Supporting information

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X-ray Test Report of samples calcined at 600 °C for 2 h



Fig. S1 The XRD patterns of samples calcined at 600 °C for 2 h

Table S1 The XRD results of 600 °C for 2 h

NO.	Angle	D value	Intensity	Intensity/%
1	25.169	3.535	224.0	80.5
2	25.325	3.514	279.0	100

When TiO2-N-S was calcined at 600 °C, two peaks were observed (Fig S1). One peak appeared at 25.169 °, while, the other peak appeared at 25.325 ° (Table S1). The intensities of these two peaks were 80.5% and 100%, respectively. According to the standard, two peaks appeared at 25.339 ° and 25.689 °, respectively. Besides, the intensities of these two peaks were 100% and 80%, respectively. Thus, research results revealed that as-prepared samples calcined at 600 °C for 2 h might be brookite phase.

The effect of reactant concentrations on the specific surface area



Fig S2: The effect of reactant concentrations on the specific surface area

As shown in Fig S2, the specific surface area increased with increased concentration of the ammonium hydroxide. When the reaction concentration exceeded 17 ml/100 ml, a sharply decrease in surface area was observed. The specific surface area increased from 154 m²/g at the titanous sulfate concentration of 10 g/100 ml to 182 m²/g when the concentration was 15 g/100 ml, following by a sharply decreased in the specific surface area. The same trend could be seen from the preparation of TiO₂-B-S and TiO₂-Fe-S.



Fig S3: The TEM image of co-doped nanoparticles prepared with different concentration of the ammonium hydroxide

Fig S3 (a-c) showed the TEM images of co-doped nanoparticles prepared with different concentration of the ammonium hydroxide calcined at 500 °C for 1 h. Crystals were formed in spite of different concentration of raw materials, which demonstrated that the ratios of reactants have little effect on the morphologies of three co-doped TiO₂ nanomaterials (Fig S3). Fig S3-b showed the TEM image of nanoparticles when the reaction concentration was 17 ml/100 ml, resulting in a crystallite size of 8 nm. However, when the concentration exceeded 17 ml/100 ml, larger nanoparticles were observed (Fig S3-c). Firstly, with more titanous sulfate, degree of supersaturation increased, resulting in smaller particle size. However, more crystal nucleus was observed with further increase in the concentration of titanous sulfate, leading to decreased degree of supersaturation. Thus, the rate of crystal growth become slower and a higher particle size was observed. The similar explanation was observed when the effect of ammonium hydroxide concentration was investigated.

The detailed XPS of TiO₂-N-S, TiO₂-B-S and TiO₂-Fe-S



Fig. S4 The XPS spectra of TiO₂-N-S

Fig S4 showed the XPS spectra of TiO₂-N-S prepared in the MFS. Fig S4 (c) showed the XPS spectra of O1s. Fig S4 (d) showed the XPS spectra of Ti2p. Fig S4 (a) showed the XPS spectra of N 1s. Two peaks were observed. One was attributed to Ti-N, while, the other one was probably assigned to some NH₃ adsorbed on the surface of TiO₂. Fig S4 (b) showed the XPS spectra of S2p. Two peaks were detected. One was attributed to S_6^+ and the other peak was assigned to S_4^+ .



Fig S5 showed the XPS spectra of TiO₂-B-S prepared in the MFS. Fig S5 (c) showed the XPS spectra of O1s. Fig S5 (d) showed the XPS spectra of Ti2p. Fig S5 (b) showed the XPS spectra of S2p. Two peaks were detected. One was attributed to S_6^+ and the other peak was assigned to S_4^+ , which indicated that the S_4^+ and S_6^+ were incorporated into the lattice of TiO₂ and substituted for titanium atoms. A peak observed at 192 eV was contributed to B1s, indicating that B atoms was incorporated into the lattice of TiO₂ and substituted for oxygen atoms (Fig S5-a).



Fig. S6 The XPS spectra of TiO₂-Fe-S

Fig S6 showed the XPS spectra of TiO₂-Fe-S prepared in the MFS. Fig S6 (c) showed the XPS spectra of O1s. Fig S6 (d) showed the XPS spectra of Ti2p. Two peaks appeared at 710.9 and 723.9 eV were assigned to Fe2p3/2 and Fe2p1/1 photoelectrons, respectively, which demonstrated that Fe was incorporated into the lattice of TiO₂ through substituting titanium atoms existing as Fe₃⁺. Two S2p peaks located at 168 and 169 eV were observed as well as the TiO₂-N-S, indicating that the S₄⁺ and S₆⁺ were incorporated into the lattice of TiO₂ and substituted for titanium atoms.

Optimization of the degradation experiments

MO concentration



Fig. S7 Effect of MO concentration on degradation efficiency without air.

5 Typically, degradation efficiency increased when the concentration of MO solution decreased on the basis of identical catalyst loading. Thus, when the concentration of MO solution increased further, a linear decrease was observed (Fig. S7).

Air flow rate



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Fig. S8 Effect of air flow rate on degradation efficiency

Mechanistically, oxygen molecule plays a vital role in the degradation of organic water pollutant. Compared with the results displayed in Fig. S7, less MO was detected with air. Just as the results revealed in Fig. S8, when air flow rate increased to 1 ml/min, the highest degradation efficiency was obtained. Interestingly, no further improvement was observed when air flow rate increased. Maybe dissolution equilibrium is achieved in the solution, hence, more oxygen has no effect on degradation efficiency.

Temperature



Fig. S9 Effect of temperature on degradation efficiency

As we all know, organic reaction proceeds better when temperature increases appropriately. On the contrary, more MO was detected 5 with higher temperature. Besides, a linear decrease was observed when temperature increased from 20 °C to 50 °C (Fig. S9). Less high reactive free radicals existed when temperature increased. Consequently, degradation efficiency decreased. **Catalyst loading**



Fig. S10 The study of catalyst loading

10 In the degradation experiments, co-doped TiO₂ was filled in the three-phase microreactor. When catalyst loading was 0.1 g, degradation efficiency was 94.23%. Higher degradation efficiency was obtained with more photocatalysts. Interestingly, when catalyst loading was from 0.5 g to 2 g, the degradation efficiency kept constant (Fig. S10). However, more MO was detected when catalyst loading exceeded 2 g. More photocatalysts suspended in the solution, therefore the contact between photocatalysts and UV light became worse.