Supporting Information

A novel $SnIn_4S_8/ZnFe_2O_4$ S-scheme heterojunction with excellent magnetic property and photocatalytic degradation activity for tetracycline

Dafeng Zhang[a,*], Ruiqi Zhang[a], Xue Jiang[a], Dong Zhang[b], Hengshuai Li[b], Junchang Liu[a], Xipeng Pu[a,*], Peiqing Cai[c]

[a] School of Materials Science and Engineering, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Liaocheng University, Liaocheng 252000, P. R. China

[b] School of Physics Science and Information Technology, Shandong Key Laboratory of Optical Communication Science and Technology, Liaocheng University, Liaocheng, 252000, P. R. China

[c] College of Optical and Electronic Technology, China Jiliang University, Hangzhou 310018, P. R. China

1. Characterization

X-ray diffraction (XRD) patterns were recorded on a diffractometer (D8 Advanced, Bruker Co., Germany) with Cu Ka-radiation operated at 40 kV and 30 mA, in a 2θ range of 10-80° with a step width of 0.02°. The morphologies of samples were obtained on a Gemini scanning electron microscope (SEM; Zeiss Ltd., Germany) equipped with an energy-dispersive X-ray system (EDX). The transmission electron microscopy (TEM) images ware recorded on a Zeiss Gemini microscope and a JEM-2100 microscope. The photoluminescence (PL) spectra were taken on an F-7000 spectrometer (Hitachi Ltd., Japan). The samples were characterized by X-ray photoelectron spectroscopy (XPS) using Thermo Fisher Scientific K-Alpha with

*Corresponding author:
E-mail address: dafengzh@hotmail.com (D. Zhang); xipengpu@hotmail.com (X. Pu)

Al $K\alpha$ line source. The magnetic properties of the ZFO and SIS/ZFO-30 photocatalysts were carried out using a vibrating sample magnetometer (Quantum Design Co., USA). The UV-vis diffuse reflectance spectrum (DRS) of the samples were determined by UV-3600 spectrophotometer (Shimadzu, Japan).

2. Photoelectrochemical measurements

The standard three-electrode system of Shanghai Chenhua Company was used for photoelectrochemical measurements with platinum wire as auxiliary electrode and saturated calomel electrode as reference electrode. 20 mg photocatalyst was suspended in 1 mL isopropanol-water (4:1) solution, and the slurry was prepared by ultrasound for 10 min. 30 μL slurry was injected into 0.5 cm × 0.5 cm SnO_2: F (FTO) glass electrode and dried to prepare working electrode. Photocurrent, electrochemical impedance spectroscopy (EIS) and Mott-Schottky diagram were measured under visible light irradiation of Na_2SO_4 (0.1 M) in aqueous solution under 300W Xenon lamp (Ceaulight Co., Ltd., China).

Photocatalytic activities and photostability test

The photocatalytic degradation performances of the as-synthesized samples were evaluated by the degradation of TC under visible light irradiation. Firstly, 50 mg photocatalyst powder was dispersed into 100 mL 50 mg/L TC aqueous solution at room temperature, and then the suspension was ultrasonically treated for 10 min and was stirred in the dark for 30 min to get the adsorption desorption equilibrium. The light source is then turned on to expose the solution to the light source. During irradiation, 3 mL TC suspension was extracted every 20 min. After centrifugation, TC concentration in different periods was calculated by UV-vis spectrophotometer.

3. Active species trapping experiments

The photocatalytic mechanism of SIS/ZFO-30 reaction system was studied by introducing different scavengers. To quench hydroxyl radicals ($^{\bullet}OH$), holes (h^+) and superoxide radicals ($^{\bullet}O_2^-$), Isopropanol (IPA), EDTA-2Na and L-histidine are used in the preparation process, respectively. The active species capture experiment was like the photocatalytic activity test except that 1mmol of the trapping agent was added to the solution. Moreover, nitroblue tetrazolium chloride (NBT) was used to confirm the generation of superoxide radicals (☙O_2^-) in an aqueous solution of NBT at 5×10^{-5} M.

4. Method and computational details

First-principle calculations were based on density functional theory (DFT) with CASTEP package of materials studio 6.0 (MS 6.0). The generalized gradient approximation (GGA) was used to deal with the electron-electron interactions and the Perde-Burke-Ernzerhof (PBE) functionals was used to deal with the exchange correlation function. Twelve electrons ($3d^{10}4s^2$) of Zn, eight electrons ($3d^64s^2$) of Fe, six electrons ($2s^22p^4$) of O, fourteen electrons ($4d^{10}5s^25p^2$) of Co, thirteen electrons ($4d^{10}5s^25p^1$) of In, six electrons ($3s^23p^4$) of S were treated as valence electrons. The thickness of the air layer is set to 15 Å to avoid the mutual influence between layers. Set 3 Å between ZFO and SIS to form a SIS/ZFO heterojunction. For the Brillouin zone, a 9×9×1 Monkhorst-pack grid was used. The geometric optimization was terminated when the energy and force of the ions fall below 1E-0.5 eV and 0.002 eV/Å.ZFO

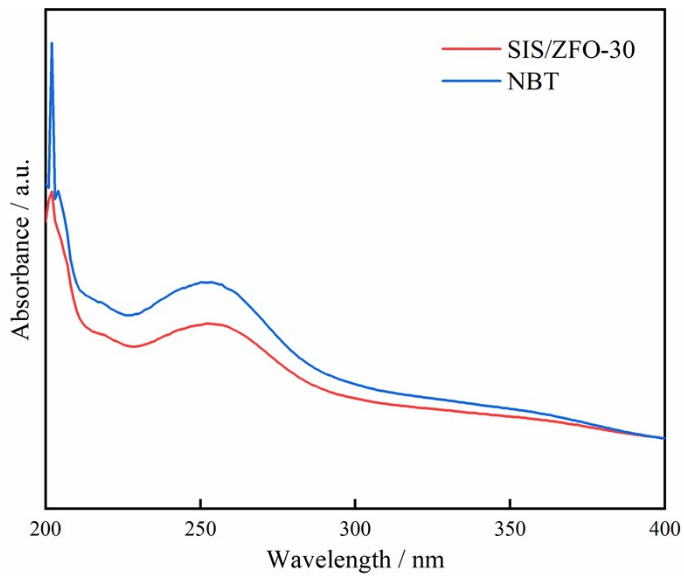

Fig. S1. UV-vis spectra of pristine NBT, SIS, and SIS/ZFO-30.

Table S1. Comparison of interpretation of tetracycline solution by different photocatalysts.

Kind of catalyst	catalyst amount (mg)	TC volume (mL)	Initial TC concentration (mg/L)	Reaction time (min)	Degradation efficiency	Reference
$SnIn_4S_8/ZnFe_2O_4$	50	100	50	120	60%	**This work**
$Ag_2O–CeO_2$	25	50	10	60	~60%	[1]

$Ag_2O/AgBr–CeO_2$	25	50	10	60	93.68%	[1]
$Bi_2S_3/BiFeO_3$	20	100	30	120	~75%	[2]
$BiFeO_3/TiO_2$	50	50	10	180	72.2%	[3]
$Bi_2O_3/BiFeO_3$	20	100	30	120	80%	[4]
TiO_2-P	80	40	100	100	~35%	[5]
$TiO_2/g-C_3N_4$	80	40	100	100	~50%	[5]
TiO_2-P/$g-C_3N_4$	80	40	100	100	~80%	[5]
$ZnO/ZnFe_2O_4$	3	20	25	240	93.68%	[6]

Reference

[1]F. Su, P. Li, J. Huang, M. Gu, Z. Liu, Y. Xu, Photocatalytic degradation of organic dye and tetracycline by ternary $Ag_2O/AgBr-CeO_2$ photocatalyst under visible-light irradiation, Sci. Rep.-UK, 11(2021).

[2]Y. Ma, P. Lv, F. Duan, J. Sheng, S. Lu, H. Zhu, M. Du, M. Chen, Direct Z-scheme $Bi_2S_3/BiFeO_3$ heterojunction nanofibers with enhanced photocatalytic activity, J. Alloy. Compd., 834(2020) 155158.

[3]X. Liao, T. Li, H. Ren, Z. Mao, X. Zhang, J. Lin, C. Lou, Enhanced photocatalytic performance through the ferroelectric synergistic effect of p-n heterojunction $BiFeO_3/TiO_2$ under visible-light irradiation, Ceram. Int., 47(2021) 10786-10795.

[4]F. Duan, Y. Ma, P. Lv, J. Sheng, S. Lu, H. Zhu, M. Du, X. Chen, M. Chen, Oxygen vacancy-enriched $Bi_2O_3/BiFeO_3$ p-n heterojunction nanofibers with highly efficient photocatalytic activity under visible

light irradiation, Appl. Surf. Sci., 562(2021) 150171.

[5]Y. Li, Q. Zhang, Y. Lu, Z. Song, C. Wang, D. Li, X. Tang, X. Zhou, Surface hydroxylation of TiO_2/g-C_3N_4 photocatalyst for photo-Fenton degradation of tetracycline, Ceram. Int., 48(2022) 1306-1313.

[6]C. Akshhayya, M.K. Okla, W.H. Al-Qahtani, M. Raaja Rajeshwari, A. Mohebaldin, Y.A. Alwasel, W. Soufan, M.A. Abdel-Maksoud, H. AbdElgawad, L.L. Raju, A.M. Thomas, S. Sudheer Khan, Novel $ZnFe_2O_4$ decorated on ZnO nanorod: Synergistic photocatalytic degradation of tetracycline, kinetics, degradation pathway and antifungal activity, Journal of Environmental Chemical Engineering, 10(2022) 107673.