Research Article

Synthesis and Photocatalytic Activity of Mo-Doped TiO₂ Nanoparticles

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The undoped and Mo-doped TiO₂ nanoparticles were synthesized by sol-gel method. The as-prepared samples were characterized by X-ray diffraction (XRD), diffuse reflectance UV-visible absorption spectra (UV-vis DRS), X-ray photoelectron spectra (XPS), and transmission electron microscopy (TEM). The photocatalytic activity was evaluated by photocatalytic degradation of methylene blue under irradiation of a 500 W xenon lamp and natural solar light outdoor. Effects of calcination temperatures and Mo doping amounts on crystal phase, crystallite size, lattice distortion, and optical properties were investigated. The results showed that most of Mo⁶⁺ took the place of Ti⁴⁺ in the crystal lattice of TiO₂, which inhibited the growth of crystallite size, suppressed the transformation from anatase to rutile, and led to lattice distortion of TiO₂. Mo doping narrowed the band gap (from 3.05 eV of TiO₂ to 2.73 eV of TiMo_{0.02}O) and efficiently increased the optical absorption in visible region. Mo doping was shown to be an efficient method for degradation of methylene blue under visible light, especially under solar light. When the calcination temperature was 550°C and the Mo doping amount was 2.0%, the Mo-doped TiO₂ sample exhibited the highest photocatalytic activity.

1. Introduction

Titanium dioxide (TiO₂) has been considered as one of good photocatalysts due to its excellent properties such as low cost, nontoxicity, chemical stability, and high photocatalytic activity [1–6]. However, TiO₂ only becomes active under irradiation with ultraviolet (UV) light (3–4% of the solar energy) because of its wide band gap (3.2 eV), and visible portion (approximately 45%) cannot get used effectively [7]. Therefore, it is a critical issue to reduce the band gap of TiO₂ for making it photosensitive to visible light. The enhancement of optical absorption in visible region will improve the photocatalytic efficiency of TiO₂, which may promote the utilization of the solar light. In the last decade, great efforts have been made to modify the band gap of TiO₂. These results show that metal ion doping is one of the effective ways. At present, the investigations about doping elements mostly focus on transition metal ions doping [8–11]. Transition metal

ions modify microstructures and electronic structures of TiO₂ and increase its photocatalytic efficiency. Molybdenum (Mo) is a transition metal and its doping into TiO₂ can shift the absorption edge towards visible region, increase the absorption under both UV and visible light, and enhance the photocatalytic activity of TiO₂ [12–15]. However, due to the large number of possible variations, it is not simple to find out the optimum doping amount and calcination temperature at the same time. Besides, obtaining optimum photocatalysts to function under solar light is very meaningful.

In this work, we successfully prepared Mo-doped TiO₂ nanoparticles by sol-gel method. The effects of doping amount and calcination temperature on the photocatalytic activity of photocatalysts were studied. Structure characteristics characterization and analysis of as-prepared samples were studied by XRD, UV-vis DRS, XPS, and TEM. By degradation of methylene blue, we investigated the optimal doping amount and calcination temperature of Mo-doped

TiO₂ nanoparticles under a 500 W xenon lamp and studied its photocatalytic efficiency under natural solar light outdoor.

2. Experimental

2.1. Materials. Tetrabutyl titanate (Ti(OC₄H₉)₄) was obtained from Tianjin Guangfu Institute of Fine Chemicals (China). Absolute ethyl alcohol (CH₃CH₂OH) was obtained from Beijing Chemical Works (China). Ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was obtained from Tianjin Guangfu Technology Development Co., Ltd. (China). Nitric acid (HNO₃) was obtained from Xilong Chemical Co., Ltd. (China). All reagents were of analytical grade.

2.2. Preparation of Photocatalysts. Mo-doped TiO₂ nanoparticles were synthesized by sol-gel method. Under continuous stirring, different amounts of ammonium molybdate were previously dissolved in a mixture solution consisting of 48.2 mL ethanol, 6 mL deionized water, and 0.6 mL nitric acid to form the mixture solution A. Then solution A was added dropwise into the mixture solution B containing 21.3 mL tetrabutyl titanate and 48.2 mL ethanol. The obtained homogeneous solution was magnetically stirred continuously for 1 h to form a gel and subsequently aged at room temperature for 24 h. The gel was then dried in an oven at 60°C until a dry gel was obtained. The dry gel was calcined in a muffle furnace at 300, 450, 550, and 650°C, respectively, to obtain Mo-doped TiO₂ nanoparticles. For comparison, the samples of pure TiO₂ and Mo-doped TiO₂ were prepared by similar procedures. Atomic ratios of Mo in the samples were 0.5%, 1.0%, 2.0%, and 3.5%, respectively. The as-prepared samples were denoted as MT(*n t*), where hereafter *n* represented the atomic ratio of Mo/Ti (%) and *t* represented calcination temperature (°C). The undoped TiO₂ was denoted as T(*t*) and used as a reference.

2.3. Characterizations. The crystal structures were examined with a powder X-ray diffraction (XRD) (BRUKER D8 ADVANCE, Cu Kα, λ = 1.54056 Å). UV-visible reflectance spectra (UV/Vis DSC) for the samples were collected on a UV-visible spectrometer (UV-2550 UV/vis Spectrometer, Shimadzu). X-ray photoelectron spectra (XPS) analysis was conducted through an X-ray photoelectron spectrometer (Thermo ESCALAB 250) with an Al Kα (1486.7 eV) X-ray source. Transmission electron microscopy (TEM) was recorded on a FEICNAI F20 microscope.

2.4. Photocatalytic Degradation Experiment. The photocatalytic activity experiment of prepared nanoparticles was conducted in a quartz glass (Φ70 × 80 mm). In each experiment, 0.2 g photocatalyst was added to 400 mL of 20 mg·L⁻¹ methylene blue solution. Two kinds of light source were used: a 500 W xenon lamp and natural solar light outdoor (July 24, 2014; N43.88°, E125.32°). Every 30 min, 5 mL suspension was sampled, centrifuged, and tested by UNICO 2100 visible spectrophotometer at 664 nm.

TABLE 1: Crystallite parameters of TiO₂ with different Mo doping amounts.

Samples	Anatase in TiO ₂ /%	Crystalline size/nm		Lattice distortion	
		A	R	A	R
T(550)	44.4	29.8	36.2	0.30	0.22
MT(0.5 550)	78.3	23.5	33.3	0.38	0.24
MT(1.0 550)	82.7	20.2	32.4	0.42	0.25
MT(2.0 550)	100	16.6		0.54	
MT(3.5 550)	100	14.6		0.61	

3. Results and Discussion

3.1. XRD Analysis. Figure 1(a) shows XRD patterns of samples calcined at 550°C with different Mo doping amounts. The XRD peaks at $2\theta = 25.6^\circ$ (101) and $2\theta = 27.7^\circ$ (110) were often taken as the characteristic peaks of anatase and rutile crystal phase, respectively [16]. The intensities of anatase peaks increased and the width of peaks became broader with Mo doping amount increasing.

The phase contents of the samples were calculated by $x_A = 1/(1 + 1.26I_R/I_A)$ where x_A is the fraction of anatase phase and I_A and I_R are the intensities of the anatase (101) and rutile (110) diffraction peaks, respectively [17]. The crystallite sizes were calculated with Scherrer formula $D = K\lambda/\beta \cos \theta$ where D is the average crystallite size in angstroms, K is a dimensionless constant (0.89 here), λ is the wavelength of the X-ray radiation (Cu Kα = 0.15406 nm), β is the full width at half maximum (FWHM). The lattice distortions were attained from $\epsilon = \beta/4tg\theta$ in which ϵ is lattice distortion and θ is the diffraction angle [18]. Results were listed in Table 1.

It could be seen that crystallite size decreased and anatase TiO₂ increased with Mo doping amount increasing. Conclusions could be derived that the Mo doping inhibited the growth of crystallite size and suppressed the transformation from anatase to rutile of TiO₂. It was noted that there was no detected MoO₃ phase. This might be ascribed to the incorporation of Mo⁶⁺ ion into the TiO₂ lattice. The ionic radius of Mo⁶⁺ is 0.062 nm, and that of Ti⁴⁺ is 0.068 nm [19]. Because of the similarity in their ionic sizes, Mo could easily be incorporated into the TiO₂ lattice, resulting in a narrower energy gap, which could be observed in the following UV-vis spectroscopy. Another consequence was that Mo doping increased lattice distortion of samples, which was confirmed by data in Table 1. Generally, smaller crystallite was attributed to greater lattice distortion caused by larger doping amount, which would also enhance the concentration of lattice defects and thus precipitate carrier recombination [20]. This implied that excessive doping, though more carriers could be generated due to smaller energy gap, would exert a negative effect on photocatalytic properties.

Figure 1(b) shows XRD patterns of samples with different calcination temperatures. With calcination temperature increasing, the diffraction peaks became sharper and stronger due to the growth of anatase crystallites. Obviously, the phase transformation from anatase to rutile occurred between 550°C and 650°C. The average crystallite sizes at 300, 450,

FIGURE 1: XRD patterns of samples: (a) MT(550) with different Mo doping amounts; (b) MT(2.0) with different calcination temperatures.

TABLE 2: The band gap energies of samples with different Mo doping amounts.

Sample	λ (nm)	E_g (eV)
T(550)	407.09	3.05
MT(0.5 550)	411.84	3.01
MT(1.0 550)	421.46	2.94
MT(2.0 550)	454.18	2.73
MT(3.5 550)	444.56	2.79

550, and 650°C were 5.3, 8.9, 16.6, and 25.7 nm, respectively. It could be observed that the crystallite size increased with temperature increasing, which might be caused by particle agglomeration under high temperature [21].

3.2. UV-Vis DRS Analysis. Figure 2 shows the UV-visible absorption spectra of samples with different Mo doping amounts. It showed that Mo doping caused a notable red shift of the absorption edge, which was beneficial to the photocatalytic activity of Mo-doped TiO_2 nanoparticles. By offering more valence electrons which could be incited easily into free carriers by photons, Mo doping introduced a donor level under the conduction band of TiO_2 , leading to a narrower band gap [20]. To MT(3.5 550), however, the absorption edge moved inversely to the shorter wavelength range. This phenomenon was a typical consequence of quantum effect and could be explained as follows: as crystallite size fell into nanoscale, the movement of electrons would be confined more intensively, resulting in the differentiation near the Fermi level and broaden the band gap [22]. The band gap was calculated by $E_g = 1240/\lambda$ where E_g (eV) is the band gap and λ (nm) is the wavelength of the absorption edge in the spectrum [23]. The wavelength of the absorption edge and the calculated band gap of samples were listed in Table 2.

FIGURE 2: UV-visible absorption of samples with different Mo doping amounts.

It could be seen that when Mo doping amount increased from 0 to 2.0%, the band gap decreased from 3.05 eV to 2.73 eV. But with Mo doping amount further increasing, the band gap increased to 2.79 eV, which corresponded to the blue shift of absorption edge as discussed above. Therefore, it could be concluded that an appropriate amount of Mo could effectively shorten the energy of TiO_2 while excessive Mo might have the opposite effect.

3.3. XPS Analysis. The XPS spectra of T(550) and MT(2.0 550) were measured. As shown in Figure 3(a), the peaks located at binding energy of 458.4 eV and 463.9 eV corresponded to $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ of TiO_2 , respectively, which

FIGURE 3: XPS spectra of samples: (a) Ti2p of T(550) and MT(2.0 550); (b) Mo3d of MT(2.0 550); (c) O1s of MT(2.0 550); (d) valance band spectra of T(550) and MT(2.0 550).

TABLE 3: Solar light intensity in the experiment.

Time/min	0	30	60	90	120	150	180	210	240	270	300
Intensity/Lux	35000	37000	47000	42000	47000	47500	48000	38000	42500	40000	27000

were consistent with the values of Ti^{4+} in TiO_2 lattice [24]. For MT(2.0 550), the binding energies of $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ were 458.55 eV and 464.25 eV, respectively; a few right shifts were caused by Mo doping, which might be an indication that molybdenum atoms indeed substituted titanium atoms in the lattice.

$\text{Mo}3d_{5/2}$ and $\text{Mo}3d_{3/2}$ peaks of MT(2.0 550) are shown in Figure 3(b). The peaks located at 232.6 eV and 235.7 eV corresponded to the feature of Mo^{6+} , while peaks located at 231.8 eV and 234.8 eV corresponded to Mo^{5+} [25]. No Mo^{4+} peak was observed, indicating that the main valances of molybdenum in the samples were +6 and +5. From the ratio of peak area, it could be obtained that the atomic percentage of Mo^{6+} and Mo^{5+} would be 72.2% and 27.8%, respectively. That was as follows: most doped Mo ions existed as Mo^{6+}

ions in TiO_2 lattice, but a small part of Mo ions existed as Mo^{5+} ions. The presence of Mo^{5+} ions signified no adequate oxygen in TiO_2 lattice to support Mo being as complemented oxidation state of Mo^{6+} ions. So, the existence of Mo^{5+} ions also implied that MT(2.0 550) was in oxygen deficiency state (as one titanium atom needed two O atoms but one molybdenum atom needed three O atoms). The surface deficiency of O could be complemented by adsorbing more oxygen, which was beneficial to photocatalytic degradation.

XPS spectrum of the O1s of MT(2.0 550) is given in Figure 3(c). The O1s spectrum could be decomposed into two peaks. The peak at 529.7 eV was assigned to crystal lattice oxygen (O_L), while the peak located at 531.5 eV could be attributed to adsorbed oxygen (O_H) [26]. The O_L was mainly attributed to the contribution of Ti-O in TiO_2 crystal lattice,

FIGURE 4: TEM images of samples: (a, b) T(550); (c, d) MT(2.0 550).

and the O_H was ascribed to lattice distortion as well as porous structure brought about by Mo doping.

According to the valance band (VB) spectra in Figure 3(d), the VB maxima of T(550) and MT(2.0 550) were 3.04 eV and 2.73 eV, respectively. It indicated that Mo doping could narrow the band gap and extend the absorption edge of TiO_2 towards visible light, which was consistent with the UV-vis spectroscopy.

3.4. TEM Analysis. Figure 4 showed the microstructures of T(550) and MT(2.0 550). It could be seen that MT(2.0 550) showed a better dispersion than T(550). All the samples consisted of highly crystalline and compact nanoparticles. For MT(2.0 550), a fine particulate morphology in porous structure could be observed. Figures 4(a) and 4(b) revealed that there were different kinds of crystalline TiO_2 . In Figure 4(b), it could be seen that the measured lattice spacing of T(550) was 0.32 nm, which was in coincidence with the spacing distance of (110) plane of rutile TiO_2 [27]. In Figure 4(d), it is indicated that in the MT(2.0 550) there existed a lattice spacing (0.35 nm) which was anatase TiO_2 [27]. So both

the XRD and TEM observations presented the coincident results and showed that MT(2.0 550) was nanocrystalline anatase TiO_2 . These results also provided evidence that the Mo doping suppressed the formation of the rutile TiO_2 and inhibited the agglomeration of TiO_2 .

3.5. Photocatalytic Activity. Figure 5 shows photocatalytic degradation of as-prepared photocatalysts with different Mo doping amounts. It could be seen that with Mo doping amount increasing from 0 to 2.0%, the degradation rate of methylene blue increased by 36%, which indicated that Mo was doped into TiO_2 lattice and enhanced the photocatalytic activity. However, with Mo doping amount further increasing to 3.5%, the degradation efficiency decreased, which was still better than that of T(550), MT(0.5 550), and MT(1.0 550) samples. This could be ascribed to the fact that the concentration of holes on the valence band increased with Mo^{6+} ions increasing and excessive Mo^{6+} ions would cause the carriers recombination. As a result, the recombination of generated electron/hole pair exceeded the carrier transition to the surface of photocatalysts. Once the concentration of

FIGURE 5: Photocatalytic degradation of samples with different Mo doping amounts.

FIGURE 6: Photocatalytic degradation of samples with different calcination temperatures.

Mo was beyond an optimum quantity, Mo^{6+} ions role as a carrier recombination center would counteract its role of trapping carriers and prolonging carrier lifetime [28]. So a decrease of photocatalytic activity was observed.

Figure 6 shows the results of photocatalytic degradation of samples with different calcination temperatures. It indicated that calcination temperature had great influence on the structure of photocatalyst. With the calcination temperature increasing from 300°C to 550°C , the degradation effect increased. However, when the calcination temperature reached 650°C , the degradation effect decreased, which might be related to the crystallite size and the ratio of anatase and rutile TiO_2 in the samples. High temperature caused particle agglomeration and decreased the surface

FIGURE 7: Photocatalytic degradation of MT(2.0 550) under different light sources (7000 Lux xenon lamp, solar light (Table 3)).

area of photocatalysts, which could also affect the efficiency. According to Figures 5 and 6, conclusions could be derived that the optimum Mo doping amount and the calcination temperature were 2.0% and 550°C , respectively.

Due to different band gap corresponding to different excitation wavelengths, light utilization of photocatalysts on different wave bands was not the same. Two kinds of light source were used in the experiments, respectively. The results are shown in Figure 7. It could be observed that MT(2.0 550) had a better performance than T(550) under both solar light and xenon lamp. It might be ascribed to the fact that Mo ions could capture the photogenerated carriers to prolong the lifetime of carriers or quicken the separation of carriers [29], which enhanced the photocatalytic activity and improved the utilization of solar light. Mo-doped TiO_2 photochemical catalysis was shown to be an efficient method for degradation of methylene blue under visible light, especially under solar light.

4. Conclusions

Undoped and Mo-doped TiO_2 nanoparticles were successfully synthesized by sol-gel method. XRD results showed that crystallite size decreased and anatase TiO_2 increased with Mo doping amount increasing. Mo doping inhibited the growth of crystallite size and suppressed the transformation from anatase to rutile of TiO_2 . For Mo-doped TiO_2 , the phase transformation from anatase to rutile occurred between 550°C and 650°C . The crystallite size increased with temperature increasing, which might be caused by particle agglomeration under high temperature. UV-vis DRS indicated the optical absorption edges of Mo-doped samples shifted to longer wavelength regions. Ti2p, Mo3d, and O1s of Mo-doped TiO_2 were detected by XPS, which suggested that molybdenum atom was doped into TiO_2 and most doped Mo ions existed as Mo^{6+} ions in TiO_2 lattice. All

the samples consisted of highly crystalline and compact nanoparticles. Mo-doped TiO₂ photochemical catalysis was shown to be an efficient method for degradation of methylene blue under visible light, especially under solar light. When the calcination temperature was 550°C and the Mo doping amount was 2.0%, the Mo-doped TiO₂ sample exhibited the highest photocatalytic activity.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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