

## Preparation, characterization and photocatalytic performance of Mo-doped ZnO photocatalysts

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A series of Mo-doped ZnO photocatalysts with different Mo-dopant concentrations have been prepared by a grinding–calcination method. The structure of these photocatalysts was characterized by a variety of methods, including N<sub>2</sub> physical adsorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, photoluminescence (PL) emission spectroscopy, and UV-vis diffuse reflectance spectroscopy (DRS). It was found that Mo<sup>6+</sup> could enter into the crystal lattice of ZnO due to the radius of Mo<sup>6+</sup> (0.065 nm) being smaller than that of Zn<sup>2+</sup> (0.083 nm). XRD results indicated that Mo<sup>6+</sup> suppressed the growth of ZnO crystals. The FT-IR spectroscopy results showed that the ZnO with 2 wt.% Mo-doping has a higher level of surface hydroxyl groups than pure ZnO. PL spectroscopy indicated that ZnO with 2 wt.% Mo-doping also exhibited the largest reduction in the intensity of the emission peak at 390 nm caused by the recombination of photogenerated hole-electron pairs. The activities of the Mo-doped ZnO photocatalysts were investigated in the photocatalytic degradation of acid orange II under UV light ( $\lambda = 365$  nm) irradiation. It was found that ZnO with 2 wt.% Mo-doping showed much higher photocatalytic activity and stability than pure ZnO. The high photocatalytic performance of the Mo-doped ZnO can be attributed to a great improvement in the surface properties of ZnO, higher crystallinity and lower recombination rate of photogenerated hole-electron (e<sup>-</sup>/h<sup>+</sup>) pairs. Moreover, the undoped Mo species may exist in the form of MoO<sub>3</sub> and form MoO<sub>3</sub>/ZnO heterojunctions which further favors the separation of e<sup>-</sup>/h<sup>+</sup> pairs.

**ZnO, Mo doping, e<sup>-</sup>/h<sup>+</sup> pairs, photocatalysis, acid orange II**

### 1 Introduction

Recently, semiconductor photocatalysis based on the utilization of solar energy has attracted a lot of attention due to its promising applications like water disinfection, and the degradation and complete mineralization of organic contaminants in waste water [1–7]. Zinc oxide, a semiconductor with a large excitation energy [8] of 60 meV, plays an important role in many application fields, such as optoelec-

tronics, photocatalysis, and gas sensing [9–12]. However, as a photocatalyst, ZnO shows a low activity compared with commercial TiO<sub>2</sub> catalysts in the photocatalytic degradation of organic compounds. Moreover, ZnO suffers from photoinstability in aqueous solution due to its problem of photocorrosion. Thus, improving both the activity and stability is important if ZnO is to be employed as an effective photocatalyst. Several methods have been reported to improve the photocatalytic performance of ZnO, such as noble metal deposition [13, 14], semiconductor coupling [15, 16], non-metal element doping [17, 18], and polymer composite formation [19, 20]. Kislov *et al.* [21] investigated the photo-

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stability and photocatalytic activity of different crystal surfaces of ZnO. They found that photostability and photocatalytic activity were strongly dependent on its surface atomic structures. If the surface is polar and has high surface energy, photolysis of ZnO easily takes place, which causes the problem of photocorrosion. Shen *et al.* [22] reported that doping of transition metals (Cr, Mn, Fe, Co, Ni, Cu) could induce a change in the cohesive energy, density of states, band structure, and optical absorption properties of ZnO. Our recent research has shown that doping of Ce into ZnO causes an increase in surface hydroxyl groups and suppresses the recombination rate of electron/hole ( $e^-/h^+$ ) pairs [23]. Inspired by these investigations, in this work, we fabricated a series of Mo-doped ZnO photocatalysts with different Mo concentrations and investigated the influences of Mo doping on the structure and photocatalytic performance of ZnO.

## 2 Experimental

### 2.1 Synthesis

All chemicals were of analytical grade and used as received without further purification. In a typical synthesis, 0.1 g of hexadecyltrimethylammonium bromide (CTAB) surfactant (AR, Sinopharm Chemical Reagent Co. Ltd.), 50 mL of deionized (DI) water and 3.673 g of  $Zn(NO_3)_2 \cdot 6H_2O$  (AR, Sinopharm Chemical Reagent Co. Ltd.) were mixed, to give solution A; 0.988 g of NaOH (AR, Sinopharm Chemical Reagent Co. Ltd.) and 50 mL of DI water were mixed, to give solution B. Solution B was added dropwise to solution A with magnetic stirring and the final mixture further stirred for half an hour. The resulting precipitate was centrifuged and washed with DI water and absolute ethanol in sequence, and finally dried at 80 °C in an oven for 12 h to obtain  $Zn(OH)_2$ . According to the required doping concentration, a certain amount of  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  (AR, Sinopharm Chemical Reagent Co. Ltd.) was mixed with the  $Zn(OH)_2$  and the mixture was ground for 1 h. The mixture was then heated in air at a ramp rate of 3 °C/min to 600 °C and calcined for 2 h, and finally naturally cooled to room temperature. The final Mo content in ZnO was determined by X-ray fluorescence analysis (Magix 601). The photocatalysts are denoted Mo(1%)/ZnO, Mo(2%)/ZnO, Mo(3%)/ZnO and Mo(8%)/ZnO indicating the wt.% amount of Mo in the photocatalyst.

### 2.2 Characterization

The Brunauer–Emmett–Teller (BET) surface areas of the sample were obtained from  $N_2$  adsorption/desorption isotherms on an automatic analyzer (NOVA 4000). The samples were outgassed for 2 h under vacuum at 350 °C prior to adsorption. Powder X-ray diffraction data (XRD) were recorded at a scanning rate of  $0.01^\circ s^{-1}$  using a Bruker D8

ADVANCE X-ray diffractometer at 40 kV and 40 mA with monochromatized Cu  $K\alpha$  ( $\lambda = 1.54178$  nm) radiation. Scanning electron microscopy (SEM) measurements were carried out on a XL30 (Philips, the Netherlands) scanning electron microscope, which was used to investigate the morphology and surface roughness of samples. The products were conductively coated with gold by sputtering for 30 s to minimize charging effects before SEM imaging was performed. Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet 470 FTIR spectrometer (USA) with a resolution of  $4\text{ cm}^{-1}$ . Samples were pressed into KBr disks. The samples were dried at 250 °C for 2 h before pressing. To investigate the recombination and lifespan of photogenerated  $e^-/h^+$  pairs in the photocatalysts, the photoluminescence (PL) emission spectra of the samples were recorded. A 320 nm He–Cd laser was used as an excitation light source. The emission from the sample was measured by a spectrometer (Spex 500M, USA) equipped with a photon counter (SR400, USA). UV–vis diffuse reflectance spectra (DRS) were measured using a UV–vis spectrophotometer (UV-2550, Shimadzu). Absorption spectra were referenced to  $BaSO_4$ .

### 2.3 Photocatalytic activity measurements

The photocatalytic activities of the samples were determined by measuring the degradation of acid orange II in an aqueous solution under ultraviolet light irradiation. In activity tests, a 365 nm UV lamp (15 W, Cole-Parmer Instrument Co.) was used as ultraviolet light source. The photocatalyst (0.05 g) was suspended in 80 mL of aqueous solution of acid orange II with a concentration of  $C_0 = 0.020$  g/L. Prior to light illumination, the suspension was strongly magnetically stirred for 40 min in the dark to establish adsorption/desorption equilibrium. The suspension was vigorously stirred in the photoreactor during the process and the temperature of the suspension was maintained at  $22 \pm 2$  °C by circulation of water through an external cooling coil. At given intervals of illumination, aliquots of the suspension were removed and centrifuged. The clear upper layer solution was analyzed using a spectrophotometer (UV-2550, Shimadzu). The dye concentration was measured at  $\lambda = 478$  nm, which is the maximum absorption wavelength for acid orange II. The degradation ratio ( $D$ ) of acid orange II was calculated according to the equation:

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

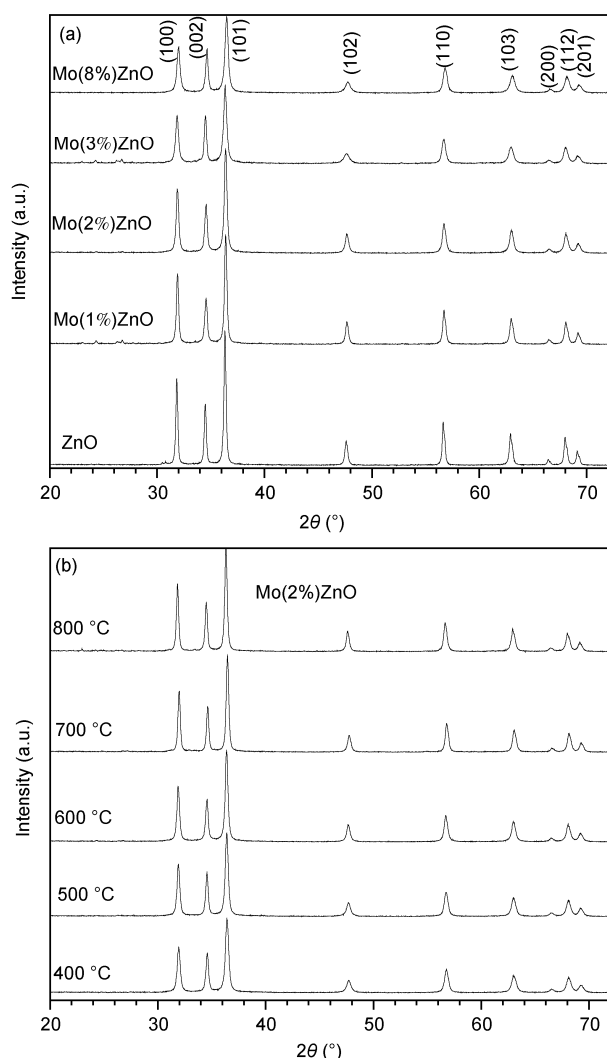
where  $C_0$  is the initial absorbance and  $C$  is the final absorbance.

## 3 Results and discussion

### 3.1 XRD analysis

XRD was used to investigate the crystalline nature of the prepared samples. The XRD patterns for the pure ZnO and

Mo-doped ZnO samples are shown in Figure 1(a). Clear characteristic peaks at  $2\theta$  values of 32.0, 34.6, 36.4, 47.8, 56.9, 63.0, 66.5, 68.1 and 69.2° are observed, and can be indexed to the standard card for hexagonal wurtzite ZnO (JCPDS No.36-1451). The sharp diffraction peaks demonstrate that these samples have high crystallinity. Moreover, no characteristic peaks of impurities, such as  $\text{MoO}_3$  and  $\text{Zn}(\text{OH})_2$ , were detected in the diffraction patterns of the composite samples, confirming that  $\text{Zn}(\text{OH})_2$  was converted to ZnO, and that Mo exists in a highly dispersed state. Figure 1(b) shows XRD patterns of Mo(2%)ZnO calcined at different temperatures. No changes in the position of the diffraction peaks were observed, which indicates that no new crystalline phases were produced. With increasing calcination temperature, the intensity of the diffraction peaks of ZnO gradually increases, indicating an improvement in crystallinity.



**Figure 1** X-ray diffraction patterns of the samples. (a) Zinc oxide and Mo-doped ZnO with different Mo contents calcined at 600 °C; (b) Mo(2%)ZnO calcined at different temperatures.

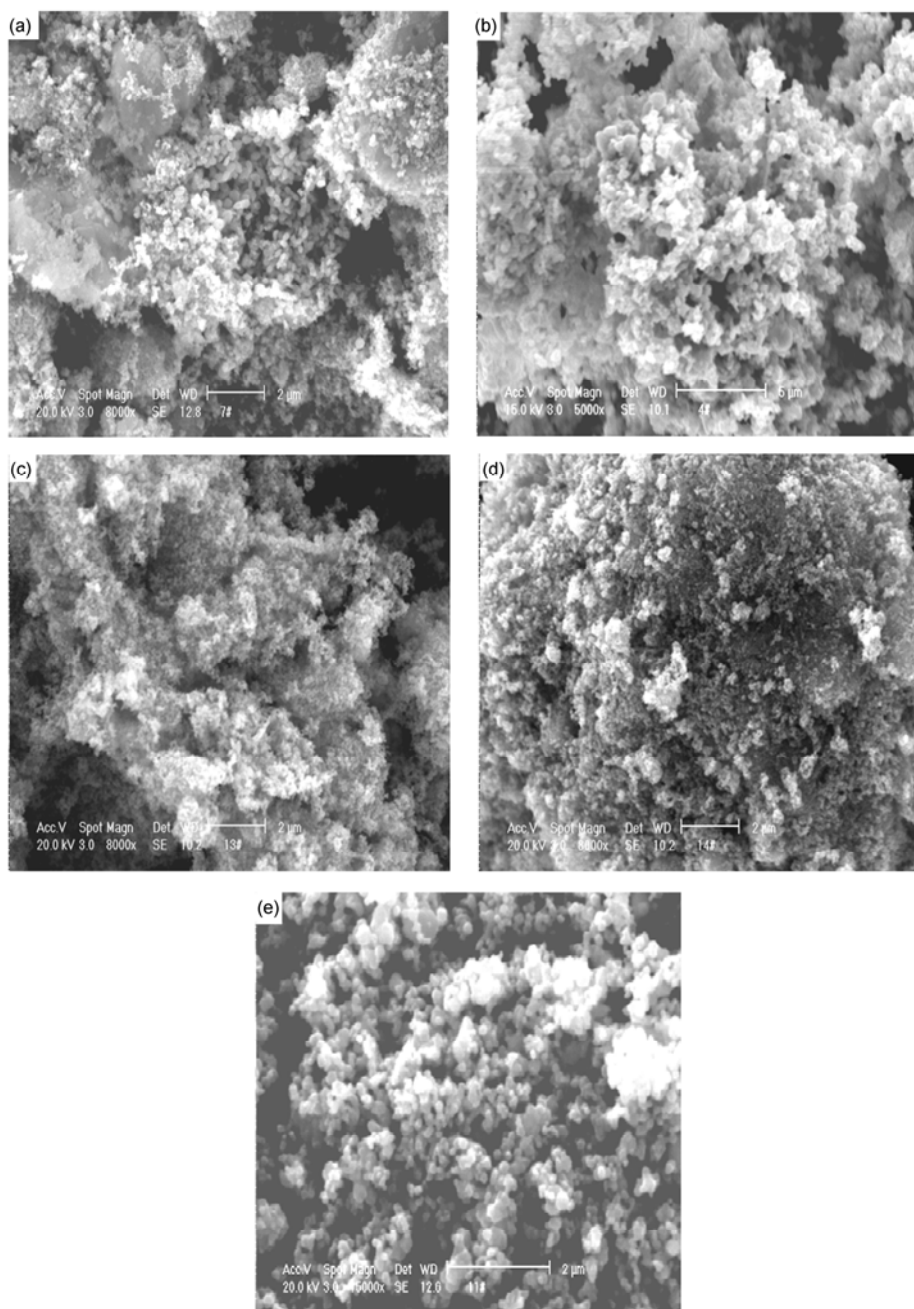
The average crystallite sizes of all samples were estimated according to the Scherrer equation [24, 25]:  $D = 0.89\lambda/(\beta\cos\theta)$ , where  $\beta$  is the width in radians of the XRD peak at half the peak height for the (101) reflection,  $\lambda$  is the wavelength of the X-rays in nanometers ( $\lambda = 0.154178$  nm),  $\theta$  is the angle between the incident and diffracted beams in degrees, and  $D$  is the average crystallite size of the powder sample in nanometers. The calculated average crystallite sizes are summarized in Table 1. It can be seen that both Mo-doping and calcination temperature have an influence on the average grain size of the sample. The presence of Mo apparently restrains the growth of ZnO crystallites. A possible reason for the decrease in ZnO crystallite size could be that some  $\text{Mo}^{6+}$  entered into the crystal lattice of ZnO and suppressed the growth of the ZnO crystal, because the radius of  $\text{Mo}^{6+}$  (0.065 nm) is smaller than that of  $\text{Zn}^{2+}$  (0.083 nm). However, increasing the calcination temperature causes an increase in grain size, which may be mainly due to the sintering of small ZnO particles at high calcination temperatures.

### 3.2 Microstructure analysis

The morphology of the synthesized samples was analyzed by SEM. Figure 2 shows the typical SEM images of the pure ZnO and Mo-doped ZnO photocatalysts. Figures 2(a)–(c) show that at the same calcination temperature, no significant differences in morphology can be observed between the pure ZnO and ZnO with different Mo-doping concentrations. All samples are composed of a large number of loose and dispersed small particles. Figures 2(d) and (e) show the effect of varying the calcination temperature on the microstructure of the Mo(2%)ZnO. It can be seen that when the sample was calcined at 800 °C, very big particles appeared and the sample showed a poor dispersion which is caused by the sintering of small particles at such an elevated temperature. The microstructures of the prepared samples were further analyzed by  $\text{N}_2$  adsorption. The BET surface area of the samples is summarized in Table 2. It can be seen that the specific surface area of the Mo-doped ZnO sample increases slightly with increasing Mo doping content, which

**Table 1** Average grain size of the zinc oxide samples with different Mo contents and Mo(2%)ZnO samples calcined at different temperatures

Sample	Calcination temperature (°C)	$D$ (nm)
ZnO	600	34.26
Mo(1%)ZnO	600	29.23
Mo(2%)ZnO	600	27.57
Mo(3%)ZnO	600	23.82
Mo(8%)ZnO	600	22.68
Mo(2%)ZnO	400	22.09
Mo(2%)ZnO	500	22.52
Mo(2%)ZnO	700	29.56
Mo(2%)ZnO	800	30.12



**Figure 2** SEM images of the samples. (a) ZnO calcined at 600 °C; (b) Mo(2%)ZnO calcined at 600 °C; (c) Mo(8%)ZnO calcined at 600 °C; (d) Mo(2%)ZnO calcined at 400 °C; (e) Mo(2%)ZnO calcined at 800 °C.

is possibly caused by the decrease in crystallite size of ZnO due to the presence of Mo. An increase in specific surface area can favor the adsorption of a dye and increase the photocatalytic activity of ZnO [26]. Moreover, increasing the calcination temperature results in a decrease in surface area. This can be attributed to sintering of the ZnO particles, in agreement with the XRD and SEM data.

### 3.3 FT-IR analysis

The FT-IR spectra of the samples are shown in Figure 3. All

the samples have a peak at around  $3440\text{ cm}^{-1}$  which can be assigned to the stretching vibration and bending vibration of surface hydroxyl groups on ZnO. From Figure 3(a), it can be seen that the intensity of the absorption peak of  $-\text{OH}$  groups markedly increases after Mo doping and the intensity of this peak reaches a maximum for ZnO with 2 wt.% Mo. In photocatalytic reactions, the activity is closely related to the number of  $-\text{OH}$  groups on the catalyst because the  $-\text{OH}$  groups can capture the photogenerated holes ( $\text{h}^+$ ) and transform to an  $\bullet\text{OH}$  radical which is the main reactive species

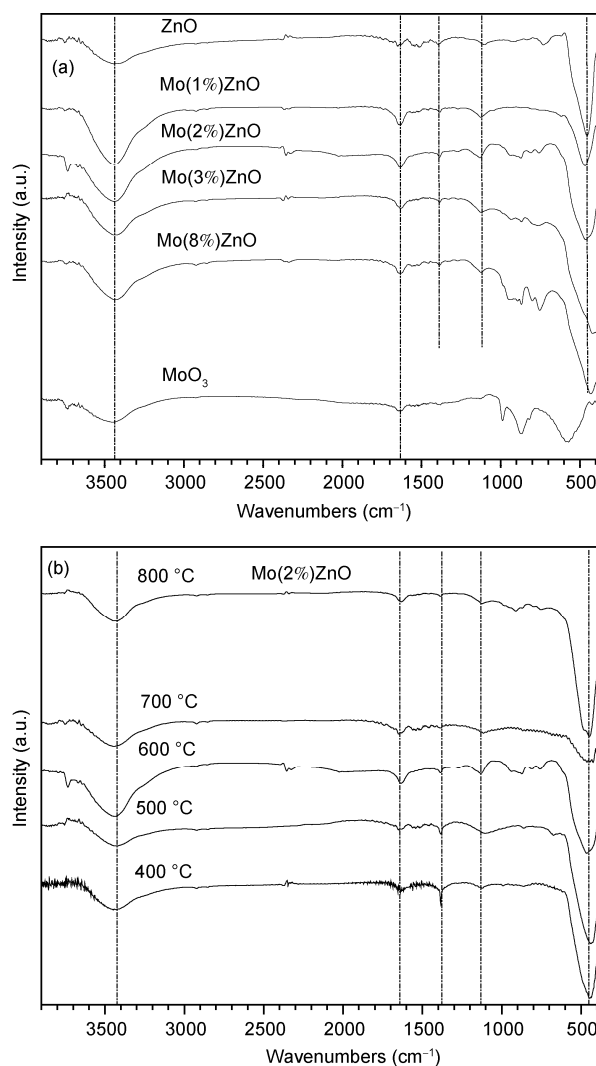
**Table 2** Specific surface areas of the zinc oxide samples with different Mo contents and Mo(2%)ZnO samples calcined at different temperatures

Sample	Calcination temperature (°C)	Surface area (m <sup>2</sup> /g)
ZnO	600	12.06
Mo(1%)ZnO	600	12.13
Mo(2%)ZnO	600	14.08
Mo(3%)ZnO	600	14.56
Mo(8%)ZnO	600	15.42
Mo(2%)ZnO	400	18.03
Mo(2%)ZnO	500	16.67
Mo(2%)ZnO	700	7.03
Mo(2%)ZnO	800	5.28

for the decomposition of dyes [27]. Therefore, an increase in the number of –OH groups can improve the photocatalytic activity. The peak at 1630 cm<sup>-1</sup> is assigned to the bending vibration of adsorbed water on the surface of the catalyst. The peak at around 440 cm<sup>-1</sup> is attributed to the stretching vibration of Zn–O bonds. It has been reported in ref. [28] that five characteristic peaks for MoO<sub>3</sub> occur at around 553, 876, 995, 1630 and 3445 cm<sup>-1</sup>, respectively. However, no such peaks for MoO<sub>3</sub> are observed for any of the doped samples. A possible reason is that a strong interaction between MoO<sub>3</sub> and ZnO may occur and the interaction could cause the disappearance of the characteristic peaks of MoO<sub>3</sub>. Two peaks at around 1388 and 1124 cm<sup>-1</sup> could be ascribed to the formation of a Mo–O–Zn bond because these two peaks were not found for either MoO<sub>3</sub> and ZnO. Figure 3(b) shows that, at the same concentration of Mo, with the increase of calcination temperature from 400 to 600 °C, the intensity of the peak at around 1124 cm<sup>-1</sup> increases gradually, which indicates that in this temperature range, an increase in calcination temperature strengthens the interactions between MoO<sub>3</sub> and ZnO and more Mo–O–Zn bonds are produced. However, when the calcination temperature was increased to 700 or 800 °C, the intensity of this peak began to decrease. The high calcination temperatures also decreased the intensity of the peak at around 3440 cm<sup>-1</sup> because treatment at elevated temperature causes the loss of –OH groups and a decrease in the specific surface area.

### 3.4 UV–vis diffuse reflectance spectra

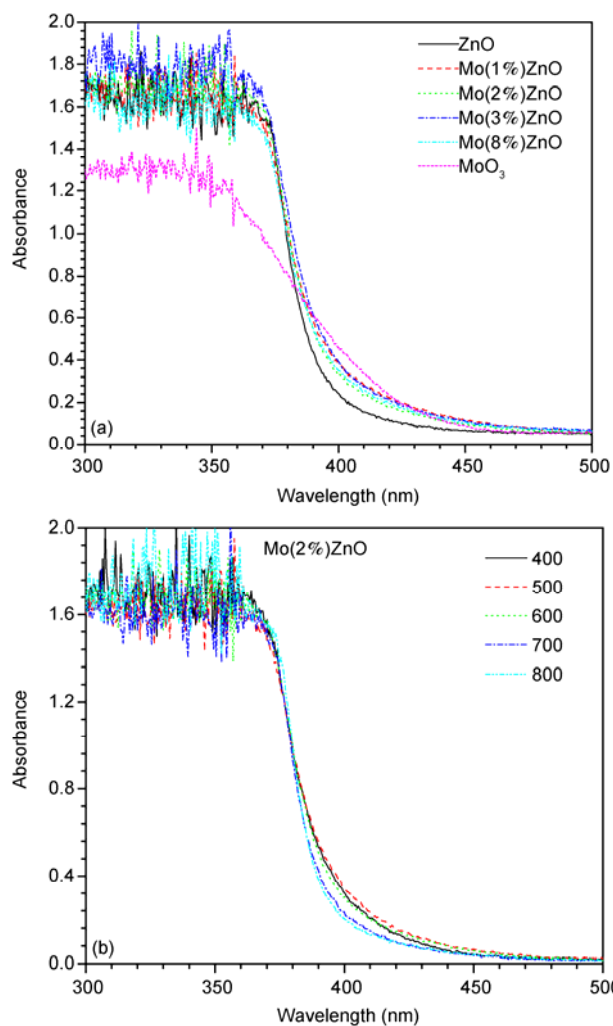
Figure 4 shows the UV–vis diffuse reflectance spectra of pristine and Mo-doped ZnO catalysts. From this figure, it can be seen that Mo doping has a slight influence on the absorption edge of zinc oxide. The band gap energy ( $E_g$ ) for the catalyst was determined using the equation  $E_g = 1240/\lambda_g$  (eV), where  $\lambda_g$  is the absorption edge which was obtained from the intercept between the tangent of the absorption curve and the abscissa. The calculated band gap energies for different samples are shown in Table 3. Figure 4(a) shows that pure ZnO has strong UV light absorption from 300 to 380 nm and very weak absorption in the visible light range.

**Figure 3** FT-IR infrared spectra of the samples. (a) Samples with different Mo contents calcined at 600 °C; (b) Mo(2%)ZnO calcined at different temperatures.

Doping with Mo causes the absorption edge of ZnO to shift slightly in the long wavelength direction and thus decreases the band gap energy. Figure 4(b) indicates that the calcination temperature has relatively little influence on the light absorption of the Mo(2%)ZnO.

**Table 3** Band gap energies of the samples

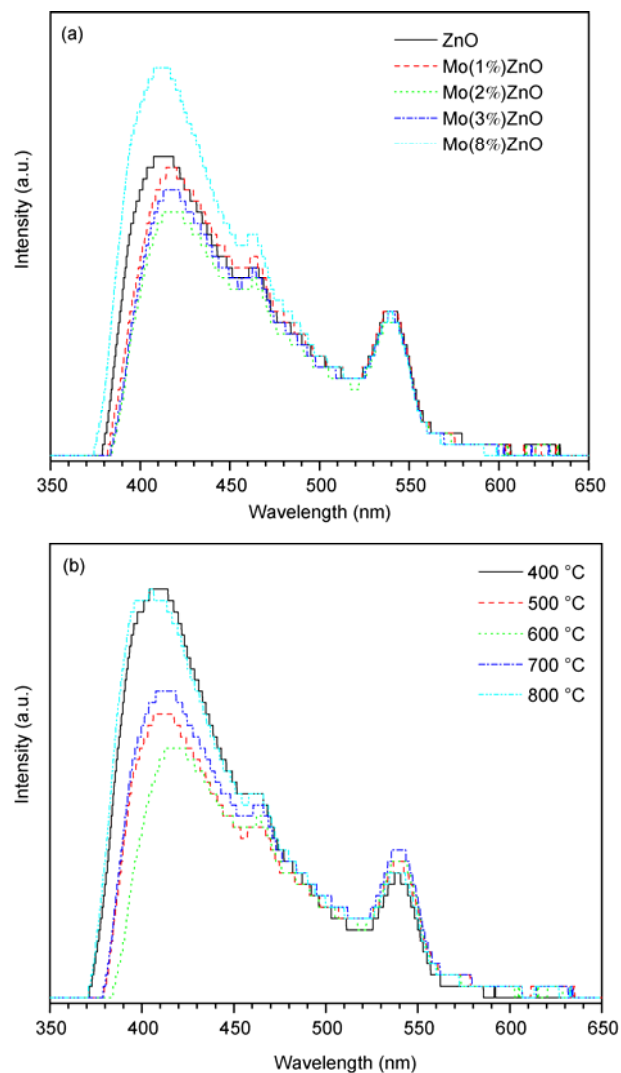
Sample	Calcination temperature (°C)	$E_g$ (eV)
ZnO	600	3.20
Mo(1%)ZnO	600	3.10
Mo(2%)ZnO	600	3.09
Mo(3%)ZnO	600	3.09
Mo(8%)ZnO	600	3.08
Mo(2%)ZnO	400	3.11
Mo(2%)ZnO	500	3.08
Mo(2%)ZnO	700	3.13
Mo(2%)ZnO	800	3.14
MoO <sub>3</sub>	600	2.87



**Figure 4** UV-vis spectra of the samples. (a) Samples with different Mo contents calcined at 600 °C; (b) Mo(2%)ZnO calcined at different temperatures.

### 3.5 PL emission spectra

To investigate the charge carrier trapping, immigration and transfer, as well as to understand the fate of photogenerated electron and hole pairs in semiconductor particles, the PL emission spectra of the pure ZnO and Mo-doped ZnO samples were recorded at room temperature as shown in Figure 5. All samples show three obvious characteristic emission peaks at around 390, 460 and 540 nm in the PL spectra. The emission peak at 390 nm near the ultraviolet range is due to the recombination of photogenerated electrons and holes [29, 30]. There is some controversy in the reference about the origins of the other two emission peaks in the range 420–620 nm. One explanation [31] is that this emission is an indirect emission which is related to surface vacancies on ZnO. Figure 5(a) indicates that Mo-doping can obviously suppress the recombination rate of  $e^-/h^+$  pairs, which causes a decrease in the intensity of the emission peak at 390 nm. In addition, the intensity of this emission peak varied with



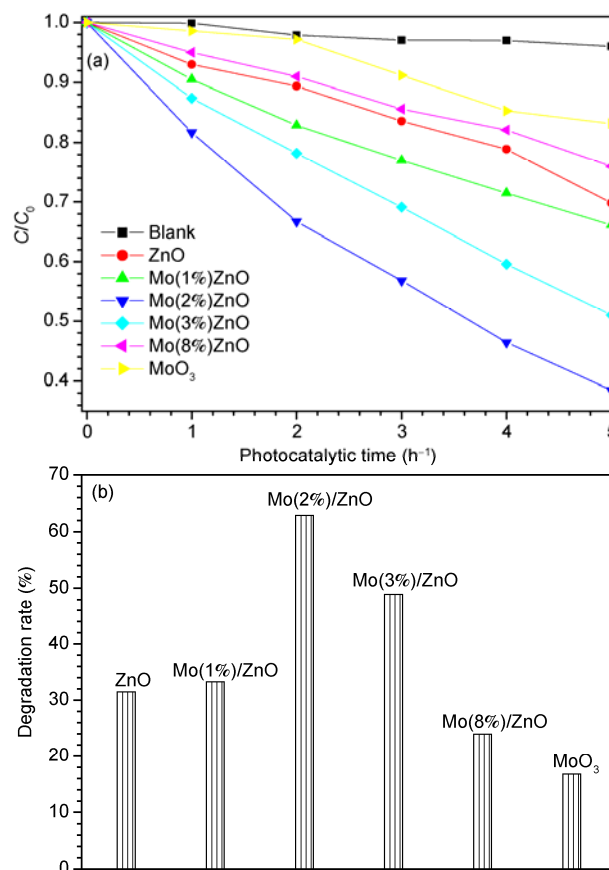
**Figure 5** Photoluminescence spectra of the samples. (a) Samples with different Mo contents calcined at 600 °C; (b) Mo(2%)ZnO calcined at different temperatures.

Mo concentration. The sample Mo(2%)ZnO calcined at 600 °C exhibited the weakest PL peak. However, higher Mo concentrations resulted in an increase in the intensity of the PL peak. Figure 5(b) shows the effects of varying the calcination temperature on the PL emission spectra of Mo(2%)ZnO. It is observed that the samples calcined at low or very high temperatures show strong and sharp emission peaks at around 390 nm. At low calcination temperatures, the poor crystallinity of ZnO could produce more recombination centers for photogenerated electrons and holes, which increases the intensity of the emission peak. However, calcination at very high temperatures may cause the displacement of  $O^{2-}$  and  $Zn^{2+}$  and produce more  $O^{2-}$  or  $Zn^{2+}$  vacancies in the ZnO crystal lattice. These vacancies also could become recombination centers for photogenerated electrons and holes. As for the emission peak in the visible light range, increasing temperature only slightly increases

the intensity of this emission peak.

### 3.6 Photocatalytic performance tests

The photocatalytic activities of the pure ZnO and Mo-doped composites were evaluated by measuring the degradation of acid orange II in aqueous solution under UV light irradiation ( $\lambda = 365$  nm). From Figure 6(a), it can be seen that acid orange II is only slightly degraded under UV light irradiation without any catalyst, indicating that direct photolysis of acid orange II can be ignored. After 5 h of light irradiation, the degradation ratios of acid orange II over ZnO, Mo(1%)ZnO, Mo(2%)ZnO, Mo(3%)ZnO and Mo(8%)ZnO reached 31.45, 33.27, 62.84, 48.96 and 23.95%, respectively, as shown in Figure 6(b). The increase in Mo concentration from 0 to 2 wt.% effectively promotes the dye degradation rate. However, a further increase in Mo content has an adverse effect. The optimal doping concentration of Mo was found to be 2 wt.%. In addition, the photocatalytic activity of ZnO doped with 2 wt.% Mo depends on the calcination temperature. From Figure 7, it can be seen that the degradation ratios of acid orange II were 51.49, 54.07, 62.84, 56.95 and 45.21% for the Mo(2%)ZnO samples calcined at 400, 500, 600, 700, and 800 °C, respectively. The sample calcined at 600 °C gives the best photocatalytic activity, which is mainly due to the recombination of photogenerated electrons and holes being suppressed by the improvement in crystallinity. However, very high calcination temperatures (700 and 800 °C) decrease the activity, which is mainly caused by the decrease in surface area, increase in crystallite size, and decrease in sample dispersion. To quantitatively understand the reaction kinetics of the acid orange II degradation in our experiments, we used a pseudo-first order model expressed by the equation:  $\ln(C_0/C) = kt$ , which can be generally used for photocatalytic degradation if the initial concentration of the pollutant is low [32].  $C_0$  and  $C$  are the concentrations of dye in the solution at time 0 and  $t$ , respectively, and  $k$  is the pseudo-first-order rate constant. The rate constants obtained from the regression of plots of  $\ln(C/C_0)$  vs.  $t$  are shown in Table 4. A good correlation with pseudo-first order reaction kinetics ( $R^2 > 0.96$ ) was found. The highest reaction rate constant was  $0.192 \text{ h}^{-1}$  for the sample calcined at 600 °C with 2 wt.% Mo. One problem associated with ZnO in photocatalytic reactions is its photo-instability due to the problem of photocorrosion. The effects of Mo-doping on photostability were investigated by reusing the catalysts. The results are shown in Figure 8. After being used four times, the degradation ratio for ZnO calcined at 600 °C decreased from 28.16 to 9.32%. However, for Mo(2%)ZnO calcined at 600 °C, there was almost no change in degradation ratio. According to the literature [12, 21], the photostability properties of ZnO are strongly dependent on its surface atomic structure. A high surface energy can cause instability of ZnO because this kind of surface is more readily attacked by photogenerated holes. The



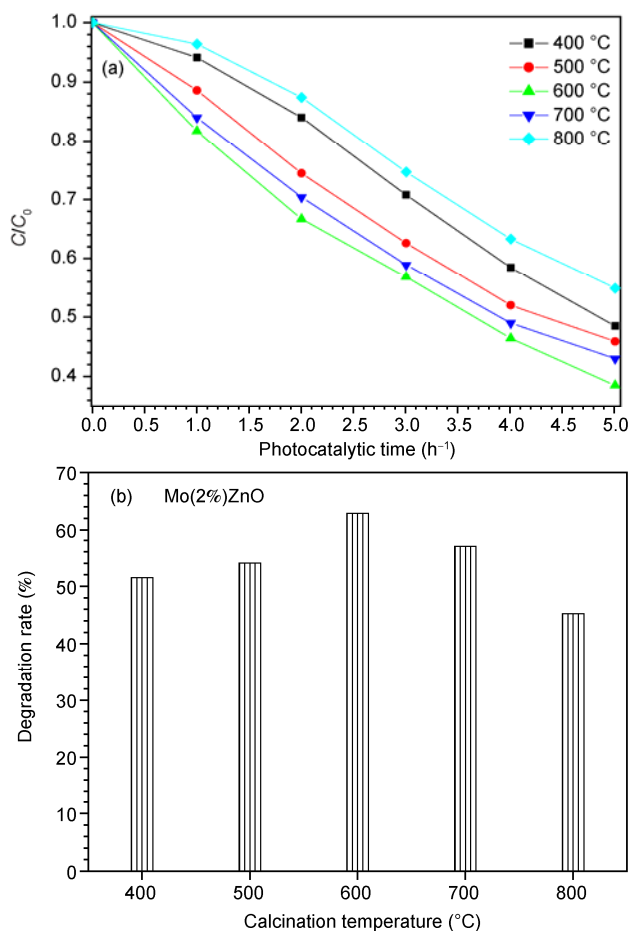
**Figure 6** Comparison of the photocatalytic activity of the catalysts with different Mo contents. (a) Changes in dye concentration as a function of irradiation time; (b) the degradation rate of the dye after 5 h irradiation.

**Table 4** First-order reaction rate constants of the catalysts in the degradation of acid orange II

Sample	Calcination temperature (°C)	$K$ ( $\text{h}^{-1}$ )	$R^2$
ZnO	600	0.065	0.98
Mo(1%)ZnO	600	0.085	0.99
Mo(2%)ZnO	600	0.192	0.99
Mo(3%)ZnO	600	0.127	0.99
Mo(8%)ZnO	600	0.051	0.99
Mo(2%)ZnO	400	0.169	0.99
Mo(2%)ZnO	500	0.192	0.99
Mo(2%)ZnO	700	0.173	0.99
Mo(2%)ZnO	800	0.145	0.99

doping of Mo changes the surface atomic structure of ZnO, which might decrease its surface energy, thus resulting in an increase in photostability.

Moreover, the undoped Mo species may exist in the form of  $\text{MoO}_3$ . Therefore, another possible reason for the high photocatalytic activity over Mo(2%)ZnO could be due to the formation of  $\text{MoO}_3/\text{ZnO}$  heterojunctions as has been reported [33, 34] for the  $\text{TiO}_2/\text{MO}_3$  system. Therefore, the valence band (VB) edge positions of  $\text{MoO}_3$  and ZnO were



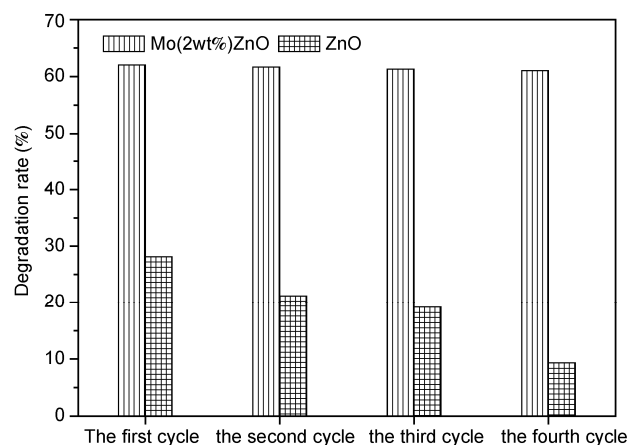
**Figure 7** Comparison of the photocatalytic performance of Mo(2%)ZnO calcined at different temperatures. (a) Changes in dye concentration as a function of irradiation time; (b) the degradation rate of the dye after 5 h irradiation.

estimated according to the concept of electronegativity [35, 36]. The conduction band (CB) and VB potentials of the two semiconductors at the point of zero charge can be calculated by the following equation:

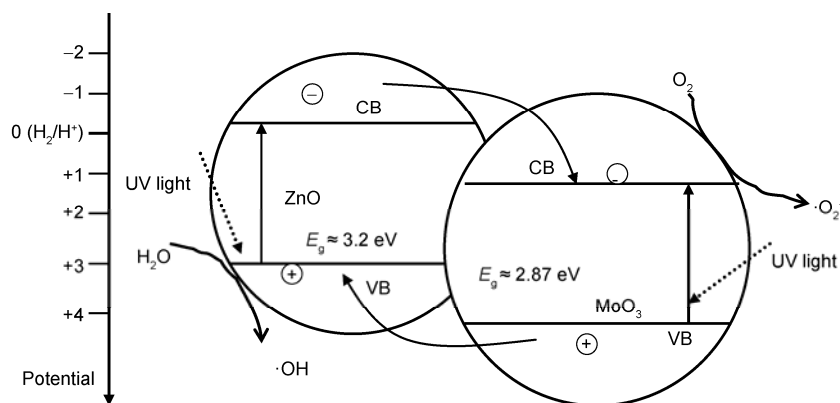
$$E_{\text{VB}} = X - E^{\text{c}} + 0.5E_{\text{g}} \quad (1)$$

where  $X$  is the absolute electronegativity of the semiconductor, which is defined as the geometric mean of the abso-

lute electronegativity of the constituent atoms;  $E^{\text{c}}$  is the energy of free electrons on the hydrogen scale (ca. 4.5 eV);  $E_{\text{VB}}$  is the VB edge potential; and  $E_{\text{g}}$  is the band gap of the semiconductor obtained from the equation  $E_{\text{g}} = 1240/\lambda_{\text{g}}$  (eV). The CB position can be deduced from the equation  $E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}}$ . The  $X$  values for MoO<sub>3</sub> and ZnO are ca. 7.2 and 6.0 eV. On the basis of the above equations, the top of the VB and the bottom of the CB of MoO<sub>3</sub> are calculated to be 4.08 and 1.21 eV, respectively. Accordingly, the VB and CB of ZnO are estimated to be 3.10 and -0.09 eV, respectively. According to our estimated  $E_{\text{g}}$  values of MoO<sub>3</sub>, the CB position of MoO<sub>3</sub> is more anodic than ZnO, and a schematic energy band model of the heterojunction composite can be depicted as shown in Figure 9. Thus, the excited electrons in the CB of ZnO can transfer to the CB of MoO<sub>3</sub>. At the same time, holes in the VB of MoO<sub>3</sub> can transfer to the VB of ZnO. Therefore, the MoO<sub>3</sub>/ZnO heterojunction could inhibit the recombination of photogenerated carriers, resulting in the enhanced performance of the MoO<sub>3</sub>/ZnO composite exhibits as compared to pure ZnO. However, if the MoO<sub>3</sub> content is too high, the dispersion of MoO<sub>3</sub> become poor and the redundant MoO<sub>3</sub> can become recombination centers, resulting in a decrease in photocatalytic activity.



**Figure 8** Comparison of the photocatalytic performance of Mo(2%)ZnO and ZnO in the recycled reactions.



**Figure 9** Photocatalytic mechanism of the MoO<sub>3</sub>/ZnO composite photocatalyst.



## 4 Conclusions

The effects of Mo doping on the structural properties of ZnO and its photocatalytic activity in the degradation of acid orange II have been investigated. The addition of Mo can effectively suppress the growth of ZnO particles and enrich the surface hydroxyl groups –OH groups in ZnO. The highest activity and good photostability were observed for Mo(2%)ZnO calcined at 600 °C. The high photocatalytic performance of the Mo-doped ZnO can be attributed to higher level of surface hydroxyl groups, high crystallinity and low recombination rate of electron/hole ( $e^-/h^+$ ) pairs. The doping of Mo also changes the surface atomic structure of ZnO, which may decrease its surface energy, thus resulting in an increase in photostability.

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