Research Article

Synthesis and Characterization of Fe-N-S-tri-Doped TiO₂ Photocatalyst and Its Enhanced Visible Light Photocatalytic Activity

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Fe-N-S-tri-doped TiO₂ photocatalysts were synthesized by one step in the presence of ammonium ferrous sulfate. The resulting materials were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflection spectrum (UV-Vis DRS). XPS analysis indicated that Fe (III) and S⁶⁺ were incorporated into the lattice of TiO₂ through substituting titanium atoms, and N might coexist in the forms of substitutional N (O-Ti-N) and interstitial N (Ti-O-N) in tridoped TiO₂. XRD results showed that tri-doping with Fe, N, and S elements could effectively retard the phase transformation of TiO₂ from anatase to rutile and growth of crystallite size. DRS results revealed that the light absorbance edge of TiO₂ in visible region was greatly improved by tri-doping with Fe, N, and S elements. Further, the photocatalytic activity of the as-synthesized samples was evaluated by the degradation of phenol under visible light irradiation. It was found that Fe-N-S-tri-doped TiO₂ catalyst exhibited higher visible light photocatalytic activity than that of pure TiO₂ and P25 TiO₂, which was mainly attributed to the small crystallite size, intense light absorbance in visible region, and narrow bandgap energy.

1. Introduction

Since the compounds in wastewater were treated by photocatalytic oxidation in 1976 by Carey et al. [1], TiO₂ nano-material has been considered as a promising photocatalyst in the degradation of organic or inorganic pollutants due to its inexpensiveness, nontoxicity, photostability and strong oxidation ability. However, TiO₂ can only be excited by UV light, which only occupies a small part of the solar spectrum [2]. In order to improve the utilization of solar energy, a great deal of efforts has been made, which include dye sensitization, coupling of TiO₂ with a narrow band gap semiconductor, noble metal deposition, and doping of TiO₂ with foreign ions [3–6]. Among which, doping of TiO₂ with foreign ions has been considered as an effective and feasible approach to enhance the photoresponse and photocatalytic activity. Very recently, it was reported that the doping of TiO₂

with two or three elements could further improve the light absorbance in visible region and photocatalytic activity [7–12]. From then on, many attempts have been carried out.

In this study, Fe-N-S-tridoped TiO₂ photocatalysts were synthesized by one step in the presence of ammonium ferrous sulfate. Fe (III) and S⁶⁺ were incorporated into the lattice of TiO₂ through substituting titanium atoms, and N might coexist in the forms of substitutional N (O-Ti-N) and interstitial N (Ti-O-N) in tridoped TiO₂. Fe-N-S-tridoped TiO₂ catalyst exhibited a higher visible light photocatalytic activity for the degradation of RhB than that of pure TiO₂ and P25 TiO₂.

2. Experimental

2.1. Synthesis of Materials. The Fe-N-S-tridoped TiO₂ photocatalysts were synthesized through sol-gel method in the

presence of ammonium ferrous sulfate. Firstly, 10 mL of tetrabutyl titanate was mixed with 40 mL of absolute ethanol. Then, the titanate-ethanol solution was added dropwise into another solution, which consisted of 10 mL of absolute ethanol, 12 mL of dilute nitric acid (1:5, volume ratio between concentration nitric acid and deionized water) and the desired amount of ammonium ferrous sulfate under vigorously stirring to carry out hydrolysis. Subsequently, the mixed solution was continuously stirred for 2 h at room temperature. After the resulting sol was aged for 6 h and dried for 36 h at 80°C, the TiO₂ precursor was obtained. Finally, Fe-N-S-tridoped TiO₂ catalysts were successfully obtained by calcining the TiO₂ precursor at 350°C for 4 h in an oven with a heating rate of 3°C·min⁻¹. For comparison, pure TiO₂ was synthesized under otherwise the identical conditions in the absence of ammonium ferrous sulfate.

2.2. Characterization of Materials. X-ray powder diffraction (XRD) patterns were performed on a Bruker D8 advance powder X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) conducted using a PHI-5700 ESCA system was employed to characterize the chemical states of tridoped ferrum, nitrogen, and sulfur atoms in the as-synthesized samples. All the binding energies were calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). The UV-visible diffuse reflectance spectra (DRS) of the samples were recorded on a UV-2550 UV-visible spectrophotometer with an integrating sphere attachment. The analyzed wavelength range was 300~700 nm, and BaSO₄ was used as the reflectance standard.

2.3. Evaluation of Photocatalytic Activity. The photodegradation experiments were performed in a self-made photoreactor containing 20 mL of 50 mg·L⁻¹ phenol and 20 mg of catalysts. A 350 W xenon arc lamp equipped with an UV cutoff filter ($\lambda > 420$ nm) was used as the visible light source. Prior to irradiation, the suspension was stirred in the dark for 60 min to establish the equilibrium of adsorption-desorption. At given time intervals, the phenol concentration was analyzed using the colorimetric method of 4-aminoantipyrine by with an UV-visible spectrophotometer (UV-2550) at the wavelength of 510 nm after centrifugation and filtration.

3. Results and Discussion

3.1. XRD Analysis. Figure 1 showed the XRD patterns of the as-synthesized TiO₂ samples. It can be seen that pure TiO₂ contained anatase (JCPDS, no. 21-1272), rutile (JCPDS, no. 21-1276) and brookite (JCPDS, no. 29-1360) with anatase phase in the majority according to their peak intensities. However, Fe-N-S-tridoped-TiO₂ consisted of anatase as the unique phase (JCPDS, no. 21-1272). Generally, brookite is a transitional phase from anatase to rutile during the calcinating process. Thus, it can be induced that tri-doping with Fe, N, and S elements could effectively retard the phase transformation of TiO₂ from anatase to rutile. In addition,

FIGURE 1: XRD patterns of pure and Fe-N-S-tridoped TiO₂ photocatalysts.

no XRD peaks related to the dopants were detected. One reason was that the concentration of the dopants was so low that it cannot be detected by XRD. The other was that the dopants were incorporated into the lattice of TiO₂ by substituting oxygen and titanium atoms or located in the interstitial sites. Further, the average crystallite sizes of the as-synthesized TiO₂ samples can be calculated by applying the Debye-Scherrer formula [13] on the anatase (101) diffraction peaks. After calculating, the crystallite sizes were found to be 10 and 5 nm for pure and Fe-N-S-tridoped TiO₂, respectively. Thus, we can conclude that tri-doping with Fe, N, and S elements could effectively retard the phase transformation of TiO₂ from anatase to rutile and growth of crystallite sizes.

3.2. XPS Analysis. In order to investigate the chemical states of dopants in Fe-N-S-tridoped TiO₂ photocatalyst, high-resolution XPS of Fe2p, N1s, and S2p were measured and shown in Figure 2. As shown in Figure 2(a), two peaks at 710.9 and 723.9 eV seen from the Fe2p core-level XPS spectrum were assigned to Fe2p_{3/2} and Fe2p_{1/2} photoelectrons [14, 15], respectively, demonstrating that Fe was incorporated into the lattice of TiO₂ through substituting the lattice titanium atoms as the form of Fe (III). As seen from Figure 2(b), two peaks at binding energies of 399.6 and 401.6 eV were observed. The first major peak was attributed to the substitutional N in the O-Ti-N structure [10, 16], indicating that some lattice O atoms were substituted by N atoms. The latter peak was attributed to the presence of interstitial N state as the characteristic of Ti-O-N in the doped TiO₂ sample [17, 18]. As seen from Figure 2(c), a single S2p peak located at 168.8 eV was observed, which was attributed to the presence of S⁶⁺, suggesting that S was incorporated into the lattice of TiO₂ through substituting titanium atoms [19, 20].

3.3. DRS Analysis. The optical properties of as-synthesized TiO₂ samples were investigated by UV-visible diffuse reflectance spectra and shown in Figure 3. As seen from

FIGURE 2: The bind energies of Fe2p (a), N1s (b), and S2p (c) of Fe-N-S-TiO₂ photocatalyst.

FIGURE 3: UV-visible DRS of pure and Fe-N-S-tridoped TiO₂ photocatalysts.

Figure 3, in both pure and Fe-N-S-tridoped TiO₂ samples, the onset of absorption edge was observed at 388 nm, corresponding to the band gap energy of 3.20 eV from

anatase TiO₂. However, the absorbance edge of Fe-N-S-tridoped TiO₂ was greatly red-shifted to visible light region. As shown in [21], the typical absorbance edge of N-doped TiO₂ was ranged from 380 to 500 nm due to the formation of localized N2p level above the top of valence band edge. Thus, in this study, the enlarged light absorbance in the range of 380~500 nm was attributed to the N doping, while the enhanced absorbance in the range of 500~700 nm was possibly due to the synergistic contribution from the tridoped species. Thus, it is reasonable that the Fe, N, and S elements were indeed incorporated into the lattice of TiO₂, leading to the difference in the crystal and electronic properties of the tridoped TiO₂.

3.4. Photocatalytic Activity. The degradation of phenol was used to evaluate the photocatalytic activities of the as-synthesized TiO₂ samples. The photocatalytic activity of P25 TiO₂ was conducted as a reference. The experimental results were shown in Figure 4. Obviously, as seen from Figure 4, Fe-N-S-tridoped TiO₂ exhibited higher visible light photocatalytic activity than that of pure TiO₂ and P25 TiO₂, for which 85.9% of phenol can be degraded after 2 h of

FIGURE 4: Photocatalytic degradation rate of phenol on different TiO₂ photocatalysts.

visible light irradiation. The enhanced photocatalytic activity was mainly attributed to small crystallite size, intense light absorbance in visible region and narrow band gap energy.

4. Conclusions

In summary, Fe-N-S-tridoped TiO₂ photocatalyst was successfully synthesized by one step in the presence of ammonium ferrous sulfate. Fe (III) and S⁶⁺ were simultaneously incorporated into the lattice of TiO₂ through substituting titanium atoms, and N might coexist in the forms of substitutional N (N-O-Ti) and interstitial N (O-Ti-N) in tridoped TiO₂. In addition, tri-doping with Fe, N, and S elements could effectively retard the phase transformation of TiO₂ from anatase to rutile and growth of crystallite size. The light absorbance edge of TiO₂ was greatly improved by tri-codoping with Fe, N, and S elements. The as-synthesized Fe-N-S-tridoped TiO₂ presented higher visible light photocatalytic activity for the degradation of phenol than that of pure TiO₂ and P25 TiO₂. The enhanced photocatalytic activity was mainly attributed to the small crystallite size, intense light absorbance in visible region, and narrow band gap energy.

Acknowledgments

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