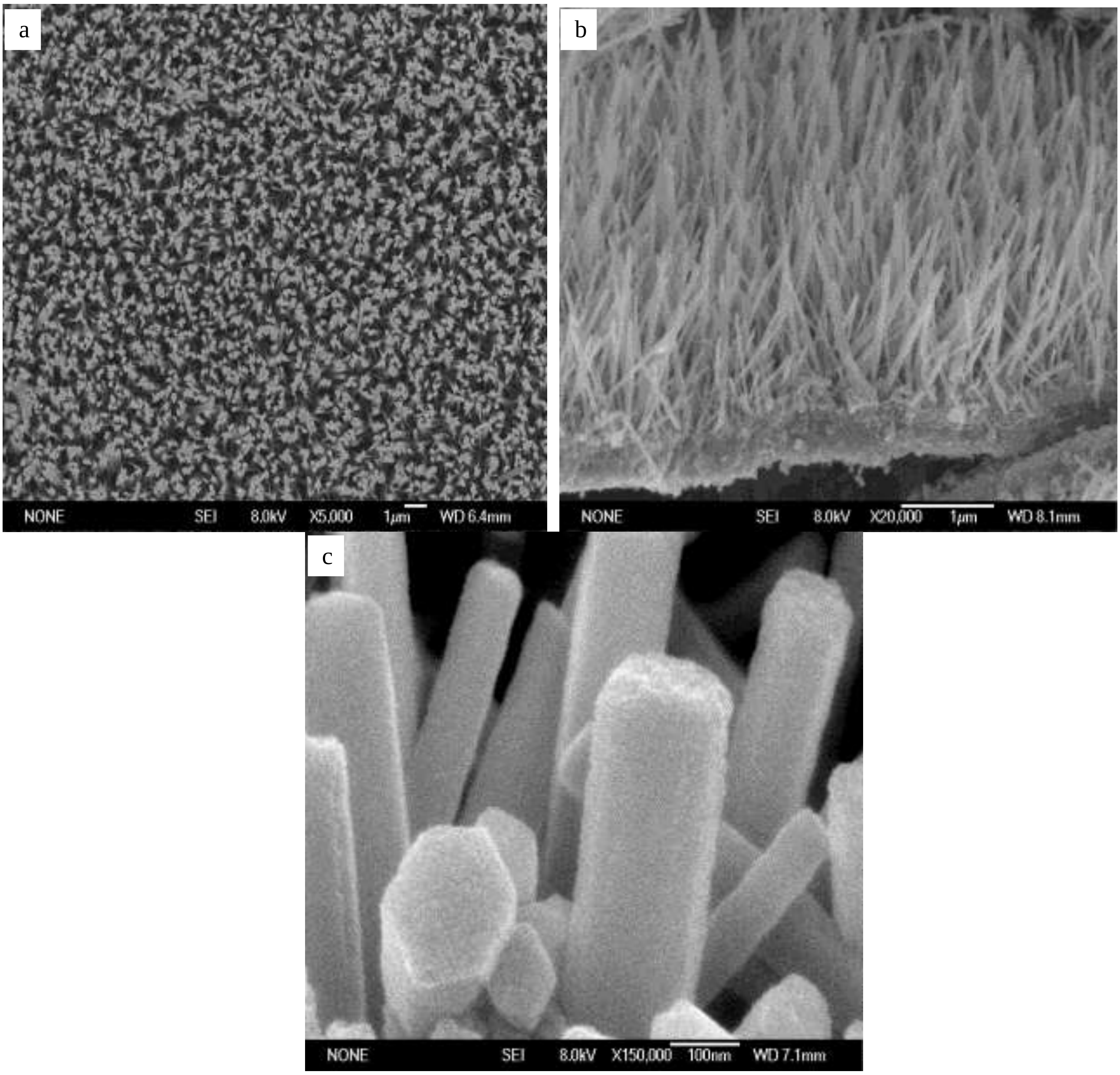
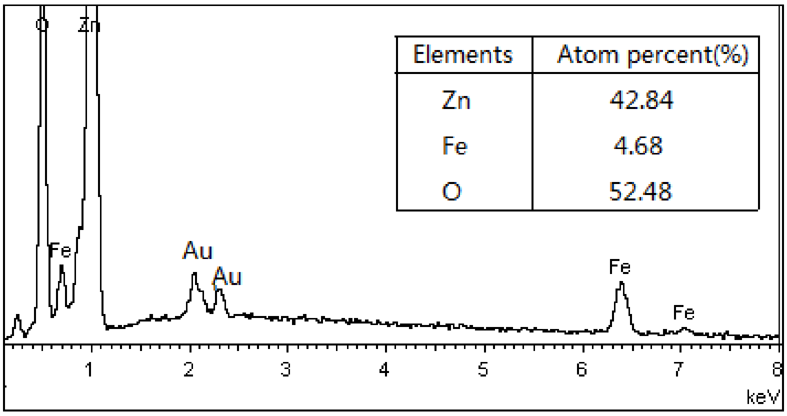


Figure S3. SEM images of ZnO NRA photoelectrode. (a) top view in low magnification, (b) cross-section view and (c) top view in high magnification.



Elements	Atom percent(%)
Zn	42.84
Fe	4.68
O	52.48

Figure S4. EDS results of ZnO-$ZnFe_2O_4$ NRA photoelectrode obtained in the image in Figure 1b.

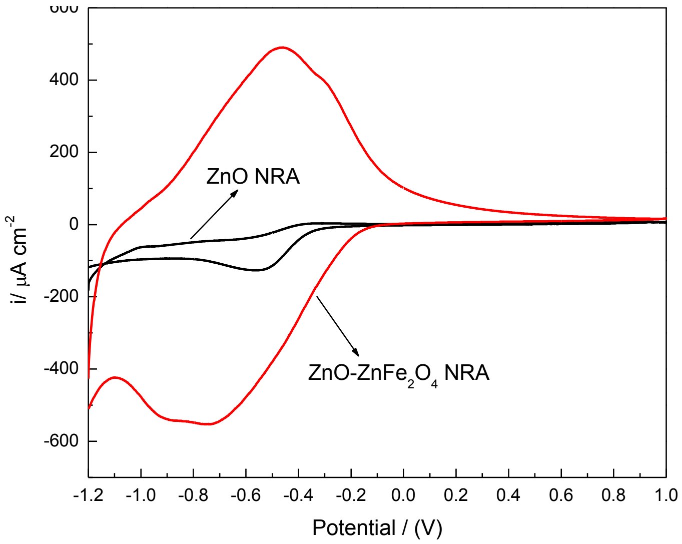


Figure S5. Cyclic voltammograms of ZnO NRA and ZnO-ZnFe$_2$O$_4$ NRA photoelectrodes in a 0.5 mol·L^{-1} Na$_2$SO$_4$ solution under dark condition. Scan rate: 50 mV·s^{-1}.

Reference

[1] H. Lv, L.Ma, P. Zeng, D. Ke, T. Peng, *J. Mater. Chem.*, 2010, **20**, 3665–3672.