# Synergy effect of Lortenz force and dissolved oxygen on photocatalytic performance under magnetic field

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We report the effect of magnetic field on photocatalytic performance for four kinds of photocatalysts( $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, SrMoO<sub>4</sub>, TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>). Different magnetic field effects are observed for four photocatalysts. For example, for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, an improvement in the photocatalytic efficiency is observed, however, the otherwise phenomenon is for SrMoO<sub>4</sub> one. For TiO<sub>2</sub>, little change of photocatalytic performance is observed. For g-C<sub>3</sub>N<sub>4</sub> sample, the photocatalytic performance increases firstly and then decreases with increasing magnetic field. The synergy effect of Lortenz force and dissolved oxygen for photocatalytic process under magnetic field is discussed.

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## 1. Introduction

In recent years, the use of photocatalysis for the degradation of harmful dyes has been continuously expanding since the polluted aqueous sources is abruptly increasing [1,2]. However, the low photodegradation efficiency limited its extensive use, the promotion of photocatalytic performance has become a hot topic in this field.

Due to the semiconductor character, it is pivotal to take full advantage of photogenerated charge carriers for enhancing the activity of photocatalysts, and thus, considerable efforts have been devoted to solving this problem. For instance, expanding the photocatalytic active spectral range of semiconductors to increase the photogenerated charge carriers density with ion implantation, metal loading or dopant-free methods [3-5]. The other method is to improve the photocatalytic performance by enhancing charge carriers separation such as structuring p-n junctions and Z-scheme heterostructure [6,7].

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External-magnetic-field as a kind of non-contact and environment friendly method, has been widely discussed on catalytic performance and has attracted extensive for a long time. Du et al propose a magnetoresistance-related strategy to boost the carrier transfer efficiency and apply it in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/reduced graphene oxide hybrid nanostructures ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/rGO) to improve the photocatalytic performance under magnetic field [8]. The catalytic performances of the ferromagnetic catalysts including Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and Fe-N-C for oxygen reduction reaction are studied under an external magnetic field, the result suggests that internal tiny magnetic fields generated by the Fe<sub>3</sub>O<sub>4</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalysts have a certain effect on photocatalytic peformance [9]. It is shown that a weak external magnetic field can increase the rate of the Suzuki cross-coupling reaction at room temperature when Pd nanoparticles supported on Co<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> nanoparticles [10]. Gao et al observed an enhancement in the photocatalytic behavior of TiO<sub>2</sub> by an applied magnetic field and suggested the enhancement is attributed to suppressing photoinduced charge recombination via the Lorentz Force [11]. Magnetically induced acceleration of photocatalysis TiO<sub>2</sub> for the degradation of phenol red solutions under visible light illumination were tested in the absence and presence of a 0.5 T magnetic field [12].

The photodegradation efficiency of  $TiO_2$  increases slightly by the increase of the magnetic field, indicating the electron-hole pairs could be separated by applying magnetic field [13]. X.L.Hao found that the application of magnetic field can enhance the adsorption ability and obviously influenced the adsorption behavior of the organo-bentonite [14]. H. Okumura [15] investigated that the magnetic field effects on photocatalytic degradation of methylene blue solution over ZnO and TiO<sub>2</sub> powders under static magnetic field up to 0.7T with light irradiation by UV light emitting diode. As a result, the positive magnetic field effects is observed for ZnO, while, the negative magnetic field effects for TiO<sub>2</sub>, and both the positive magnetic field are increased with the increase of the applied magnetic field. The cause of magnetic field effect is attributed to the dissolved oxygen in the methyl blue (MB) and magnetic adsorption molecules [16].

In the current work, four different kinds of photocatalyst ( $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, SrMoO<sub>4</sub>, TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>) are selected to study the photodegradation of MB variation with applying magnetic field. As a result, four kinds of different magnetic field effect is observed for four photocatalysts. For example, for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, an improvement in the photocatalytic efficiency is observed, however, the otherwise phenomenon is for SrMoO<sub>4</sub> one. For TiO<sub>2</sub>, little change of photocatalytic performance is observed. For g-C<sub>3</sub>N<sub>4</sub> sample, the photocatalytic performance increases firstly and then decreases with increasing magnetic field.

#### 2. Experimental

#### 2.1. Materials

The raw materials include  $Bi(NO_3)_3 \cdot 5H_2O$ ,  $Na_2MoO_4 \cdot 2H_2O$ ,  $Sr(NO_3)_2$ , NaOH, melamine, ethylene glycol,  $Na_3Cit$ , and de-ionized water, commercial  $TiO_2$ .

#### 2.2. Preparation

1)  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample: Stoichiometric amounts of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were dissolved in ethylene glycol. Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and NaOH were separately dissolved in the deionized water with stirring for 30 min using a magnetic stirrer. NaOH solution was added to adjust pH value to 7.0.

An amount of EDTA was dissolved in the deionized water with magnetic stirring and added dropwise to the above mixed solution under vigorous magnetic stirring for 30 min. Finally, the mixture was placed in a 1000-mL Hastelloy autoclave (Parr 4577) and reacted at 160 °C for 12.0 h. After the autoclave was cooled to room temperature naturally, the products were separated by centrifugation, washed with ethanol and deionized water several times, and subsequently dried at 80 °C to obtain the final samples.

2) SrMoO<sub>4</sub> sample: In hydrothermal preparation, stoichiometric amounts of Sr(NO<sub>3</sub>)<sub>2</sub>, Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, and NaOH were separately dissolved for 20 min in deionized water stirred with a magnetic stirrer. Na<sub>3</sub>Cit was also dissolved in deionized water and mixed into the above solution for 60 min at 40 °C under stirring. A diluted NaOH solution was added to this solution to adjust its pH between 6 and 9. Finally, the mixture was placed in a 1000 mL hastelloy autoclave (Parr 4577) and reacted at 120 °C for 6.0 h. The autoclave was then naturally cooled to the room temperature, the products were separated in a centrifuge, washed with ethanol and deionized water several times, and then dried at 80 °C to obtain the final samples.

3) TiO<sub>2</sub>: The commercial TiO<sub>2</sub> powder is used as a photocatalyst for magnetic field effect measurements.

4) g-C<sub>3</sub>N<sub>4</sub> sample: Stoichiometric amount of melamine was separately dissolved in deionized water stirred with a magnetic stirrer. Na<sub>3</sub>Cit was also dissolved in deionized water and mixed into the above solution for 5 min by ultrasound. Finally, the mixture was placed in a 200 ml hastelloy autoclave at 200 °C for 4.0 h.The autoclave was then naturally cooled to the room temperature, the products were separated in a centrifuge, washed with ethanol and deionized water several times, and then dried at 80 °C to obtain the final samples.

#### 2.3. Characterize

The crystal structures of these products were characterized using an X-ray diffractometer (Dx-2000 SSC, Smart Lab 9 KW, Rigaku Industrial Corporation, Osaka, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5408$  Å) over the scanning range of 10-80° with a step size of 0.04°. UV-vis absorbance spectra were recorded using BaSO<sub>4</sub> as a reference. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250Xi instrument.

The photocatalytic activities of our samples were evaluated based upon the degradation of MB under a 300 W Xe lamp light with and without a magnetic field. Typically, without a magnetic field, aqueous solution of MB (100 mL, 10 mg/L) was mixed with our samples (50 mg) in a vessel. Before the irradiation, the mixed solution was stirred in the dark for 120 min until an adsorption-desorption equilibrium was established. Samples of solution were extracted every 20 or 10 min from the reactor and the concentration of MB was analyzed using an ultraviolet-visible (UV–vis) spectrometer (UV-3200S, MAPADA, Shanghai, China). The concentration of MB was calculated based upon a calibration curve.

Under various magnetic fields, the degradation of MB was studied following the same procedure. The various magnetic fields were produced by  $Nd_2Fe_{14}B$  magnets. The magnetic field intensity was changed by the number of magnets: 0, 1, 2, 3 and 4. The magnetic field intensity is 450 Gauss when there is only one magnet applied. Two and three magnets showed a magnetic induction intensity of 620 and 1000 Gauss, respectively. Four magnets installed in series, with an intensity of 1200 Gauss, was defined as the large magnetic field.

## 3. Result and discussion.

### 3.1. Phase constitution of photocatalysts

The phase of the prepared photocatalysts was examined by X-ray diffraction (XRD) technique. Here, we only provide the XRD patterns for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> and SrMoO<sub>4</sub> sample as shown in Figure 1(a) and (b).

Fig. 1(a) shows the XRD patterns of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample prepared at 160°C for 12 h with a pH value of 7. The diffraction peaks are carefully indexed and assigned to the lattice planes of (020), (111), (131), (002), (060), (151), (202), (260), (131), (191), and (262) for the corresponding 2 $\theta$  values of 10.75°, 23.46°, 28.21°, 32.52°, 34.47°, 36.04°, 46.78°, 47.20°, 55.58°, 56.37°, and 58.52°, respectively. The observed pattern indicates that all of the prepared  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> samples have pure orthorhombic structure. The diffraction peaks can be indexed to the orthorhombic  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>(JCPDS 21-0102). Moreover, no other impurity phases are observed for all samples.



Fig. 1. the XRD patterns of sample: (a)  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>,(b) SrMoO<sub>4</sub>.

Fig. 1(b) is the XRD patterns for  $SrMoO_4$  sample. The sample are well indexed as the pure scheelite tetragonal structures (I41/a space group), which are in good agreement with the standard card (JCPDS 08-0482).



Fig. 2. Survery (a), Bi 4f(b), Mo 3d (c), O1s (d) XPS spectra for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> samples.

The sharp and well-defined peaks suggest that these samples have well crystallization. The 2 $\theta$  values of 27.66°, 29.76°, 33.10°, 45.20°, 47.56°, 51.58°, 55.94°, and 72.71° are corresponding with the (112), (004), (200), (204), (220), (116), (312), and (316) lattice planes, respectively.

Besides, the chemical composition of the as-synthesized materials was examined by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of the composition catalysts was presented in Fig. 2(a)-(d) for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> catalyst. The wide scanning spectrum of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> and individual bands are both presented. There are some obvious peaks corresponding to Bi 5d, Bi 5p, Bi 4f, Bi 4d, Bi 4p, Mo 3d, Mo 3p, C 1s and O 1s, as shown in Fig. 2(a). The small C peak, corresponding to carbonates, is attributed to organic materials and contamination caused by air exposure. Figure 2(b)-(d) provides the high-resolution Bi 4f, Mo 3d, and O 1s spectra. The Bi signal can be fitted the two peaks, as shown in Fig. 2(b). Specifically, the binding energy of 159.01 and 164.32 eV is ascribed to Bi  $4f^{7/2}$  and Bi  $4f^{5/2}$ , indicating that the Bi species of our samples are in the form of Bi<sup>3+</sup> [17]. In addition, according to the fitting calculation of peak area, the proportions of Bi 4f<sup>7/2</sup> and Bi 4f<sup>5/2</sup> is 46.20 and 53.80%, respectively. Four peaks as presented in Fig. 2c can be observed in the Mo spectrum at 231.80, 232.36, 235.05, and 235.66eV, which are attributed to  $Mo^{5+}$  and  $Mo^{6+}$  [18, 19]. Additionally, the proportions of  $Mo^{5+}$  and  $Mo^{6+}$  are found to be 13.40 and 86.6%, respectively. Figure 2d provides the O1s core level XPS spectrum for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, it can be seen that the spectrum is divided into three component peaks. The binding energy peaks at about 530.06, 531.29 and 532.35eV are assigned to the lattice oxygen in perovskite structure ( $O_L$ ), the surface hydroxyl species ( $O_{OH}$ ), and the vacancy oxygen ( $O_{\nu}$ ). The lattice oxygen, surface hydroxyl, and absorbed content were about 82.20, 14.30, and 3.50%, respectively [20]. In addition, the percentage of  $O_{OH}$  signal links to the quantity of surface oxygen

vacancies. The oxygen vacancies have a great influence on the optical properties and the separation of charge-carries. The oxygen vacancies can react with  $H_2O/OH^-$  to form strong oxidizing hydroxyl radicals to degrade pollutants.

Fig. 3(a-d) provides the XPS patterns of survey, Sr, Mo, and O elements for SrMoO<sub>4</sub> sample. From the survey spectrum( Figure 3a), Sr, Mo and O elements were identified. The obvious peaks corresponding to Mo 3p, Mo 3d, and Sr 3d, O 1s can be detected in our sample. Fig. 3(b) gives the high-resolution XPS spectrum of Sr 3d, the binding energy peaks at 134.20 and 132.56 eV is attributed to Sr  $3d^{3/2}$  and Sr  $3d^{5/2}$ . In addition, according to the fitting calculation of peak area, the proportions of Sr  $3d^{3/2}$  and Sr  $3d^{5/2}$  is 47.20 and 52.80%, respectively. Figure 3(c) gives the high-resolution XPS spectrum of the Mo element, and the two peaks at 235.70eV and 232.36eV can be assigned to Mo  $3d^{3/2}$  and Mo  $3d^{5/2}$ . Mo ion is the form of hexavalent (+6) oxidation state for our sample. Similar to the  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, three binding energy peaks at about 530.42, 531.43 and 532.20 eV can be observed for the O 1s core level XPS spectrum, which are attributed to the lattice oxygen in perovskite structure (O<sub>L</sub>), the surface hydroxyl species (O<sub>OH</sub>), and the vacancy oxygen (Ou), respectively. The lattice oxygen, surface hydroxyl, and the absorbed content were about 69.30, 27.30, and 3.40%, respectively. The O<sub>OH</sub> and Ou signal are related to the photodegradation performance during the photocatalytic process.



Fig. 3. Survery (a), Sr 3d(b), Mo 3d (c), O1s (d) XPS spectra for SrMoO<sub>4</sub> samples.

Fig. 4(a-d) provides the XPS for TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> samples. Ti 2p and O 1s peaks are detected for TiO<sub>2</sub> sample. The Ti signal can be fitted the two peaks, as shown in Fig. 4(b). Specifically, the binding energy of 458.97 and 464.68 eV is ascribed to Ti  $2p^{3/2}$  and  $2p^{1/2}$ , indicating that the Ti species of our samples are in the form of Ti<sup>3+</sup>.





Fig. 4. Survery (a), Ti 2p(b), O1s (c) XPS spectra for SrMoO<sub>4</sub> samples; and Survery (d), C 1s(e), N1s (f) XPS spectra for g-C<sub>3</sub>N<sub>4</sub> samples.

Fig. 4(c) provides the O 1s core level XPS spectrum for  $TiO_2$  sample, similar to  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> and SrMoO<sub>4</sub>, the binding energy peaks at about 530.27, 531.70 and 532.20 eV are observed and they are corresponding to the lattice oxygen in perovskite structure (O<sub>L</sub>), the surface hydroxyl species (O<sub>OH</sub>), and the vacancy oxygen (Ov), respectively. The lattice oxygen, surface hydroxyl, and the absorbed content were about 94.20, 5.60, and 0.20%, respectively. Fig. 4(d)-(f) provides the survey and high-resolution C1s, N1s, and O1s spectra. The high-resolution XPS spectrum of C1s and N1s are provided too, the binding energy peaks at 285.4 and 288.7eV is attributed to C-C and C-N. In addition, three binding energy peaks at about 399.2, 400.0, and 401.2 eV can be observed for the N 1s core level XPS spectrum, which are attributed to C-N=C, N-C<sub>3</sub>, and C-O, respectively.

#### 3.2. Morphology of photocatalysts

The morphologies and microstructures of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>(a,c) and SrMoO<sub>4</sub>(b,d) samples were further presented by SEM and TEM images shown in Fig. 5. As is known, crystal growth was strongly related to the intrinsic crystal structure. The structure of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> consists of alternating (Bi<sub>2</sub>O<sub>2</sub>)<sub>n</sub><sup>2+</sup> layers and perovskite-like (MoO<sub>4</sub>)<sub>n</sub><sup>2-</sup> layers, and octahedral Mo chains usually play an important role on the high intrinsic anisotropic growth. Moreover, the chemical potential is also important, if the chemical potential of two surfaces is much higher than others, the two-dimensional growth occurs. Therefore, the chains of octahedral-Mo equally exist along a and c axes. As a result, the crystal growth of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample is preferentially along the layer, and irregular and thin flake-like structure are observed as shown in Fig. 5(a,c).





Fig. 5. SEM and TEM images for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>(a,c) and SrMoO<sub>4</sub>(b,d) samples.

For  $SrMoO_4$  sample, as shown in Fig. 5(b,d), broccoli-shape morphology can be observed. These broccoli structures are constituted of small particles, and these particles have been partially oriented and attached on the irregular faces. Moreover, these particles overlapped each other closely. It is reasonable to suggest that several nanocrystallites nucleate and grow into small seed system, and then a great number of these seed particles tend to aggregate together [21].

## 3.3. UV result of photocatalysts

The optical absorption property of a semiconductor is one key factor in estimating its photocatalytic activity. The optical absorption property is frequently deemed to be relevant to the electronic structure feature. Therefore, the absorption spectra of our samples are measured. For  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, as shown in Fig. 6(a), the absorption regions ranges from visible light region to UV light region, which suggests it has photocatalytic activity under visible light radiation. For SrMoO<sub>4</sub> sample, as shown in Fig. 6(b), from the absorption spectra, it is clearly found that, there exists strong and broad absorption band between 200 and 300nm. This board absorption band is attributed to the charge transfer from the oxygen (2p) electrons that move into the central molybdenum atom inside the [MoO<sub>4</sub>]<sup>2-</sup> ion.



Fig. 6. UV-vis diffuse reflectance spectra and plots of  $(\alpha hv)^2$  vs photo energy (hv) for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>(a,c)and SrMoO<sub>4</sub>(b,d) samples.

The optical band gap energy  $(E_g)$  is also calculated. According to the reference [22], the optical band gap is associated with the absorbance and the photo energy by the following equation:  $ahv = A(hv-E_g)^n$ , where  $a, h, v, E_g$  and A are absorption coefficient, Plank constant, photo frequency, photonic energy gap and a constant, respectively. n is a constant associated with the different types of electronic transitions (n=1/2, 2, 3/2 or 3 for directly allowed, indirectly allowed, directly forbidden, and indirectly forbidden transitions, respectively). The parameter n depends on the characteristics of the transitions in the semiconductor. According to the reference [23], n is adopted as 1 for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample. However, for SrMoO<sub>4</sub> sample, according to the Lacomba-Perales et al [24], n=1/2 value was adopted in above equation. The energy gap  $E_g$  for the absorption edge is determined by extrapolating the linear portion of the plot  $(ahv)^2$  vs hv to zero absorbance. The energy gap  $E_g$  are calculated as shown in Fig. 6(c) and 6(d), and the obtained value is 4.165 and 2.43 eV for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> and SrMoO<sub>4</sub> sample, respectively.



*Fig.* 7 UV-vis diffuse reflectance spectra and plots of  $(ahv)^2$  vs photo energy (hv) for  $TiO_2(a,c)$ and  $g-C_3N_4$  (b,d) samples.

Fig. 7 (a) and (b) provides the absorption spectra of  $TiO_2$  and  $g-C_3N_4$  samples. The absorption spectra indicate that there exists strong and broad absorption band between 200 and 400 nm for  $TiO_2$  and 200-500 nm for  $g-C_3N_4$ , respectively. The energy gap are also calculated as shown in Figure 7(c) and (d), 3.47 eV and 2.687 eV are obtained, respectively.

The positions for valence band  $(E_{VB})$  and conduction band  $(E_{CB})$  are theoretically calculated using the following equations:

$$E_{VB} = X - Ee + 0.5Eg$$
$$E_{CB} = E_{VB} - Eg$$

on the hydrogen scale (4.50 eV), and Eg is the band gap energy of the semiconductor. The X value for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> and SrMoO<sub>4</sub> is 5.50 and 5.42 eV, respectively. The E<sub>VB</sub> and E<sub>CB</sub> values are estimated. For  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, E<sub>VB</sub> and E<sub>CB</sub> is 2.215 and -0.215 eV; for SrMoO<sub>4</sub> sample, E<sub>VB</sub> and E<sub>CB</sub> is 3.002 and -1.162 eV, respectively. As we known, the redox potential of O<sub>2</sub> to  $\cdot$ O<sub>2</sub><sup>-</sup> and OH<sup>-</sup> to  $\cdot$ OH is -0.33 eV and 1.99 eV, respectively. Obviously, for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, the valence band potential is positive enough to oxide OH to  $\cdot$ OH, however, the conduction band potential is not negative enough to redox O<sub>2</sub> to  $\cdot$ O<sub>2</sub><sup>-</sup>. The otherwise phenomenon is for SrMoO<sub>4</sub> sample, the E<sub>VB</sub> values for SrMoO<sub>4</sub> sample is more positive that the redox potential of OH<sup>-</sup>/ $\cdot$ OH and hence the transferred electrons in the valence band are favorable to reduce OH<sup>-</sup>. Moreover, due to the lower negative potential of conduction band against standard redox potential of O<sub>2</sub>/ $\cdot$ O<sub>2</sub><sup>-</sup>, the O<sub>2</sub> may generated to radical  $\cdot$ O<sub>2</sub><sup>-</sup>. For TiO<sub>2</sub> sample, the valence band potential (3.045 eV) is positive enough to oxide OH to  $\cdot$ OH, and the conduction band potential (-0.425 eV) is negative enough to redox O<sub>2</sub> to  $\cdot$ O<sub>2</sub><sup>-</sup>. For g-C<sub>3</sub>N<sub>4</sub> sample, the valence band potential is positive enough to oxide OH to  $\cdot$ OH, however, similar to the  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, due to the conduction band potential of g-C<sub>3</sub>N<sub>4</sub> is positive but not negative, the O<sub>2</sub> can not be reduced to  $\cdot$ O<sub>2</sub><sup>-</sup>. Therefore, the electrons can only reduce O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> (O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> is 0.695eV), and the generation of  $\cdot$ OH might result from the transfer from OH to  $\cdot$ OH and  $\cdot$ O<sub>2</sub><sup>-</sup> through  $\cdot$ O<sub>2</sub><sup>-</sup> $\rightarrow$ H<sub>2</sub>O<sub>2</sub> $\rightarrow$  $\cdot$ OH process.

### 3.4. Photocatalytic result of photocatalysts

To detect the magnetic field effect on photocatalyst, the photocatalytic degradation of MB dye with  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, SrMoO<sub>4</sub>, TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub> samples was performed with and without a magnetic field. The degradation of MB under visible light illumination was monitored by recording the decrease of the UV-vis absorption spectra ( $\lambda = 663$  nm) when the applied magnetic field is 0, 450, 620, 1000, and 1200 Gauss, respectively.

Fig. 8 presents the variation of MB concentration (C/C<sub>0</sub>) with irradiation time at different magnetic field for  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>(a), SrMoO<sub>4</sub>(b), TiO<sub>2</sub>(c) and g-C<sub>3</sub>N<sub>4</sub>(d) sample, where C and C<sub>0</sub> are the initial and final concentration of MB solution. For  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, as shown in Fig. 8(a), the general photocatalytic reaction without non-magnetic field, the photodegradation rate of MB was 66% after 100 min of UV illumination.



Fig. 8. The degradation rates of MB dye under the magnetic field effect for all samples: (a)  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, (b) SrMoO<sub>4</sub>, (c) TiO<sub>2</sub>, (d) g-C<sub>3</sub>N<sub>4</sub>.

Notably, the photodegradation rate of MB after 100 min was 80% when the applied magnetic field is 450 Gauss under the same reaction conduction, that is to say, the inclusion of magnetic field resulted in 14% improvement in the photocatalytic properties. Moreover, the degradation efficiency reaches 85%, 90%, and 90% when the applied magnetic field is 620, 1000, and 1200 Gauss, respectively. Obviously, the degradation efficiency is enhanced largely with applying of magnetic field during the photocatalytic performance of  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> is measured. It suggests that the existence of a permanent magnetic field plays a remarkable role in improving the photocatalytic efficiency. Fig. 8(b) presents the photocatalytic performance for  $SrMoO_4$  sample at different applied magnetic field intensity. With non-magnetic applied, the photocatalytic degradation of MB dye is 65%. However, the degradation rates of MB with the SrMoO<sub>4</sub> product were kept about 50% for different magnetic field applying. The results demonstrate a noticeable decrease in the photocatalytic performance as the magnetic field is used. Obviously, this is different from the  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> result. Fig. 8(c) reveals the relation between C/C<sub>0</sub> and variation time for TiO<sub>2</sub>, the photocatalytic performance is almost not changed. The C/C<sub>0</sub> value is kept 100% in 40min for different magnetic field intensity. The photocatalytic performance with magnetic field for TiO<sub>2</sub> has been observed in previous reports, and opposite results have been reported. For example, the  $C/C_0$  value decreases with increasing magnetic field intensity [16], that is to say, the negative magnetic field effect is observed for TiO<sub>2</sub>. However, the positive magnetic field effect is exhibited for  $TiO_2$  where the C/C<sub>0</sub> value is enhanced with increasing magnetic field intensity [11]. Fig. 8(d) presents the photocatalytic performance for  $g-C_3N_4$  sample with different magnetic field intensity. The  $C/C_0$  value is about 90% for without magnetic field. When the applied magnetic field is adopted 450 Gauss, the photocatalytic performance is almost not varied. However, when the magnetic field intensity is 620 and 1000 Gauss, the photodegadation efficiency decrease to 80% and 70%, respectively. Surprisingly, the photocatalytic performance is enhanced again to 75% when H=1200 Gauss.

As we known, there are three key steps to determine the photocatalytic performance for semiconductor photocatalyst: absorption of light, separation and migration of electron-hole pair, oxidation-reduction reaction on the surface photocatalyst. Therefore, the magnetic field effect will be discussed based on the above three steps.

At first, the absorption of light for semiconductor photocatalyst is not influenced by magnetic field. That is to say, the Zeeman energy caused by the magnetic field is several orders of magnitude lower than the band gap of semiconductors and thus has slight influence on the photocatalytic performance. Hence, the variation of photocatalytic property with magnetic field can not be attributed to the absorption of light.



Fig. 9. Schematic diagram of charge carrier transfer process and possible photocatalytic mechanism of sample under the magnetic field effect.

Secondly, after light absorption, the electron-hole pairs generate in the semiconductors at the same time. However, the photogenerated electron and hole can recombine easily. Once magnetic field is applied during photocatalysis, both the moving electrons and holes in the magnetic field experience a Lorentz force vertical to their direction of movement,  $\vec{F} = \vec{q} \cdot \vec{v} \times \vec{B}$ ,

where q is the particle charge and  $\vec{v}$  is the velocity of a particle moving in magnetic field with

magnetic intensity B. Obviously, the electron and hole will experience opposite forces due to their opposite charges and enhance charge carrier separation, which means that more charge carriers can participate in the photocatalytic process, as a result, the photocatalytic efficiency is improved by a applying a magnetic field to our photocatalytic system, as shown in Figure 9.

Thirdly, according to the reference [25,26], the dissolved oxygen in the solution plays an important role for magnetic field effect on the MB photodegration. When MB solids is mixed with water, there is a bonding interaction between oxygen molecules and MB dye ones, at the same time, the reaction sites of the MB dye molecule is blocked. In addition, since the MB dye molecule is much larger than oxygen molecule in size, the oxygen molecules can be attached to the MB molecules, as a result, MB-oxygen complex are formed. On the contrary, if the formation of the MB-oxygen complex is not complete, an appropriate amount of dissolved oxygen and photogenerated-electrons may efficiently react to produce the superoxide radicals to decompose the MB dye, and the higher photodegradation rate is achieved. Therefore, the state and amount of dissolved oxygen meeting or near the photocatalyst powder surface is the key parameter. In addition, it is well known that the dissolution of the oxygen molecules are dissolved into water are promoted by a magnetic field.

Under light irradiation, γ-Bi<sub>2</sub>MoO<sub>6</sub> is easily excited due to the narrow band gap, and corresponding photogenerated electrons and holes are generated. Once magnetic field is applied during photocatalysis process, the charge carriers separate more efficiently due to the Lortenz force, which prolongs the lifetime of carriers and inhibits the recombination of photogenerated electrons. For  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> sample, the valence band potential is positive enough to oxide OH to  $\cdot OH$ , however, the conduction band potential is not negative enough to redox  $O_2$  to  $\cdot O_2^-$ . However, the photo-electrons reduce  $O_2$  to  $H_2O_2$  through  $O_2 \rightarrow H_2O_2 \rightarrow OH$  process, as a result, O<sub>2</sub> is changed to ·OH. The ·OH hydroxyl radicals as active species can directly attack MB molecules to decolorize the dye, and the small molecules can be eventually mineralized to form  $CO_2$ and  $H_2O$ . Therefore, an appropriate amount of dissolved oxygen and photogenerated-electrons may efficiently react to produce the superoxide radicals to decompose the MB dye, and the higher photodegradation rate is achieved with the enhancement of magnetic field. Meanwhile, the photogenerated holes of the valence band can react with H<sub>2</sub>O and OH<sup>-</sup> to generated  $\cdot$ OH hydroxyl radicals as strong oxidizing agents. The  $\cdot$ OH hydroxyl radicals and  $\cdot$ O<sub>2</sub> superoxide radicals can directly attack MB molecules to decolorize the dye, and the small molecules can be eventually mineralized to form CO2 and H2O. With increasing magnetic field intensity, more and more oxygen is dissolved into the MB solution, and more and more  $O_2^{-1}$ superoxide radicals are produced, as a result, the photodegradation property is enhanced as shown in Fig. 8(a). Finally, higher photodegradation rate is observed, the photocatalytic performance increases from 70% for without magnetic field to 90% with 1200 Gauss applied magnetic field.

For SrMoO<sub>4</sub> sample, based on the UV-vis spectrum discussion, the oxygen absorbed on the SrMoO<sub>4</sub> surface can be oxidized as  $\cdot$ O<sub>2</sub><sup>-</sup> superoxide radicals without magnetic field. When the quantity of  $\cdot$ O<sub>2</sub><sup>-</sup> superoxide radicals is enough to reach saturation value for our SrMoO<sub>4</sub> sample, which can hinder the  $\cdot$ O<sub>2</sub><sup>-</sup> superoxide radicals further generating. Therefore, with increasing magnetic field, more and more oxygen is dissolved, more and more MB-oxygen complex is formed. Hence, the photocatalytic degradation of MB dye decreases from 65% to 50% with increasing magnetic field, as shown in Figure 8(b).

Similar phenomena are also observed in TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>. Specially for g-C<sub>3</sub>N<sub>4</sub> sample, based on the XPS result, similar to  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, the valence band potential is positive enough to oxide OH to ·OH, the O<sub>2</sub> can not be reduced to ·O<sub>2</sub><sup>-</sup> due to the conduction band potential of g-C<sub>3</sub>N<sub>4</sub> is positive. A certain amount of superoxide radicals ·O<sub>2</sub><sup>-</sup> are produced when the oxygen is dissolved. As a result, The ·OH hydroxyl radicals and ·O<sub>2</sub><sup>-</sup> superoxide radicals attack the MB molecules to decolorize the dye. With increasing magnetic field, more and more oxygen is dissolved into MB soultion, the oxygen molecules would form a complex with the MB dye, which hinder the MB dye photodegradting. Based on the above discussion, it is suggested that there is a competition between the formation of MB-oxygen complex and the degradation of MB solution. As a result, for TiO<sub>2</sub>, the C/C<sub>0</sub> value would not vary with increasing magnetic field, and for g-C<sub>3</sub>N<sub>4</sub>, the C/C<sub>0</sub> value decreases and then increases with magnetic field.

#### 4. Conclusions

In summary, four different photocatalyst  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub>, SrMoO<sub>4</sub>, TiO<sub>2</sub>, and g-C<sub>3</sub>N<sub>4</sub> are choosed to detect the photocatalytic perfromance variation with applying magnetic field.  $\gamma$ -Bi<sub>2</sub>MoO<sub>6</sub> exhibits highly enhanced photocatalytic activity for MB photodegradation with increasing magnetic field. However, the opposite phenomenon is observed for SrMoO<sub>4</sub>. The photocatalytic property would not change almost for TiO<sub>2</sub> sample with magnetic field variation. For g-C<sub>3</sub>N<sub>4</sub>, the degration of MB solution C/C<sub>0</sub> decreases and increases with magnetic field.

Under light irradiation, the photogenerated electrons and holes are formed. The electrons in the valence band are stimulated to the conduction band, whereas correspondingly, the same amount of holes are generated in the valence band. When a magnetic field was present during photocatalysis, both the photogenerated electrons and holes experience a Lortenz force vertical to their direction of movement. Moreover, the forces acting on the negative charge electron and positive hole are in oppsite directions, which results in the deviation of the electron and hole in opposite directions. Therefore, the photogenerated electron-hole pairs would be separated in a magnetic field. However, another factor should also be considered. The dissolved oxygen in the solution plays an important role for magnetic field effect on the MB photodegration. When MB solids is mixed with water, there is a bonding interaction between oxygen molecules and MB dye ones, at the same time, the reaction sites of the MB dye molecule is blocked. Therefore, there exists competetion between Lortenz force and dissolved oxygen for photocatalytic process in magnetic field.

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