

Electronic Supplementary Information (ESI)

Ti³⁺:TiO₂/TiF₃ hybrid with enhanced visible-light photocatalytic reactivity

Xiaodong Meng,^a Baibiao Huang,^{*a} Xiangchao Ma,^b Zeyan Wang,^{*a} Zhaoke Zheng,^a Junpeng Wang,^a Xiaoyan Qin,^a Xiaoyang Zhang^a and Ying Dai^b

^aState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China,

^bSchool of Physics, Shandong University, Jinan 250100, China

E-mail: bbhuang@sdu.edu.cn, wangzeyan@sdu.edu.cn

1. Experimental Details

1.1 Synthesis

Synthesis of Ti³⁺:TiO₂/TiF₃ hybrid photocatalyst: Ti³⁺:TiO₂/TiF₃ hybrid was synthesized by a one-step solvothermal method. In a typical procedure, 0.275mL TiCl₄ (2.5mmol) and 0.31g TiF₄ (2.5mmol) powder were added into 45ml absolute ethanol under vigorous stirring. After that, a given amount of Zn powder with different Zn/Ti molar ratios (R_{ZT}=0, 2:8, 3:8, 4:8, 5:8 and 3:4, respectively) was added into the solution and the solution was stirred vigorously for 10 minutes. The color of the solution differed from light yellow to brown depending on the amount of Zn powder. The above-mentioned synthesis procedure was carried out at room temperature (25°C). Then the solution was transferred to a dried 120mL Teflon autoclave, and kept at 180°C for 24 hours. After being cooled to room temperature, the acquired samples were washed with ethanol for several times and dried out at 40 °C.

NaOH washing treatment: 0.3g as-prepared Ti³⁺:TiO₂/TiF₃ sample with R_{ZT}=4:8 was dispersed in 100mL sodium hydroxide solution (1M). Then the solution was stirred for 4 hours at room temperature. After stirring, the sample was collected by pumping filtration, washed with distilled water several times and dried at 40 °C.

Annealing treatment: 0.3g as-prepared Ti³⁺:TiO₂/TiF₃ sample with R_{ZT}=4:8 was annealed in dried Teflon autoclave at 140 °C for 2 hours. After being cooled to room temperature, the sample was collected.

1.2 Characterization

X-ray diffraction (XRD) patterns were obtained by using a Bruker D8 advanced X-ray powder diffractometer with Cu_{kα} radiation (λ=0.15418nm). Scanning electron microscope (SEM) images were obtained with a Hitachi S-4800 microscope. Transmission electron microscope (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL-2100 microscope. The binding energies were characterized by using X-ray photoelectron spectroscopy (XPS; VG Micro Tech ESCA 3000 X-ray photoelectron spectroscope with

monochromatic Al_{Kα} with a photon energy of 1486.6 eV at a pressure of 1×10⁻⁹ mbar). The XPS spectra energy was charge corrected to the adventitious C 1s peak at 284.8 eV.

1.3 Photocatalytic measurement

Methyl orange (MO) was chosen to evaluate the photocatalytic properties of as-prepared samples. In a typical procedure, 0.1g of as-prepared samples were dispersed in a Pyrex glass reactor (with the cross section of 30cm² and the height of 5cm) containing 100mL MO solutions with a concentration of 20mgL⁻¹. Prior to illumination, the suspension was kept in the dark with stirring for 30 min to form absorption equilibrium. The optical system for detecting the catalytic reaction consists of a 300W Xe arc lamp (PLS-SXE300, Beijing Trusttech Co. Ltd) with an ultraviolet cutoff filter to provide visible light (λ≥400nm), and the degradation of MO was monitored by UV/Vis spectroscopy (UV-7502PC, Xinmao, Shanghai).

2. Calculation Details

2.1 DFT Calculation of TiF₃

Calculations of electronic structures: The electronic structures are obtained based on the spin-polarized density functional theory (DFT) calculations using the projector augmented wave (PAW) pseudopotentials as implemented in the Vienna ab initio Simulation Package (VASP) code¹⁻². In order to overcome the general underestimation of band gap, we carried out DFT plus on-site repulsion U (DFT + U) calculations³ with effective on-site repulsion U_{eff} = U - J = 4eV. A unit cell with the lattice parameters (a = 3.872 Å) is used to simulate the bulk TiF₃. The plane wave cutoff energy of 400 eV was employed to provide sufficient precision. The Brillouin zone is sampled with 4×4×4 Γ-centered k-points.⁴ The atomic positions of all atoms are fully relaxed until the residual force is smaller than 0.02eV/Å. The total and projected densities of states (TDOS and PDOS) are calculated at the equilibrium volume using the tetrahedron method with Blöchl corrections for accuracy.⁵

2.2 Estimation of the VB and CB edges of TiF₃

Charges must redistribute until the electrochemical potentials of the compound reach the equilibrium when the atoms are connected to a compound.⁶ According to the bond length arguments, Sanderson speculate that electronegativity of a compound X_{comp} is defined by the geometric mean of the electronegativities of the constituent atoms:

$$\chi_{comp} = \sqrt[N]{\chi_1^r \chi_2^s \cdots \chi_{n-1}^p \chi_n^q} \quad (1)$$

The X_n, n and N are the electronegativity of the constituent atom, the number of species and the total number of atoms in the compound. The superscripts r, s, p and q demonstrate the numbers of atoms 1, 2, n-1 and n. The X_{comp} of TiF₃ is calculated to be 7.9eV.

The CB edge of a semiconductor at the point of zero charge (E⁰_{CB}) is empirically

defined as follows:

$$E_{CB}^0 \approx E_{CB} = \chi_{comp} - E^e - \frac{1}{2}E_g \quad (2)$$

E_g and E^e are the bandgap of the semiconductor and the energy of free electrons on the hydrogen scale (i.e. $E^e=4.5$ eV).

Through the UV/Vis diffuse reflectance spectrum of TiF_3 , the band gap of spin-up electrons is estimated to be 6.06eV. Thus, from Eq. 2, the CB of TiF_3 is estimated to be 0.37eV with respect to the normal hydrogen electrode (NHE). Then the VB edge and occupied spin-up states of TiF_3 can be calculated to be 6.42eV and 3.13eV, respectively.

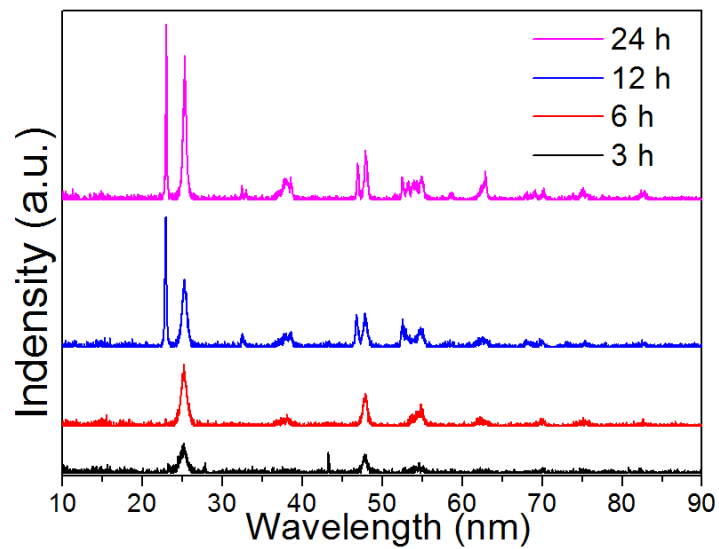


Fig. S1 XRD patterns of $\text{Ti}^{3+}:\text{TiO}_2/\text{TiF}_3$ samples obtained with $R_{\text{Zr}}=4:8$ under different reaction time.

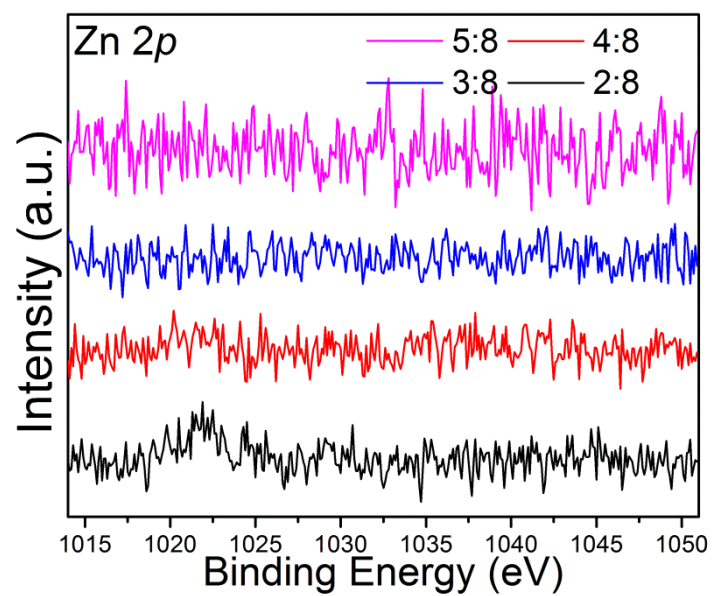


Fig. S2 $\text{Zn } 2p$ XPS spectra of TiO_2 samples obtained with different R_{Zr} .

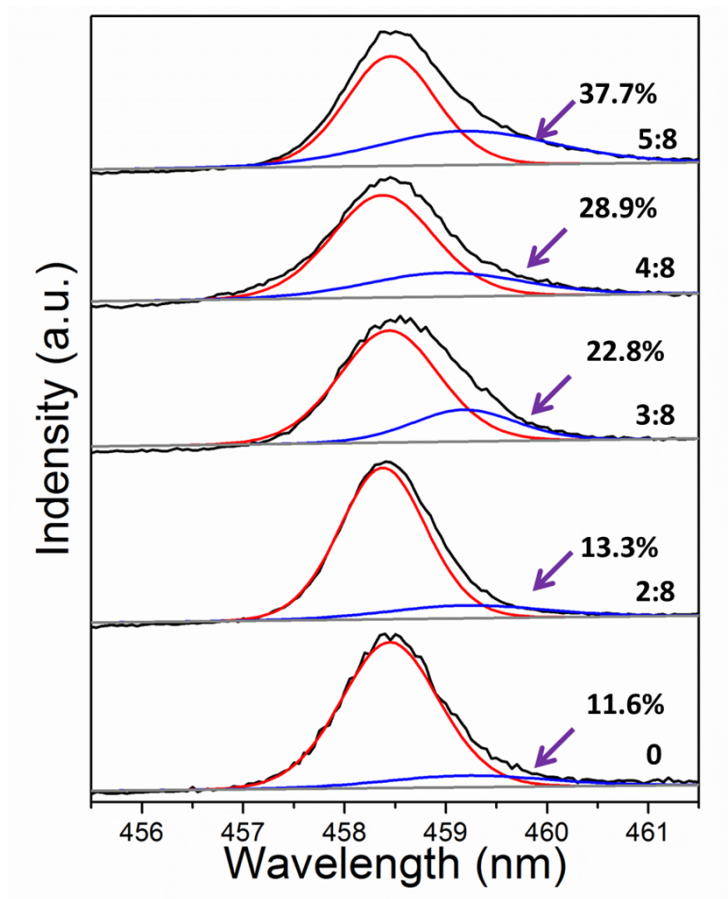


Fig. S3 Ti 2p_{3/2} XPS spectra of TiO₂ samples obtained with different R_{ZT}.

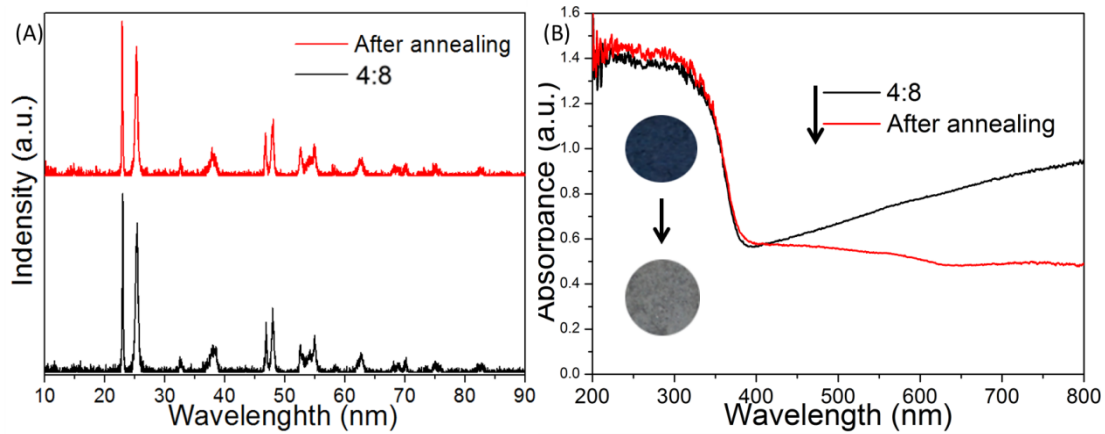


Fig. S4 (A) XRD patterns and (B) UV-Vis diffuse reflectance spectra of $\text{Ti}^{3+}:\text{TiO}_2/\text{TiF}_3$ samples obtained with $R_{\text{ZT}} = 4:8$ before and after annealing under 140°C for 2 hours.

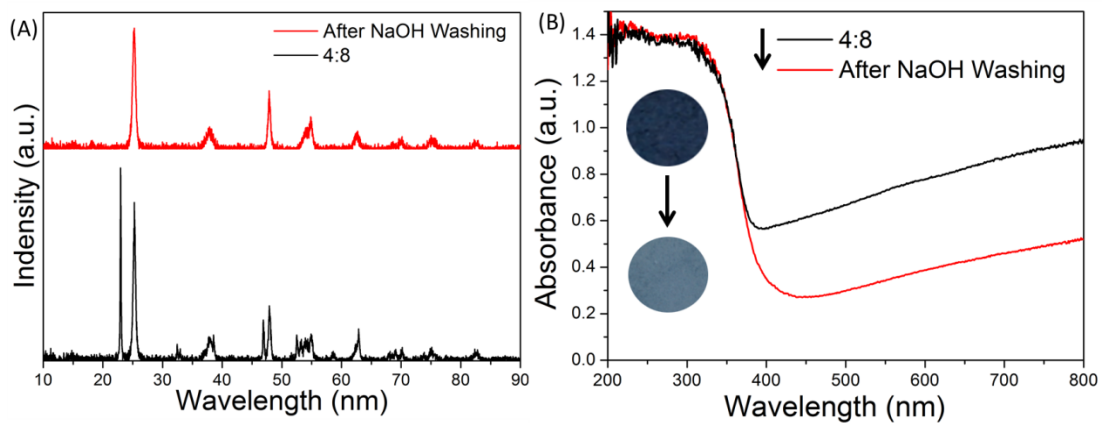


Fig. S5 (A) XRD patterns and (B) UV-vis diffuse reflectance spectra of $\text{Ti}^{3+}:\text{TiO}_2/\text{TiF}_3$ samples obtained with $R_{\text{ZT}} = 4:8$ before and after NaOH washing for 4 hours.

- 1 G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.
- 2 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 3 S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B*, 1998, **57**, 1505 - 1509.
- 4 H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
- 5 P. E. Blöchl, O. Jepsen and O. K. Andersen, *Phys. Rev. B*, 1994, **49**, 16223.
- 6 P. Wang, B. B. Huang, X. Y. Zhang, X. Y. Qin, Y. Dai, H. Jin, J. Y. Wei and M. H. Whangbo, *Chem. Eur. J.*, 2008, **14**, 10543 – 10546.