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Electronic Supplementary Information:

A facile phase transformation strategy for fabrication of novel Z-scheme ternary heterojunctions with efficient photocatalytic propertiesconcisely

Changlin Yu[a,b]*, Fanyun Chen*[b]*, Wanqin Zhou*[a]*, Debin Zeng*[b]*, Zhen Liu*[a]*, Longfu Wei*[a]*,*
Kai Yang[b]*, Dehao Li*[a]

[a]*Faculty of Environmental Science and Engineering, Key Laboratory of Petrochemical Pollution Process and Control, Guangdong Province, Guangdong University of Petrochemical Technology, Maoming 525000, Guangdong, China ;*
[b]*School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, 86 Hongqi Road, Ganzhou 341000, Jiangxi, China*

*Corresponding Authors: yuchanglinjx@163.com (C.Y.); dehlee@163.com (D.L.).

Experimental section

Materials and reagents. $Zn(CH_3COO)_2$•$2H_2O$, ethylene glycol, tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), ethanol, methanol, Chloroplatinic acid (H_2PtCl_6), potassium dichromate ($K_2Cr_2O_7$), silver nitrate ($AgNO_3$), potassium bromate ($KBrO_3$), manganese sulfate ($MnSO_4$), phenol, rhodamine B (Rh B), and methyl orange (MO) were of analytical grade, which purchased from Sinopharm Chemical Reagent Co. Ltd. China, and used without further purification. The mobile phase of high performance liquid chromatography (HPLC) was HPLC-grade methanol and Mill-Q ultrapure water.

$ZnTiO_3$ and $ZnTiO_3/Zn_2Ti_3O_8/ZnO$ preparation. Samples were prepared via a solvothermal-calcination method. Specially, 8 mmol $Zn(CH_3COO)_2$•$2H_2O$ was first dissolved in 60 mL ethylene glycol. The mixture was magnetically stirred overnight. Then 10mmol tetrabutyl titanate was added. After stirring for 30 min, the solution was placed in a 100 mL Teflon lined strainless autoclave and heated to 180°C for 24 h. After the solution was cooled down to room temperature, the precursors of white precipitates were collected, washed three times with ethanol, and vacuum dried at 60°C for 10 h. Finally, the powder was placed in a furnace and calcinated at 400, 500, 600, 700 and 800°C for 2 h, respectively. And the samples were denoted as ZTO-X (ZTO represents a composite of three elements of Zn, Ti and O. X represents the calcination temperature and X= 400, 500, 600, 700, 800°C, respectively). For the preparation of pure $ZnTiO_3$, the mixed solution was not treated by solvothermal process and only aged at 180°C for 24 h. Then obtained powder was calcinated at 700°C for 2 h.

Photodeposited Ag. 0.2 g of ZTO-700, 50 ml of water, 5 ml of methanol and 0.0093g of $AgNO_3$ (the mass fraction of Ag is 3%) were respectively taken into the photoreactor. The circulating water was used to keep the temperature at 25°C. Xenon lamp (500W) was used as the light source. After 2 hours of illumination under magnetic stirring, it was filtered and washed with deionized water, and then vacuum dried at 60 °C for 10 hours, which was denoted as 3% Ag-ZTO-700.

Photodeposited Mn_2O_3. 0.2 g of ZTO-700, 55 ml of water, 0.09185g of $KBrO_3$ and 0.0186 g of $MnSO_4$ (the mass fraction of Mn is 3%) were respectively taken into the photoreactor. The circulating water was used to keep the temperature at 25°C. Xenon lamp (500W) was used as the light source. After 3 hours of illumination under magnetic stirring, it was filtered and washed with deionized water, and then vacuum dried at 60 °C for 10 hours, which was denoted as 3% Mn_2O_3-ZTO-700.

Characterization. The powder X-ray diffraction (XRD) patterns of the synthesized samples were recorded on a Bruker D8-advance X-ray diffractometer using Cu Ka (λ =0.15418 nm) radiation under 40 kV and 40 mA with scanning angles of 10-80^o. The Brunauer–Emmett–Teller (BET) surface areas of the sample were calculated from N_2 adsorption/desorption isotherms determined at liquid nitrogen temperature (77 K) on an automatic analyzer (ASAP 2020). The samples were outgassed for 2 h under vacuum at 90°C prior to adsorption. The morphology of samples was tested by scanning electron microscopy (SEM) with FLA650F type of the FEI company. Transmission electron microscopy (TEM) images were performed on a Tecnai 20 FEG microscope. The light absorption properties of the samples were measured by UV-Vis diffuse reflectance spectra (DRS) on a UV-Vis spectrophotometer (UV-2550, Shimadzu) and $BaSO_4$ as the reference. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 FT-IR spectrometer, and samples were pressed by a KBr disk preparation apparatus. The surface compositions and elemental valence analysis were done by X-ray photoelectron spectroscopy (XPS) using a PHI Quantum 2000 XPS system with a monochromatic Al Ka source and a charge neutralizer. All the binding energies caused by the relative surface charging were referenced to the C1s peak at 284.8 eV. The photoluminescence (PL) emission spectra of samples were tested by a fluorescence spectrometer (Hitachi F-7000, Japan) using an excitation wavelength of 297 nm.

The electron spin resonance (ESR) spectra were performed on an electron spin resonance spectrometer (Bruker ER200-SLC, Germany), using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO: 50 mM, 0.2 mL) as the stabilizer of active species in the aqueous with the suspended photocatalyst. The parameter settings for ESR spectrometer were as follows: center field = 323.467 mT, sweep width = 5 mT, microwave frequency = 9069 MHz, and microwave power = 0.998 mW. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were performed on a Simultaneous DSC/TGA (SDT) Thermal Analyzer at a heating rate of 10°C/min in air flow.

Photoelectrochemical measurements were carried out on an electrochemical workstation with three-electrode (CHI-660E, China). 0.1 M of Na_2SO_4 solution was used as electrolyte solution. Saturated Ag/AgCl was used as reference electrode and platinum wires were utilized as the counter electrode. The working electrode was done by dropcoating method on indium tin oxide (ITO) conducting glass. The homogeneous mixtures of 1 mL ethanol and 10 mg samples were spread onto ITO with the area of $1cm^2$ and dried at 60°C for 5 h. A xenon lamp (CEL-HXF300) was used as the excitation light source for photocurrent test.

Photocatalytic performance evaluation. Photocatalytic performance evaluation was carried out for dyes and phenol degradation, the reduction of Cr(VI), and hydrogen production. For the degradation of Rhodamine B (Rh B) and methyl orange (MO), 30 mg photocatalyst was suspended on the aqueous solution of the above dye (50 mL, 10 mg/L). 400 W metal halide lamp was used as light source. Before light irradiation, the suspension was magnetically stirred in the dark for 30 min to attain the physical adsorption and desorption equilibrium. The suspension was magneticly stirred during the reaction process, and the reaction temperature was maintained at room temperature by circulation of water. After the interval of illumination time, approximately 2 mL suspension was taken out and centrifuged to remove photocatalyst powders for targeted pollutants analyzed by UV-Vis spectrophotometer. For Cr(VI) reduction, after centrifugation, the concentration of Cr(VI) was measured according to the diphenylcarbazide colorimetric method at 540 nm (GB 7466-87, Standards of China).

The synergistic reaction of Cr(VI) reduction and phenol degradation were carried out under 500W xenon lamp (Solar-500N) illumination. 50 mg photocatalysts was suspended in 80 mL mixed aqueous solution of Cr(VI) (20 mg/L) and phenol (20 mg/L). As for the concentration of Cr(VI) was measured according to above determination of Cr(VI). The concentration of phenol was analyzed by the high performance liquid chromatograph (HPLC, Sykam, German) equipped with fluorescence fetector and a Waters XTerra RP18 column (3.9 mm × 150 mm, particle size 5 μm). The mobile-phase was 55% methanol and 45% water with a flow rate of 0.7 mL min^{-1}. Total organic carbon (TOC) was measured with a (Vario TOC, German Elementar Company) analyzer. The removal ratio (R) of Rh B, MO, Cr(VI) and phenol (or TOC) was determined as follows:

$$R = (1-C/C_0) \times 100\%$$

Where C_0 is the initial concentration of pollutant and C is the concentration at given irradiating time intervals.

For the photocatalytic hydrogen production, 50 mg photocatalyst was dispersed in 80 mL distilled water and 0.165 mL H_2PtCl_6 solution (1 mg/L) and 20 mL methanol were added as sacrificial agents. A 300 W xenon lamp (PLS-SXE300C) was used as a simulated solar source. The above solution was vacuumed degassed for 10 min before the light irradiation to remove the dissolved oxygen under the condition of stirring and then illuminated for 30 min to deposit Pt on the catalysts. After the light deposition, the light source was turned off and the inside of the reactor was again evacuated into vacuum state. And then the light source was turned on to start the test. During the course of the reaction, the circulating cooling water kept the temperature of the reactor at about 25 °C. The amounts of evolved hydrogen were measured at intervals of 1 h and were analyzed by gas chromatography and the catalytic activity of the catalysts was evaluated by the total hydrogen production time of 5 h.

The stability of sample. The recycling experiment of the best composite photocatalyst (ZTO-700) was carried out through degrading 10 ppm Rh B and reducing 10 ppm Cr(VI) solution under the irradiation of 400 W metal halide lamp to test the stability of ZTO-700. The results as shown in Figure S4, indicating that the activity of ZTO-700 decreased slightly with the increase of the cyclic number. It may be that the surface of the catalyst was not cleaned enough after each reaction and adsorbed certain simulated pollutants. But the activity of ZTO-700 is relatively stable.

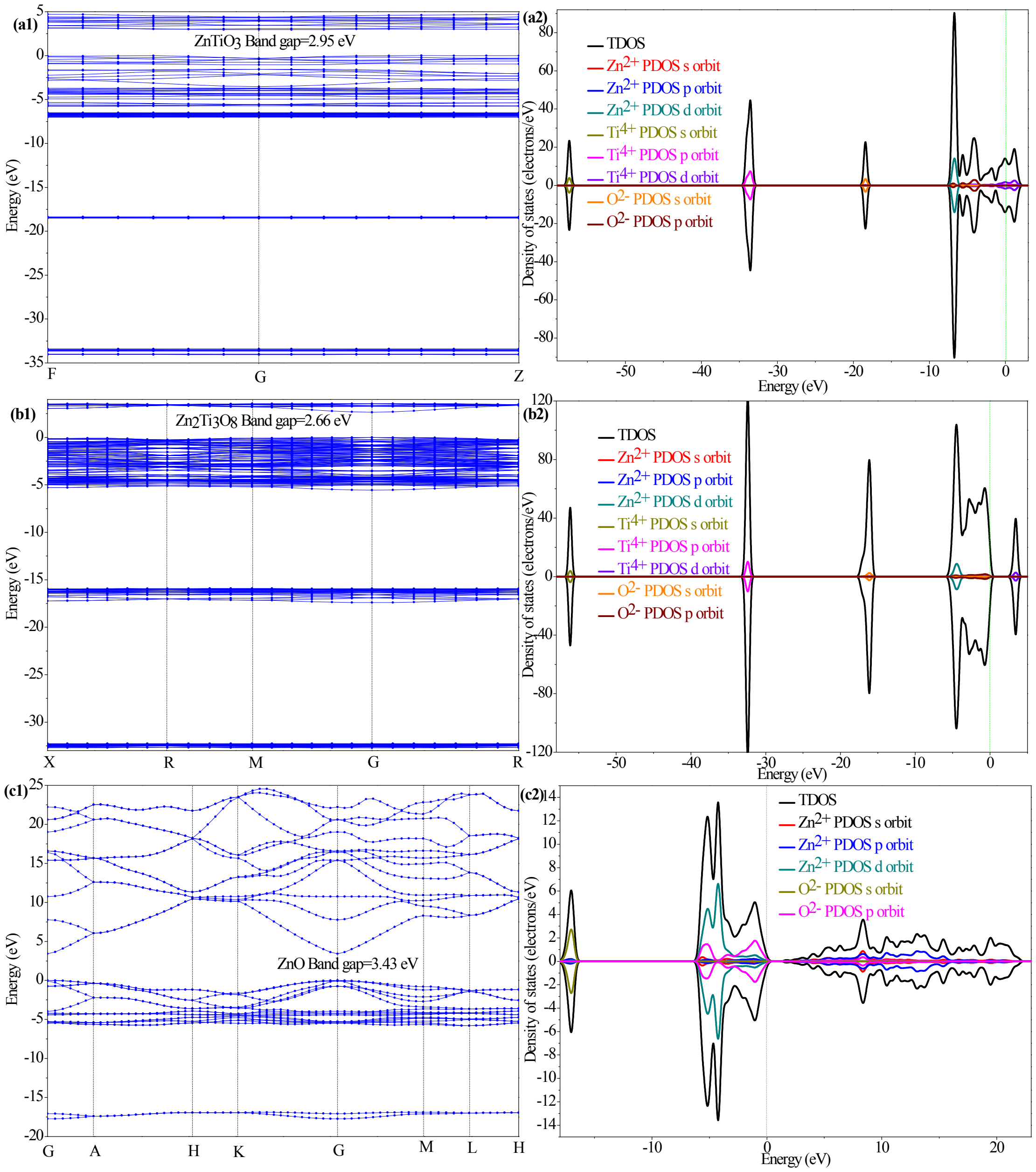

Figure S1. The pristine and optimized crystal structures. $ZnTiO_3$ (a), $Zn_2Ti_3O_8$ (b) and ZnO (c).

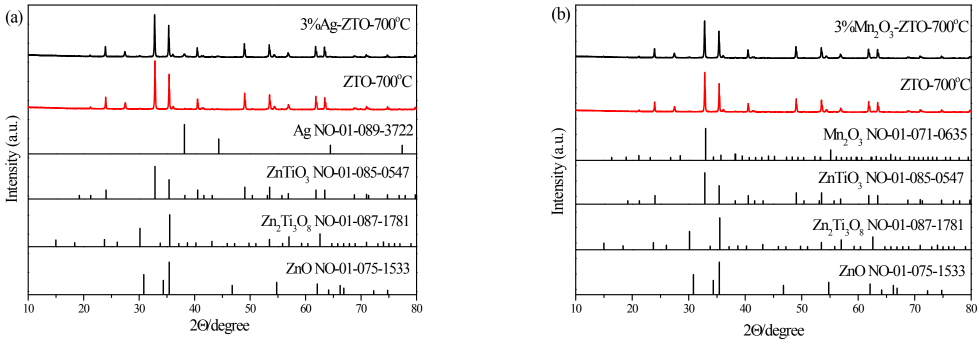

Figure S2. XRD patterns of 3% Ag-ZTO-700 and 3% Mn_2O_3-ZTO-700

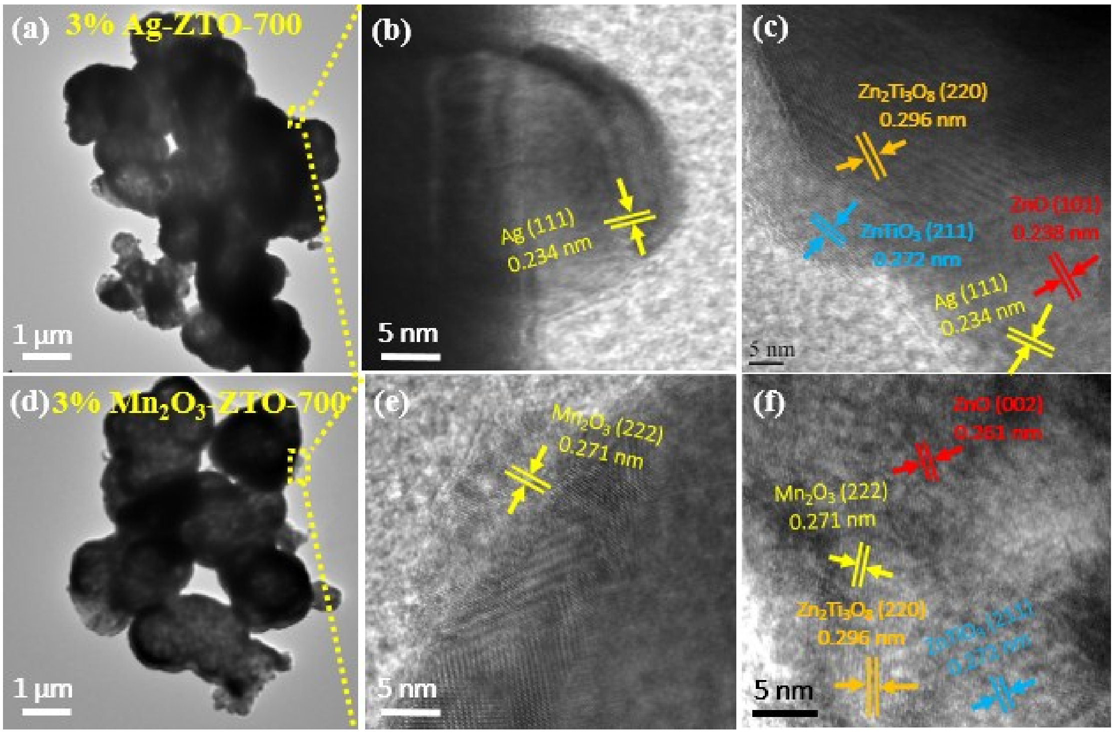

Figure S3. HRTEM images of the samples 3% Ag-ZTO-700 (a)-(c) and 3% Mn_2O_3-ZTO-700 (d)-(f)

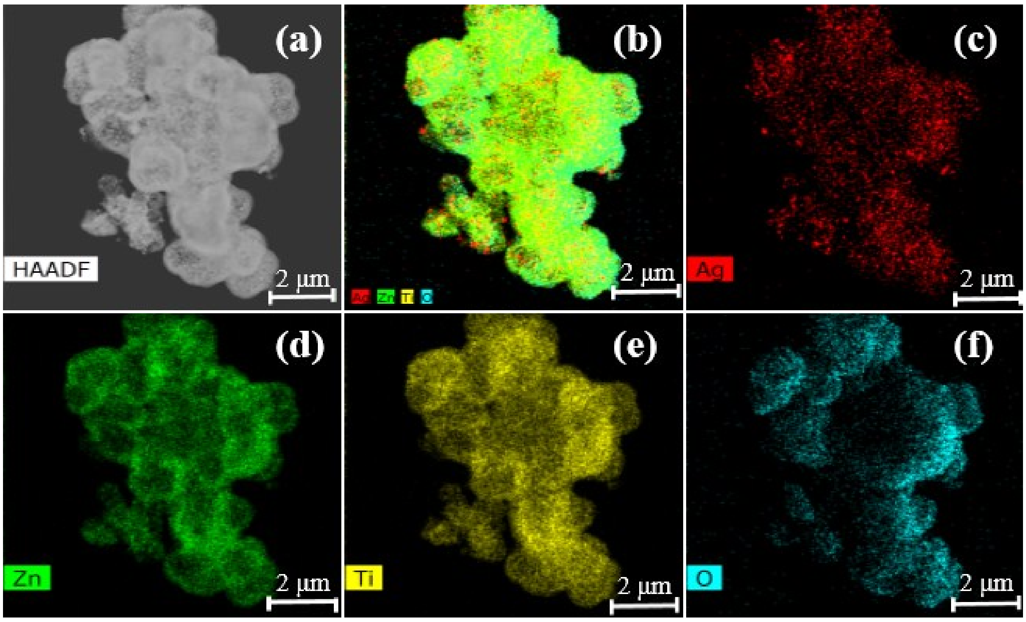

Figure S4. HAADF image and element mapping images of the sample 3% Ag-ZTO-700: (b) all elements; (c) Ag; (d) Zn; (e) Ti; (f) O.

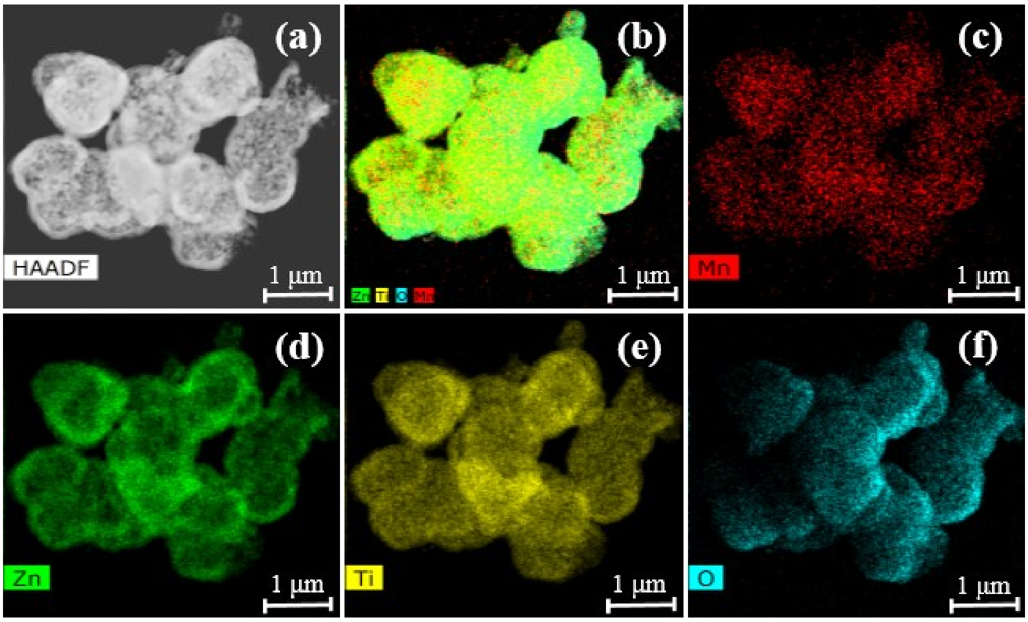

Figure S5. HAADF image and element mapping images of the sample 3% Mn_2O_3-ZTO-700: (b) all elements; (c) Mn; (d) Zn; (e) Ti; (f) O.

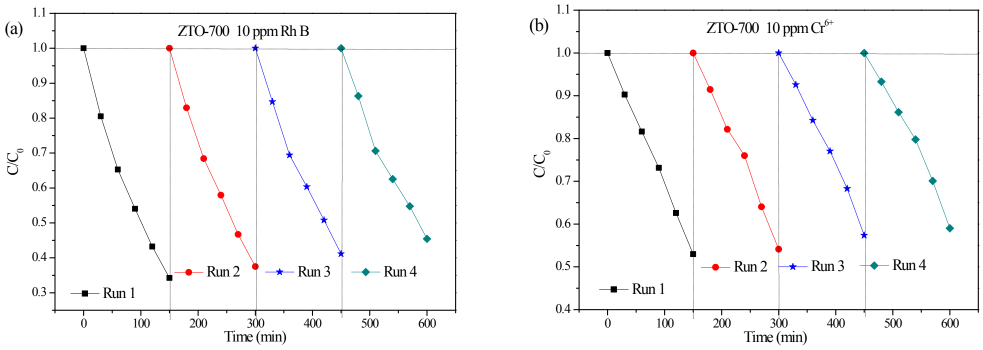

Figure S6. Photocatalytic stability of ZTO-700 in recycling reactions for the degradation of Rh B (a) and the reduction of Cr(VI) solution (b)