

Magnetic field assisted photocatalytic degradation of organic dyes in the presence of Ag/TiO₂ coated composite

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ABSTRACT

Ag/TiO₂ coated composite was prepared via sol-gel method in order to elucidate its application in magnetic field assisted photocatalytic degradation of dyes. Through the degradation of organic dyes, the key influences such as Ag amount, heat-treated temperature and time on the photocatalytic activity of Ag/TiO₂, as well as UV irradiation time, rotational speed, dye concentration and magnetic sheet number on the photocatalytic degradation were studied. Results showed that the Ag/TiO₂ with 25 wt% Ag content heat-treated at 550 °C for 60 min has the best photocatalytic activity. With the increase of UV light irradiation time, rotational speed and magnetic sheet number, the degradation rate is improved. Different dye degradation proved that the method could universally be used.

Key words | Ag/TiO₂, assisted photocatalysis, dye degradation, magnetic field

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INTRODUCTION

In recent years, azo dyes have been widely used in textile, paper, food, leather, cosmetics and pharmaceutical industries (Chang *et al.* 2001). Once these azo dyes are intentionally or accidentally discharged into rivers, lakes and the sea, themselves or their intermediates can lead to serious environmental problems and affect the ecosystem balance and human health (Saratale *et al.* 2009). Fortunately, photocatalysis has been used as an efficient pollution control technology (Czili & Horvath 2009). From the discovery of TiO₂ photocatalysis in 1972 (Hoffmann *et al.* 1995), various semiconductors have widely been used as photocatalyst to tentatively degrade the organic pollutants (Luo *et al.* 2010). However, TiO₂ is a poor absorber of photons in the solar spectrum. To effectively destroy the organic pollutants, the ultraviolet (UV) light ($\lambda < 387$ nm) must be required to irradiate the TiO₂ for its broad band-gap (3.2–4.5 eV) (Sivalingam *et al.* 2004). In addition, because of rapid recombination of photogenerated electrons and holes the TiO₂ cannot show high photocatalytic activity. Therefore, for enhancing photocatalytic activity of TiO₂ two key problems, narrow scope of light response and easy recombination of electron–hole pair, must be solved.

For a long time, much attention has been focused on extending the range of absorption wavelength of TiO₂, namely, making the TiO₂ absorb the visible light to a

large extent. Many reformative methods have been adopted such as doping of transition-metal ions (Hung *et al.* 2007), combination of narrow band-gap semiconductors (Bessekhouad *et al.* 2006) and aggradation of noble-metals (Ohtani *et al.* 1997). For the past few years, in the use of visible light, great achievements have been made. However, so far there is no good method for restraining recombination of electrons and holes. Once, people used the method of capturing electrons to restrain the recombination of photo-generated electrons and holes (Kim *et al.* 2011). In fact, because of limited doping of transition-metal (Fe³⁺, Co³⁺ or Cr³⁺) and depositing of noble-metal (Pt, Pd or Ag), the number of captured electrons soon becomes saturated (Gao *et al.* 2011). Afterwards, those superfluous electrons will consume the newly generated holes, which reduce the photocatalytic activity of TiO₂. In view of the deficiency of electron capture theory, we propose that the photocatalytic activity of TiO₂ might be improved through the effective consumption of electrons or holes. Due to the long spacing distance, these residual electrons and holes can not recombine but carry out their respective chemical reactions.

Ag has been deposited on the surface of TiO₂ particles to restrain the recombination of photogenerated electron–hole pairs (Behnajady *et al.* 2006). As an electronic

capture agent, Ag only can briefly enhance the photocatalytic activity of TiO₂ without other supplementary means. In recent years, magnetic field was generally used to recover the artificial-combined photocatalyst with magnetic materials (Ao *et al.* 2009). In this work, by using magnetic field the Ag can play a new role of consumption of electrons or holes. As a natural phenomenon, cutting magnetic induction lines will beget an induced electromotive force at both ends of Ag conductor in the magnetic field. The anode electric potential can effectively consume electronics and the cathode electromotive force can consume more holes. So the TiO₂ surface will produce isolated electrons and holes, thereby increasing the degradation rate of dye.

MATERIALS AND METHODS

Materials and apparatus

Nd-Fe-B magnetic round sheet (10 mm diameter and 1.0 mm thickness, Shenyang Zhanbo Magnet Technology Co. Ltd, China) was used to form magnetic field. Nano-sized silver powder (FAgN80, Jiaozuo Companion Nano-Materials Corporation, China) and Tetra-*n*-butyl titanate (Ti(O-Bu)₄, 99.99%, Sinopharm Chemical Reagent Co. Ltd, China) were bought to prepare the Ag/TiO₂ coated composite. Several organic dyes (99.99%, Tianjin Kaiyuan Reagent Corporation, China) were used to undergo photocatalytic degradation. The degradation process was tracked by UV-vis Spectrometer (LAMBDA-17, Perkin-Elmer, USA).

Preparation of Ag/TiO₂ coated composite

The Ag/TiO₂ coated composite was prepared by the sol-gel method. The molar ratio of Ti(O-Bu)₄:C₂H₅OH:H₂O:acetic acid was controlled as 1:10:2:1 and the mass ratio of TiO₂ and Ag was controlled as 1.0-x:x (x = 0.00–0.25). At first, a homogeneous ethanol solution of Ti(O-Bu)₄ was used as titanium dioxide precursor. The mixed solution of ethanol, acetic acid and deionized water were gradually added into the above solution under stirring magnetically. When the microemulsion was vigorously stirred for 30 min, xg Ag powders were added into the final solution. The obtained suspension was kept stirring until the gel was formed. The gel was dried at 110 °C for 24 h and grounded into powder in succession. After filtration and lavation, the separated powder was put into a crucible and heated in a muffle furnace at the calefactive rate of 20 °C/min and then the powders

were calcined at 550 °C for 40–80 min and at 400–700 °C for 60 min, respectively.

Experiments of photocatalytic degradation

Reactions were carried out in a 150 mL beaker placed in an UV irradiation apparatus (35 W mercury lamp, Philips, The Netherlands). The temperature of 25.0 ± 0.2 °C was maintained by circulating-cooling water and monitored constantly by a thermograph. One hundred milliliter of Acid-Red B solution (20 mg/L) and 1.0 g/L photocatalyst were used in all the experiments unless otherwise stated. The samples were magnetically stirred in order to achieve the complete adsorption/desorption equilibrium of dye on the catalyst surface and the suspensions were irradiated for 120 min using UV light. Ten milliliter of sample was withdrawn with a syringe every 20 min to determine the UV-vis spectra. The dye adsorption and reduction ratios were calculated based on the absorbance of Acid-Red B solution at maximum absorption wavelength (λ_{\max}).

RESULTS AND DISCUSSION

X-ray diffraction (XRD) and scanning electron microscopy (SEM) of Ag/TiO₂ coated composite

From Figure 1(a), in comparison with the diffraction diagram of the basic TiO₂ crystal structure, two new peaks can be seen that belong to characteristic diffraction peaks of Ag at $2\theta = 44.5^\circ$ and $2\theta = 38.0^\circ$. They become higher and higher along with the increase of Ag content, which indicates that different contents of Ag have been well combined with TiO₂.

As shown in Figure 1(b), according to the characteristic diffraction peaks at $2\theta = 25.5^\circ$ (101), $2\theta = 37.9^\circ$ (004), $2\theta = 48.2^\circ$ (200), $2\theta = 54.1^\circ$ (105), $2\theta = 55.2^\circ$ (211) and $2\theta = 62.8^\circ$ (204), the crystal phase of TiO₂ heat-treated at 400 °C for 60 min can be judged to be a single anatase phase. When the heat-treated temperature reached 700 °C, as observed from Figure 1(b-2) the TiO₂ part can mainly be identified as rutile phase. As seen, the intension and positions of these diffraction peaks hardly changes, but the peaks slightly widen by increasing the heat-treated time for 40 and 80 min. It can be seen from Figure 1(c), along with the increase of time some not obvious peaks were also enhanced. This phenomenon may be produced by agglomeration reaction. It could be inferred that heat-treatment for longer time or at a higher temperature should have an

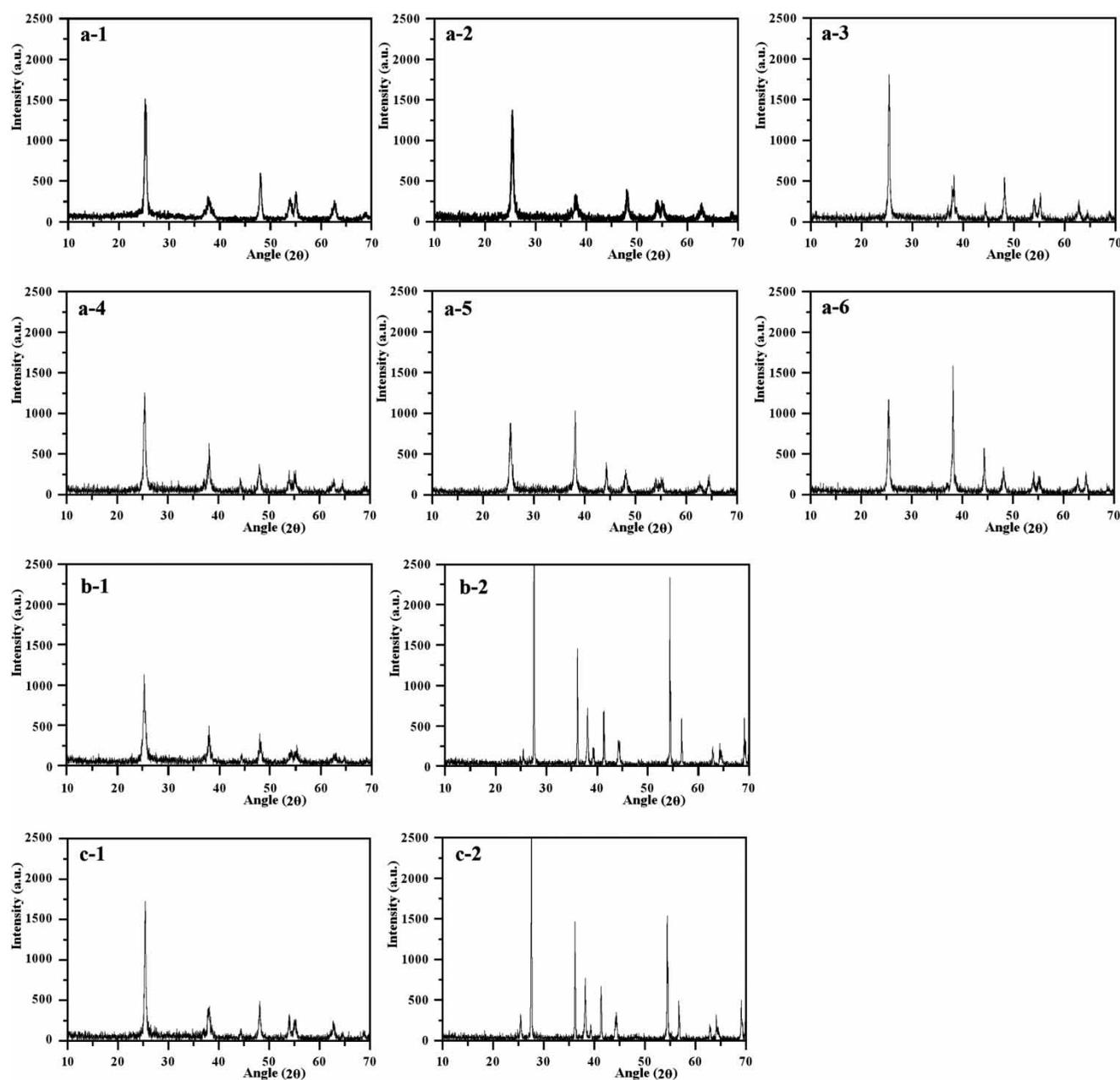


Figure 1 | The XRD of Ag/TiO₂ coated composite with: (a) different Ag contents (a-1: 0.0 wt%; a-2: 5.0 wt%; a-3: 10.0 wt%; a-4: 15.0 wt%; a-5: 20.0 wt%; a-6: 25.0 wt%) heat-treated at 550 °C for 60 min, (b) different heat-treated temperatures (b-1: 400 °C; b-2: 700 °C) for 60 min with 10 wt% Ag content and (c) different heat-treated times (c-1: 40 min; c-2: 80 min) at 550 °C with 10 wt% Ag content.

influence on Ag/TiO₂. Hence, during the preparation of Ag/TiO₂ the heat-treated temperature and time both should have the effects on the surface structure and crystal phase, which are directly related to the photocatalytic activity.

As seen in Figure 2(a), there are a large number of square species belong to anatase TiO₂ with an average size

of approximately 1.0 μm. In Figure 2(b), there are also some small grainy balls with an average size of approximately 0.5 μm encased on the surface of TiO₂ particles. It indicates that the Ag particles have been well coated with the TiO₂. From Figure 2(c), it can be found that a large number of blocky square species with average size of approximately 0.5 μm, suffered the reunion reaction.

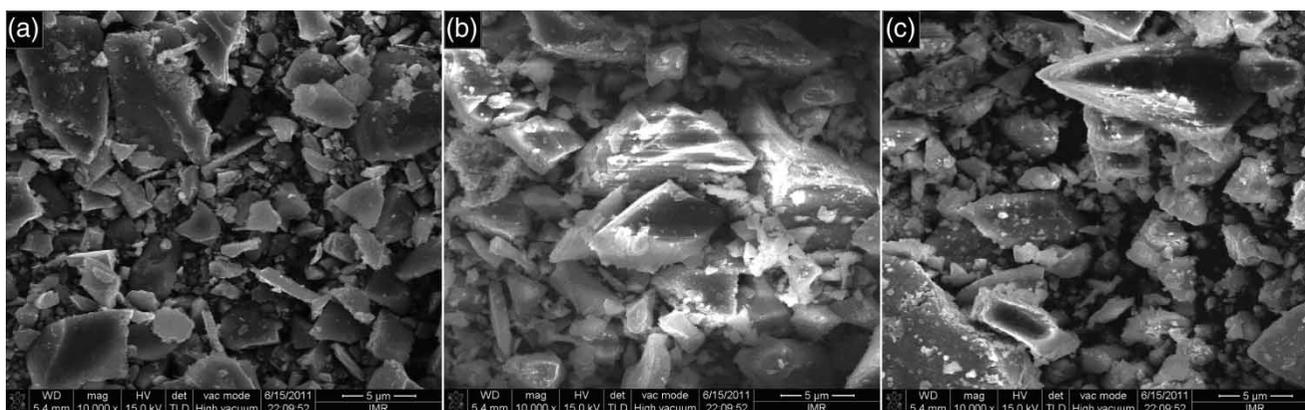


Figure 2 | The SEM of Ag/TiO₂ coated composite with different Ag contents (a: 0.0 wt %; b: 10.0 wt %; c: 25.0 wt %) heat-treated at 550 °C for 60 min.

Photocatalytic activity of Ag/TiO₂ in magnetic field

As shown in Figure 3(a), the maximum absorption peak appears at 514 nm. It corresponds to the azo bond (–N=N–) as the most active site for oxidative attack in Acid-Red B molecule. Besides, the absorption peaks at 292 and 321 nm in the ultraviolet regions are related to the naphthyl rings. In the dark, the decrease of the absorption peaks hardly happens, which indicates that the adsorption ability of catalyst for Acid-Red B is weak. After 30 min one-fold UV irradiation, three absorption peaks all decline, which may be caused by self-sensitization of dye, but the reduction ratios are not high. In Figure 3(b), under identical conditions the Ag/TiO₂ shows high activity. Of which, the degradation ratio based on the maximum absorption peak reaches 73.29% under magnetic field, which is obviously higher than the corresponding degradation ratio (68.9%) without magnetic field. Hence, it can

be concluded that the high degradation ratio may be achieved when the magnetic field is used.

Effect of Ag content, heat-treated temperature and time on photocatalytic activity of Ag/TiO₂ in magnetic field

It is found from Figure 4(a) that the degradation ratio obviously increases with the increase of coated Ag content in the range 0–15 wt%, but it hardly changes after 15 wt%. Apparently, the photocatalytic activity of Ag/TiO₂ with any Ag content is higher than that for the similar system with only TiO₂. For 15 wt% Ag, the degradation ratio reached above 85.0%. It is only 28.0% in the case of TiO₂ only. This is because Ag can enhance the electron–hole separation, thereby improving the photocatalytic activity. Of course, even if Ag amount is further increased over 15 wt%, the photocatalytic activity will not be

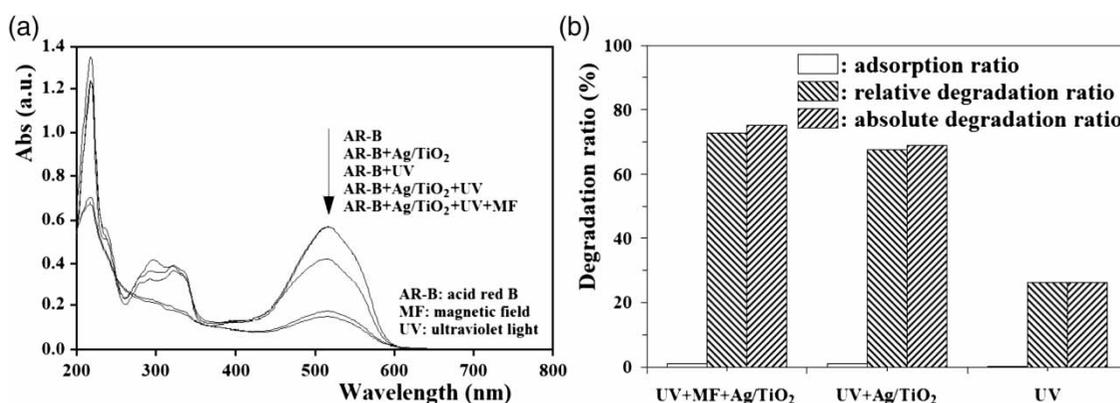


Figure 3 | UV-vis spectra (a) and degradation ratio (b) of Acid-Red B in aqueous solutions under different experimental conditions. (20 mg/L Acid-Red B initial concentration, 1.0 g/L Ag/TiO₂ photocatalyst (with 10 wt% Ag content heat-treated at 550 °C for 60 min) amount, 2.0 h UV light irradiation, 1,000 r/min revolution speed and 10 magnetic sheets.)

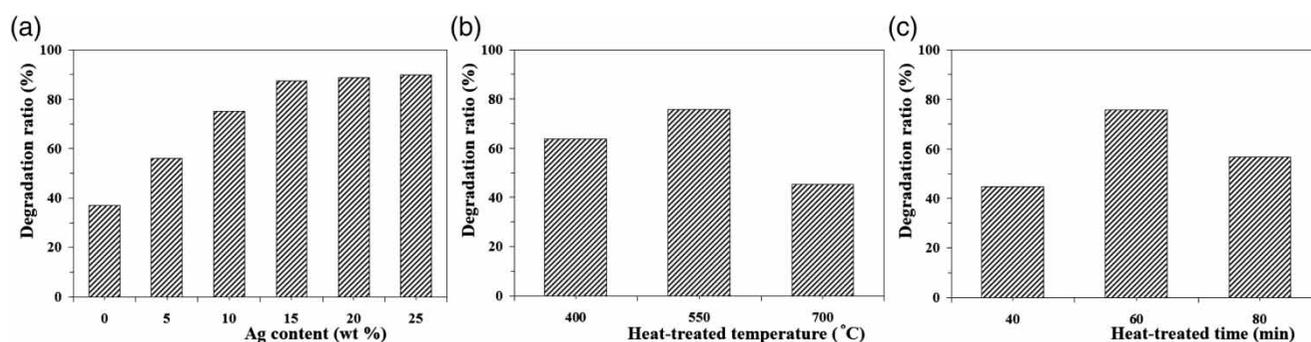


Figure 4 | Effect of (a) Ag content (heat-treated at 550 °C for 60 min), (b) heat-treated temperature (with 10 wt% Ag content heat-treated for 60 min) and (c) heat-treated time (with 10 wt% Ag content heat-treated at 550 °C) on the photocatalytic activity of Ag/TiO₂ coated composite. (20 mg/L Acid-Red B initial concentration, 1.0 g/L Ag/TiO₂ catalyst (with 10 wt% Ag content heat-treated at 550 °C for 60 min) amount, 2.0 h UV light irradiation, 1,000 r/min revolution speed and 10 magnetic sheets.)

enhanced. It indicates that there is a limit to the Ag amount. When the coated Ag is more than a certain amount, incomplete coating Ag or excessively thin TiO₂ film must occur. It is clearly not conducive to increase of the photocatalytic activity of Ag/TiO₂ in organic dye degradation.

The effect of heat-treated temperature on the photocatalytic activity of Ag/TiO₂ is shown in Figure 4(b). The Ag/TiO₂ heat-treated at 550 °C exhibits the highest degradation ratio unexpectedly compared with that at 400 and 700 °C. For 400–700 °C, the corresponding degradation ratios are 63.35, 75.13 and 45.73%, respectively. That is because, at low calcination temperature (400 °C), the structure of the prepared composite is too loose to restrain the recombination of the electrons and holes. For the high calcination temperature (700 °C), the lower catalytic activity is due to the formation of inactive rutile phase. Therefore, 550 °C is favorable to activate the photocatalyst.

The influence of heat-treated time on the photocatalytic activity of Ag/TiO₂ is shown in Figure 4(c). As seen, after 2.0 h UV irradiation, the highest degradation ratio is attained in the presence of Ag/TiO₂ calcined at 550 °C for 60 min and the corresponding degradation ratio is 75.13%. It indicates that this photocatalyst has the highest photocatalytic activity. In addition, the degradation ratios are 45.06 and 56.18% for 40 and 80 min heat-treatment, respectively. The explanation is that the connection of components with heat-treatment for 40 min is not tight, which induces failure to separate the holes and electrons. The transformation of crystal phase of the part TiO₂ from anatase to rutile takes place for 80 min heat-treatment, which decreases the photocatalytic activity of TiO₂. Thus, it could be concluded that a suitable heat-treated time is good for the enhancement of photocatalytic activity of Ag/TiO₂.

Effect of UV irradiation time, initial dye concentration, organic dye kind, revolution speed and magnetic sheet number on photocatalytic degradation

The photocatalytic degradations of Acid-Red B along with the increase of UV irradiation time are shown in Figure 5(a). Apparently, the degradation ratio in MF + Ag/TiO₂ increases much faster than that without any catalyst. After 3.0 h UV irradiation, the degradation ratio reaches 92.08% for MF + Ag/TiO₂. It can be speculated that most Acid-Red B molecules soon could be degraded in the MF + Ag/TiO₂.

The effect of wide concentration range of Acid-Red B on the photocatalytic degradation was studied. As seen in Figure 5(b), the reduction ratio decreased with increasing concentration. That is because the high concentration results in the deep color solution, which restrains the absorption and transmission of light. In this case, the photons get intercepted before reaching the photocatalyst surface, consequently, the reduction percentage is reduced. Hence, an appropriate initial concentration is necessary for photocatalytic degradation of any organic dye.

The photocatalytic activity of Ag/TiO₂ to degrade various dyes, such as Congo-red, Methylene-blue, Azofuchsine, Methyl-orange, Rhodamine-B and Acid-Red B, was studied. As shown in Figure 5(c), all of these dyes could be degraded in MF + Ag/TiO₂ under UV irradiation. Apparently, the degradation ratios of various dyes are somewhat related to their adsorption ratios. The appropriate adsorption ratio is conducive to the degradation of dyes on the Ag/TiO₂ surface. These dye molecules have different charges after ionization, indicating that the electrostatic attraction or repulsion has occurred between organic molecules and photocatalyst particles. It results in the different adsorption and degradation ratios. In any case,

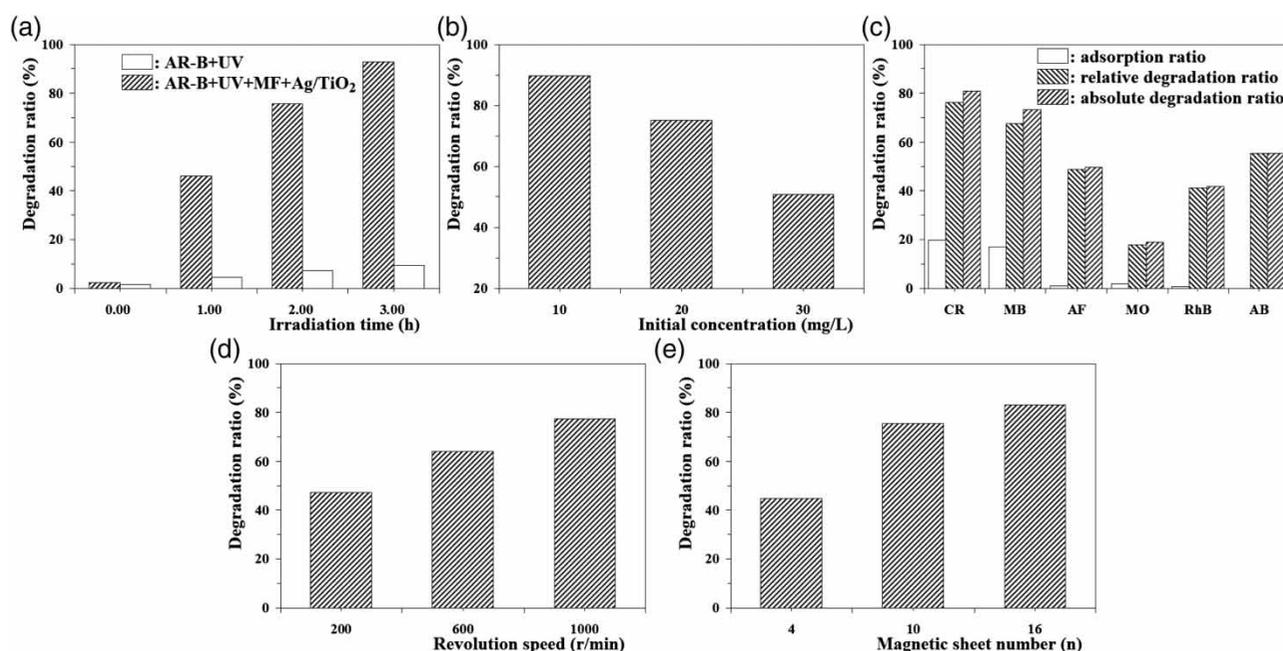


Figure 5 | Effect of UV light irradiation time (a), dye initial concentration (b), organic dye kind (c), revolution speed (d), and magnetic sheet number (e) on the photocatalytic degradation. (20 mg/L dye initial concentration, 1.0 g/L Ag/TiO₂ catalyst (with 10 wt% Ag content heat-treated at 550 °C for 60 min) amount, 2.0 h UV light irradiation, 1,000 r/min revolution speed and 10 magnetic sheets. CR: Congo-red, MB: Methylene-blue, AF: Azo-fuchsine, MO: Methyl-orange, RhB: Rhodamine-B and AB: Acid-Red B.)

experimentally, Ag/TiO₂ has promising applied perspective in the degradation of azo dyes.

The revolution speed has an important influence on the photocatalytic degradation as shown in Figure 5(d). The degradation ratio increases with the enhancement of revolution speed. The 1,000 r/min revolution speed exhibits the highest degradation ratio. Apparently, the faster the revolution speed, the higher the degradation ratio becomes. It is also based on Faraday's law of electromagnetic induction ($E = BLV\sin\theta$; E induced electromotive force, B magnetic flux density, L conductor length, V rotation speed and θ : intersection angle between conductor and magnetic induction line). When the magnetic field strength and the conductor length are fixed, the fast rotation speed can induce large electromotive force, which can move photo-generated electrons causing electron-hole separation.

According to Faraday's law, the induced electromotive force (E) is proportional to magnetic flux density (B). Therefore, the magnetic sheet number is another important influence factor on the photocatalytic degradation. It can be seen in Figure 5(e), for the highest degradation rate the magnetic sheet number is 16. As the revolution speed and conductor length are fixed, the induced electromotive force increase with the enhancement of magnetic field strength. Then increasing the number of magnetic sheet is to increase the strength of the magnetic field. The

enhancement of anode electric potential can better move electronics to consume holes.

Mechanism discussion of photocatalytic reaction of Ag/TiO₂ in magnetic field

The mechanism of magnetic field assisted photocatalytic degradation in the presence of Ag/TiO₂ is first proposed. The enhancement of the photocatalytic activity is because the effective separation of the electrons and holes. When the Ag/TiO₂ is irradiated by UV light, the electron transition should take place. That is, the electrons in the valence band (VB) are transitioned to conduction band (CB). As a result, electrons and holes are generated at the same time. However, the recombination of photogenerated electron-hole pairs restrains further reactions. Theoretically, whether electron or hole is removed, the photocatalytic activity of TiO₂ will be enhanced. According to our ideas, with the help of magnetic field this purpose can be achieved. Based on Faraday's law of electromagnetic induction, the cutting magnetic lines will beget an induced electromotive force at both ends of the Ag conductor. The anode electric potential can consume electrons and the cathode electromotive force can consume holes. So it can lead to the effective separation of the electron and hole. Thus, the photocatalytic activity is improved through

respective consumption of electron or hole in magnetic field.

CONCLUSIONS

The present study aimed at investigating magnetic field assisted photocatalytic degradation of dyes. When 25.0 wt% Ag content, 550 °C and 60 min heat-treatment were adopted, the Ag/TiO₂ revealed the highest photocatalytic activity. It was also learned that the degradation degree of organic dye was obviously affected by Ag/TiO₂ amount, irradiation time, initial dye concentration and magnetic field intensity. In summary, the magnetic field can effectively assist photocatalytic degradation and display a better prospect in future applications.

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