

Effects of pH value on photocatalytic performance of ZnO composite graphene for degradation of methyl orange

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The ZnO nanoparticles were coated with an appropriate amount of graphene oxide. The structure, surface morphology and Band gap of ZnO/graphene were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-vis absorption spectra. The effect of PH on the photocatalytic degradation of methyl orange using ZnO/ graphene composites under visible light was studied. The research indicated that ZnO/graphene photocatalyst showed enhanced effect for the degradation of Methyl orange in pH=3-5. Cycle degradation in different pH environment, and a cyclic degradation of recovered sample by scanning electron microscope showed that the presence of graphene has a protective effect on ZnO, which was able to inhibit the corrosion of ZnO in acidic environment, and improve the stability of its repeated degradation. As can be seen from photoluminescence spectroscopy experiments of ZnO /graphene and ZnO, the existence of graphene can effectively accelerate the separation efficiency of ZnO photogenerated electrons and holes, improving the photocatalytic degradation efficiency, which provides a theoretical basis for ZnO/graphene degrading dye wastewater in different pH especially in acidic environment.

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1. Introduction

As an excellent multi-functional and wide band gap semiconductor material with excellent optical and electrical properties (Band gap at room temperature is 3.37 eV), ZnO has the characteristics of cheap, non-toxic, high efficiency and easy to prepare and so on [1-3]. Besides, having a higher electron mobility ($205\text{-}300\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$) and a variety of morphologies and crystal structures, ZnO is considered to be a new generation of optoelectronic semiconductor materials [4-6]. Therefore, ZnO has been paid much attention, especially in the field of environment, and the researchers have done a lot of research [7-9]. Among them, the study on the influence of pH on photocatalytic performance is more than other factors. In Parida's study [10], the effect of different pH on photocatalytic degradation of phenol by ZnO under solar irradiation was investigated. The result showed that ZnO had the best effect on phenol degradation at pH 5 and the photocatalytic efficiency reached 88% at the time of 4 h. Satish et al. [11] found that ZnO was beneficial to the degradation of phenol in weak acid or neutral solution, and

after the ZnO was reused for 5 times, its photocatalytic efficiency could be maintained with high efficiency. Senthilraja et al. [12] found that the photocatalytic efficiency of ZnO was decreased due to the easy dissolution of ZnO under acidic conditions. And ZnO had the best effect on AR18 when pH was 11. Behnajady et al. [13] studied the changes of Zn^{2+} concentration with the treatment of AY23 by ZnO under different pH value. The result showed that when pH was 7.5, Zn^{2+} was not detected. But when pH value was 5.2 and 2.5, the amount of Zn^{2+} was 365 and 430 mg/L, respectively. In the process of application, ZnO could be corroded under acidic or alkaline conditions, which led to difficulties in recovery of ZnO and did not fully exert its photocatalytic advantages [14]. With regard to improving the photocatalytic efficiency of ZnO under various pH conditions and inhibiting the corrosion of ZnO under acidic conditions, domestic and foreign researchers had conducted a large number of composite experiments on ZnO. Through the research of Randeep [15], the mixture of ZnO and SnO_2 showed better photocatalytic performance for methylene blue at pH being 10 compared with ZnO. What's more, a

new heterostructure Bi₂O₃/ZnO prepared by Balachandran S. et al. [16] showed better photocatalytic activity for AB1 and the degradation efficiency was higher at the pH of 7, comparing with ZnO. TiO₂/ZnO/ chitosan compound was prepared successfully by Zhu H et al [17]. It was found that the chitosan played a good protective effect on ZnO, making the degradation efficiency of methyl orange reach 99.8% when pH was 2.

Recently, graphene has aroused wide concern of researchers due to its excellent electrical conductivity, excellent chemical stability and high specific surface area [18-20]. Similar to carbon nanotubes, graphene can also be used as an excellent electron acceptor/transport material [21-23]. And the semiconductor oxides and graphene composites with excellent photocatalytic properties have been reported [24-27]. Wu et al. [28] has successfully prepared the dissection of ZnO/graphene by a simple chemical method, which has higher photocatalytic efficiency and sensing properties than pure ZnO. Li et al [29] doped ZnO and graphene to form a compound system, and the photocatalytic activity of rhodamine B under visible light was studied. It was found that ZnO/graphene has higher photocatalytic efficiency than ZnO. Research on graphene composite semiconductor oxides is far more than these. Recent studies have also found that the semiconductor oxides of composite graphene have three advantages [30]: enhancing the adsorption of pollutants, broadening the absorption range of light, transporting and separating effectively charges and being chemically stable. Therefore, we can believe that the excellent properties of graphene can improve the photocatalytic efficiency of ZnO in different pH and inhibit the corrosion of ZnO under acidic and alkaline conditions, and thus play a very good role in the protection of ZnO.

In this paper, ZnO/graphene composite photocatalysts were synthesized and characterized in the laboratory. Besides, the photocatalytic degradation of methyl orange by ZnO/ graphene under different pH conditions was studied.

2. Experimental materials and methods

2.1. Synthesis of ZnO/grapheme compounds

Graphene was prepared by Hummer-hydrazine hydrate reduction [31-32] method, and ZnO was prepared by chemical precipitation method [33]. Then 4g ZnO and 0.1g graphene were dispersed in 100ml distilled water respectively for 30min with ultrasonic frequency being 400 Hz. 1mg/ml graphene solution was slowly added dropwise to a 40 mg/ml ZnO solution for a strong agitation of 2 hours. After 30 min with ultrasonic, the mixture was rapidly heated to 200°C, then ZnO/ graphene composite samples were obtained.

2.2. Characterization of samples

Scanning electron microscopy (SEM) (JSM-6700F, JEOL, Tokyo, Japan) was used to characterize the microstructure of ZnO, graphene and ZnO/graphene composites. XRD (D/MAX-2500/PC; Rigaku Co, Tokyo, Japan) was used to study the crystal structure of the samples. UV-Vis diffuse reflectance spectroscopy (UV41000, HITACHI, Tokyo, Japan) was used to study the absorption of different samples at different wavelengths and determine the band gap.

2.3. Experiments of photocatalytic degradation of methyl orange

In this experiment, the dosage of ZnO/graphene photocatalyst is 0.1g, the concentration of methyl orange (MO) solution is 10mg/L, the volume is 100ml. When the pH (pH=1, 3, 5, 7, 9, 11) was changed, the degradation ability of ZnO/graphene and ZnO on methyl orange was investigated by decolorization rate. The

decolorization rate = $\frac{C_t}{C_0}$. Where C₀ was the concentration

of dye before reaction, C_t was the concentration of dye after light at the time of t. The linear relationship was between the concentration and the absorbance. The absorbance was measured by 1100 spectrophotometer (Shanghai Tian Mei Instrument Co., Ltd.). After degrading, ZnO/graphene and ZnO were characterized by scanning electron microscopy (SEM). Then 5 times of photocatalyst reused experiments were carried out to observe the corrosion and recovery of photocatalyst under different pH conditions. The dye methyl orange solution and the photocatalyst were mixed in the dark state to stir up for 30 min before the degradation experiment to achieve adsorption equilibrium. The visible light can be obtained through the filter (lambda > 420 nm) to filter out UV from the external 300W Xe light source illumination (PLS-SXE300, Beijing Co. Ltd., China). The distance of the light source and the dye solution is 15 cm, and the reaction temperature kept at 20 °C by condensate water system. The photocatalytic reactor was shown in Fig. 1.

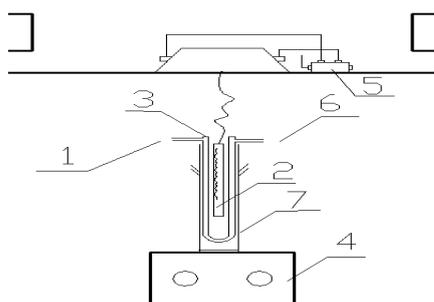


Fig. 1. The photocatalytic reactor (1 Intake; 2 300 xenon lamp; 3 Quartz liner; 4 Agitator; 5 Transformer; 6 Outfall; 7 Glass cover Fig. 1 The photocatalytic reactor)

3. Results and discussion

3.1. Characterization of ZnO and ZnO/graphene

X-ray diffractograms of ZnO/graphene was shown in Fig. 2.

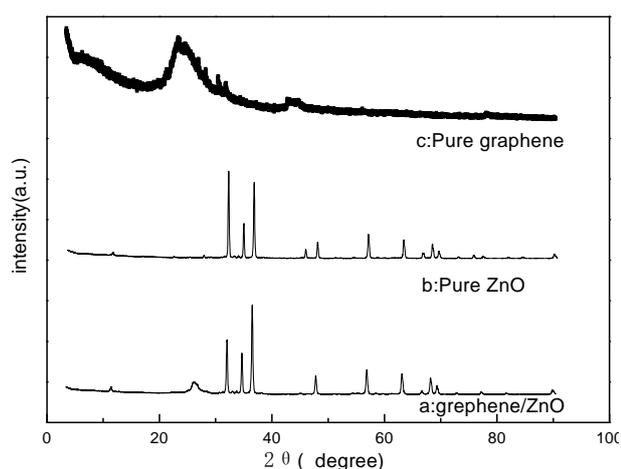


Fig. 2. X-ray diffractograms (a) ZnO/graphene, (b) ZnO, (c) Graphene

As can be seen from Fig. 2(b), there was a series of strong diffraction peaks in 31.8, 34.4, 36.3, 47.5, 56.6, 62.9 and 68.1 degree, and the diffraction peak corresponding to (100), (002), (101), (102), (110), (103), (200) crystal planes (JCPDS No. 89 - 0511) of the zinc oxide hexagonal system. These results were in agreement with the standard card which meant that the ZnO crystals were successfully prepared. Fig. 2(c) shows the XRD pattern of graphene, which showed a strong diffraction peak at about 25.8 degrees, which was consistent with the standard card and is consistent with the (002) crystal plane reported by Bu [34] so that graphene has been successfully prepared. Fig. 2a shows the XRD pattern of ZnO/graphene composite. On this curve, in addition to the diffraction peak of graphene appearing at 25.8 degrees. At the same

time, the ZnO diffraction peak of the composite material was also exactly the same as that of the pure ZnO diffraction peak (as shown in Fig. 2b), indicating that ZnO/graphene composites were successfully prepared.

The scanning electron microscopes of graphene, pure ZnO and ZnO/graphene were shown in Fig. 3.

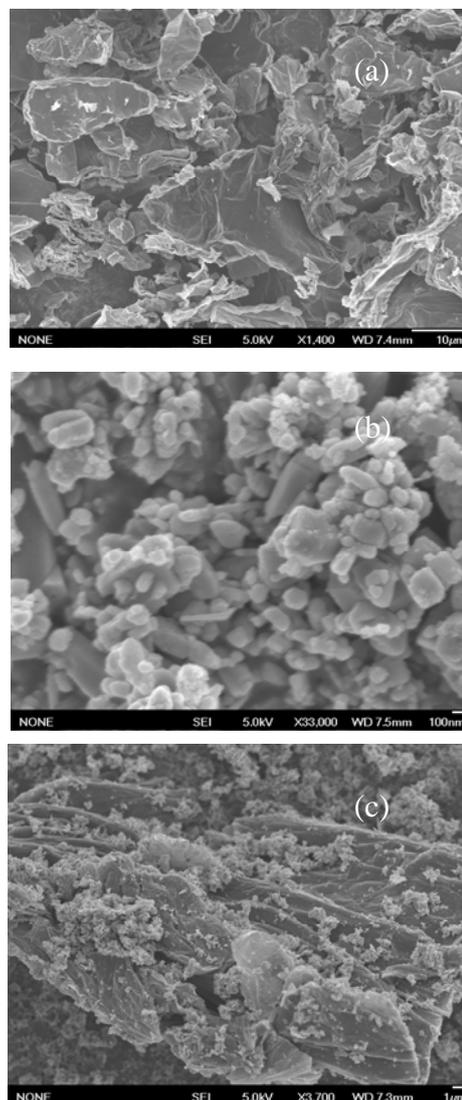


Fig. 3. SEM diagram (a) graphene (b) ZnO (c) ZnO/graphene

Fig. 3(a) is a SEM image of graphene. It could be seen from Fig. 3(a) that it had a layered structure of graphene with good transparency, but the surface was not even and the wrinkled surface. The reason was that the oxygen containing groups at the edges of graphene were removed in the electrochemical reduction process, resulting in the natural folding of the edges in the absence of oxygen containing groups [35]. Besides, this was similar to that of graphene prepared by Xiang [36]. Fig. 3(b) was SEM morphology of pure ZnO, from which it could be observed

that many ZnO clustered together with the structure of rodlike, which indicated that ZnO was well prepared. As could be seen from Fig. 3(c), a lot of short rods of ZnO are superimposed on each other and distributed on the surface of graphenes, which showed that the ZnO/graphene composites had been successfully prepared.

The UV-Vis analysis of ZnO/graphene was shown in Fig. 4.

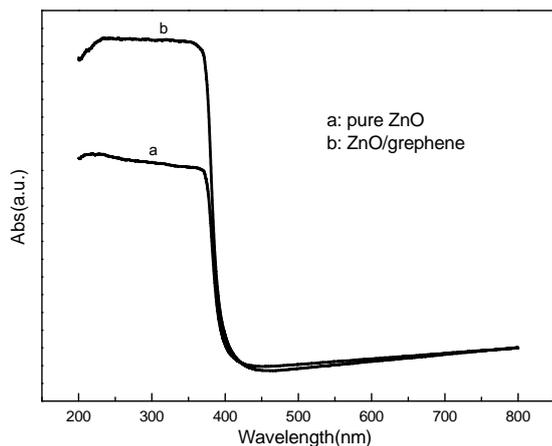


Fig. 4. UV-vis spectrum (a) ZnO; (b) ZnO/grapheme

As can be seen from Fig. 4, on the one hand, both ZnO and ZnO/graphene samples had strong absorption at 400 nm and the absorption intensity was stronger in the presence of graphene. On the other hand, compared with curve a and curve b, when graphene was compounded with ZnO, the maximum absorption was slightly red shifted and extended the straight line of the curve a and b to the horizontal axis. According to the formula $\lambda_0 = \frac{1240}{E_g} (eV)$, it could be known that the absorption characteristic of ZnO/graphene became wider and the band gap became narrow, indicating that the addition of graphene had changed the absorption performance of ZnO making the absorption range wider, which was more conducive to the absorption of visible light [37]. This provides a possibility for ZnO/graphene to improve ZnO photocatalytic performance under different pH conditions.

3.2. Photocatalytic degradation of methyl orange by ZnO/graphene under different pH conditions

The photocatalytic degradation of methyl orange by ZnO/graphene under different pH conditions was shown in

Fig. 5.

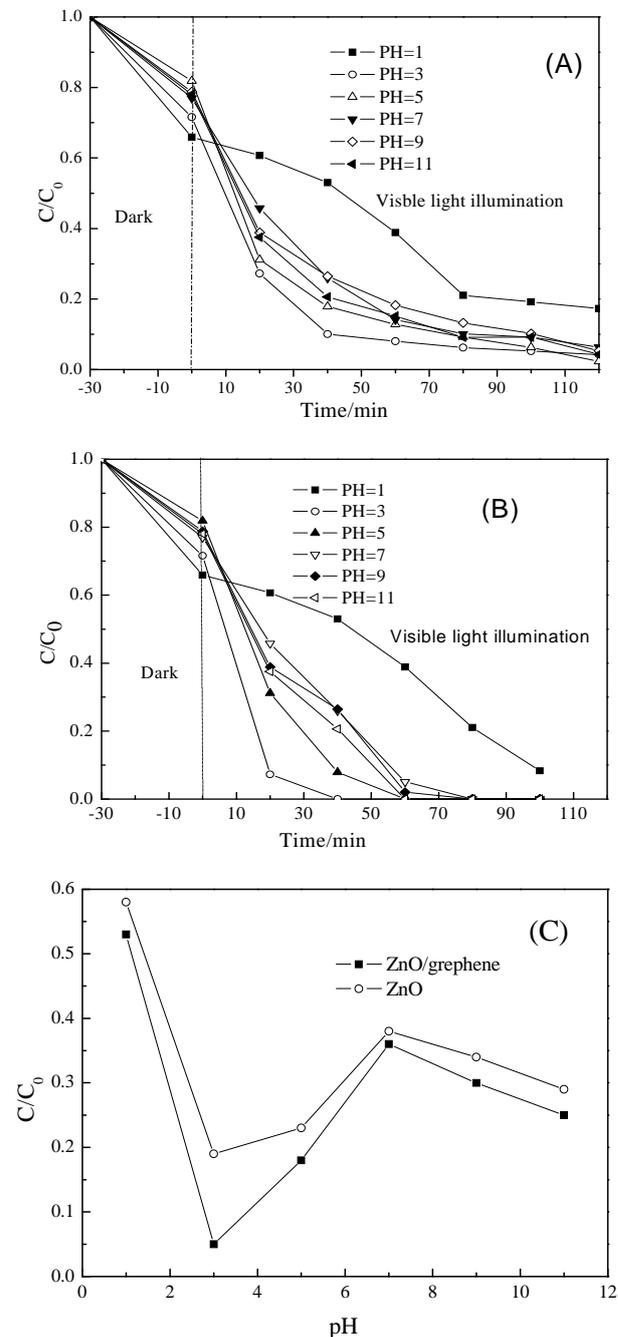


Fig. 5. Photocatalytic degradation of methyl orange under different pH conditions (A) by pure ZnO (B) by ZnO/graphene (C) by pure ZnO and ZnO/graphene

The degradation of methyl orange (MO) in 120 min by ZnO and ZnO/graphene under different pH conditions was investigated. Fig. (A) shows the degradation curve of ZnO to MO, after 30 min of dark state adsorption, about 20%~30% of MO was adsorbed. When pH value was 3 and 5, ZnO showed better photocatalytic degradation effect on MO. However, the effect of pH on the

photocatalytic performance of ZnO was various. On the one hand, when the methyl orange solution was acidic, $\text{pH} < \text{pH}_{\text{zpc}}$ (the zero potential of ZnO is about 8 [38]), the surface of ZnO is positively charged, and the adsorption capacity of methyl orange was enhanced because of the electrostatic attraction of the anionic dye methyl orange. On the other hand, when the $\text{pH}=3$ and $\text{pH}=5$, the molecular structure of methyl orange had been changed to the quinone structure [39,40] which was unstable and can be easily destroyed. Under the condition of weak alkaline, the ZnO surface being negatively charged was favorable for the hole to migrate to its surface and reacted with the electron donor to produce hydroxyl radical. Thus it reduced the surface recombination probability of photogenerated electrons and holes [41]. However, ZnO is amphoteric oxide. When the basicity was strong, the surface of ZnO may had begun to form hydroxyl complexes which changed the structure of the catalyst surface affecting its photocatalytic activity. In addition, the degradation ability of ZnO to methyl orange was poor under the condition of $\text{pH}=1$, which due to the high concentration of H^+ in the process of catalytic degradation and the directly reaction with ZnO, making ZnO corroded. So the photocatalytic activity of ZnO was decreased. Fig. (B) shows the degradation curve of ZnO/graphene to MO, and compares the degradation curve of (A) ZnO to MO, the catalytic degradation ability of ZnO/graphene was obviously improved under the same pH conditions. This can be explained by the mechanism of photocatalytic reaction. On the one hand, the reason may be that the existence of graphene had a good protective effect on ZnO and inhibited the chemical corrosion of ZnO. And the photogenerated electrons can be easily transferred to the surface of ZnO, and the hydroxyl radical was formed by combining with O_2 , which reduced the recombination of electrons and holes, thus enhanced the photocatalytic performance of ZnO/graphene [42-44]. In the third aspect, the addition of graphene made the ZnO band gap become narrow which could be reflected from the above-mentioned UV-visible diffuse reflectance. This was consistent with the experimental results of Xu [21], and thus improved the photocatalytic activity of ZnO. The efficiency made it easier to be excited by the sunlight and the generated hole has stronger oxidation ability, making the photocatalytic efficiency of methyl orange become higher under different pH conditions. Moreover, in the low pH conditions ($\text{pH} \leq 5$), the corrosion of ZnO occurs, the lower the pH is, the more serious the corrosion is. Although the photocatalytic reaction rate is faster in acid condition, the methyl orange degradation efficiency has no obviously improvement compared with basic condition. Because the existence of graphene had a good protective effect on ZnO and inhibited the chemical corrosion of ZnO,

the methyl orange degradation efficiency is obviously improved by ZnO/graphene in acid condition ($\text{pH} \leq 5$). In figure (C), the photocatalytic activities of ZnO/graphene and ZnO in different pH conditions were compared synthetically for 30 minutes. Compared with ZnO photocatalyst, when $\text{pH}=1\sim 11$, the photocatalytic degradation of methyl orange with ZnO/graphene had obvious improved, especially when $\text{pH}=3$, the photocatalytic effect was more significant. The result showed that graphene played a promoting role for the photocatalytic effect of ZnO under different pH conditions. In addition, from the respective curves of the photocatalytic degradation performance of methyl orange of ZnO/graphene and ZnO under different pH conditions, it can be seen that the degradation rate of ZnO/graphene and ZnO to methyl orange is $\text{pH}=3$ max. Comparing with acidic conditions, the degradation rate of methyl orange in the alkaline environment was significantly reduced, which was another expression of Fig. (A) and Fig. (B).

3.3. SEM of ZnO/ graphene corrosion under different pH conditions

At the end of the photocatalytic reaction under different pH, the SEM of the recovered ZnO and ZnO/graphene corrosion were shown in Fig. 6.

Under the condition of $\text{pH}=1$, there existed more serious corrosion of ZnO, either pure ZnO or composite graphene. By the end of the photocatalytic reaction, the ZnO had been completely dissolved in the solution and the ZnO/graphene also had a large degree of dissolution, so that the material can not be recycled. This was consistent with what was reflected in Fig. 4 (C)—when $\text{pH}=1$, the photocatalytic degradation efficiency of ZnO and ZnO/graphene was the lowest. As can be seen from figure a-j, the corrosion degree of ZnO was more serious in acidic condition. However, under the alkaline condition, the corrosion degree of ZnO was lighter and maintained the initial morphology, compared with pure ZnO and ZnO in acidic condition. In addition compared with the SEM photographs of ZnO and ZnO / graphene, the corrosion degree of ZnO doped graphene was lighter than that of pure ZnO indicating that the presence of graphene had a protective effect on ZnO in the acid condition and improved the photocatalytic degradation efficiency. As a result, it was very important to deal with the wastewater containing methyl orange in the actual process.

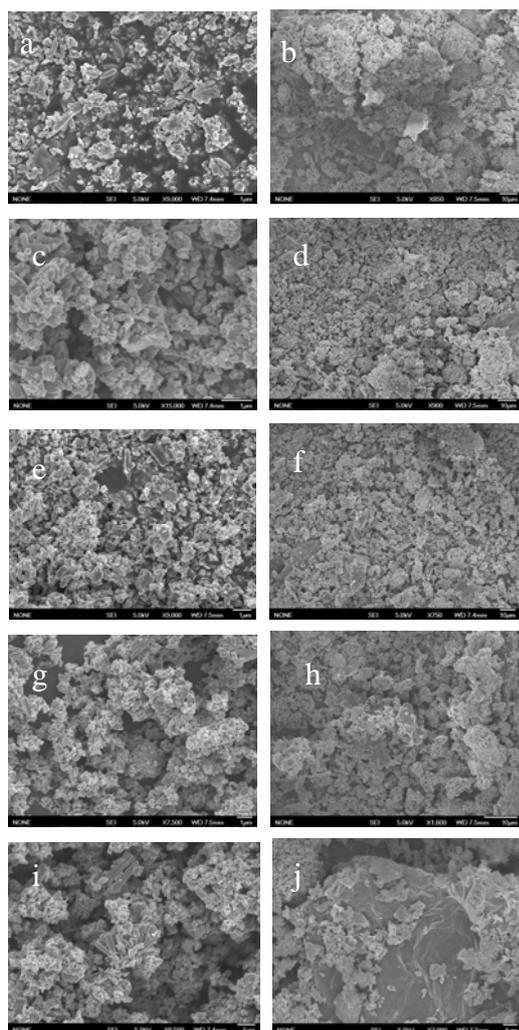


Fig. 6. SEM of ZnO/graphene and ZnO corrosion under different pH conditions (a. ZnO under pH=3; b. ZnO/graphene under pH=3; c. ZnO under pH=5; d. ZnO/graphene under pH=5; e. ZnO under pH=7; f. ZnO/graphene under pH=7; g. ZnO under pH=9; h. ZnO/graphene under pH=9; i. ZnO under pH=11; j. ZnO/graphene under pH=11)

3.4. Reused of ZnO / graphene under different pH conditions

In order to investigate the stability of ZnO/graphene, the reused of ZnO/graphene was tested under the condition of respective pH. The cycle time is one hour. For each new cycle, the methyl orange was decolorization after the photocatalyst samples being filtered and dried. The results were shown in Fig. 7.

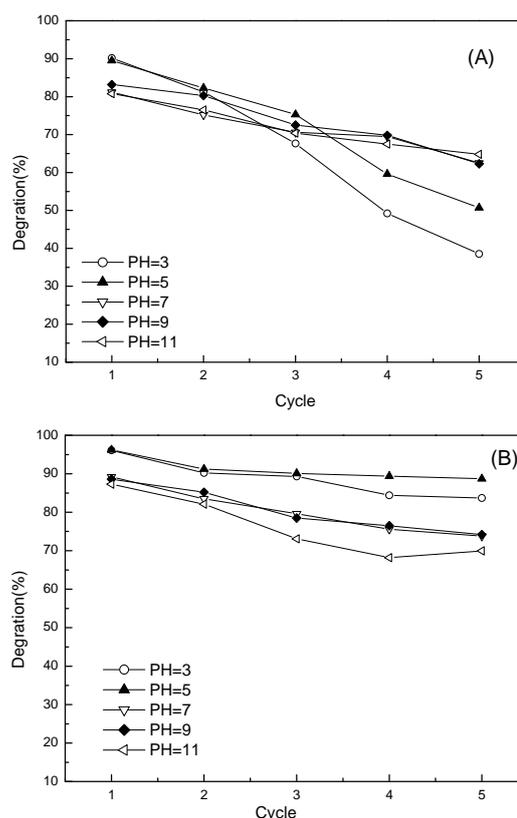


Fig. 7. Stability of photocatalytic degradation of methyl orange (A) ZnO; (B) ZnO/graphene

As can be seen from the graph (A), with the increase of the reused number, the degradation rate of methyl orange by ZnO decreased gradually. Especially when pH=1, the degradation rate of methyl orange by ZnO was reduced so fast indicating that the stability of ZnO was destroyed leading to the serious corrosion by H^+ making the recycling difficult. It was consistent with SEM of graph 6. In addition, although the photocatalytic efficiency was high at pH=3 and pH=5 at first, the photocatalytic efficiency of ZnO decreased quickly with the increase of the reused numbers, especially in the third cycle. This meant that the pure ZnO had high photocatalytic efficiency in acidic conditions, but it was unstable in acidic environment which was adverse to deal with effluent containing methyl orange. However, under the alkaline condition, although the degradation efficiency of ZnO was feeble, the photocatalytic degradation efficiency of ZnO remained stable after 5 cycles. In figure (B), except pH=1, the ZnO doped with graphene can maintain good stability under various pH conditions. Especially when the pH values were 3 and 5, the ZnO doped with graphene enabled to prevent from slipping of the photocatalytic efficiency. And after the sample was reused by 5 cycles, the degradation efficiency of methyl orange with ZnO/graphene remained at about 85%. Compared with figure (A) and (B), in each cycle, the degradation rate of the ZnO doped graphene was better than that of pure ZnO

under various pH conditions, which indicating the addition of graphene could improve photocatalytic degradation rate with Zn under various pH conditions.

4. Photocatalytic degradation mechanism by ZnO/graphene

The mechanism of photocatalytic degradation of methyl orange by ZnO/graphene was shown in Fig. 8.

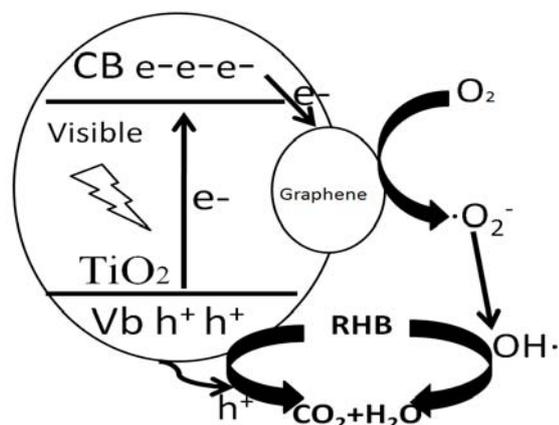


Fig. 8. Mechanism of photocatalytic degradation of methyl orange by ZnO/graphene

Equipping with good stability [22], graphene didn't react with methyl orange under different pH conditions. Instead, graphene could focus on protecting ZnO, preventing ZnO from being corroded and improving the stability of ZnO. On the other hand, graphene had high conductivity [45]. The experimental results suggested that the carrier mobility of graphene can reach $15000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature. When graphene was mixed with ZnO, it could be involved in the transfer of photogenerated carriers. ZnO was excited by the incident light, then the photogenerated electrons could be rapidly transferred to the surface of graphene and combined with the dissolved oxygen in solution so that the $\text{O}_2^{\cdot-}$ with strong reducing ability was formed making the hole h^+ on the valence band fail to be combined with the electron. This was consistent with the results of the photoluminescence spectra of ZnO/graphene and ZnO in Fig. 9. The photoluminescence spectrum to some extent reflected the recombination efficiency of photogenerated electrons and holes. The two recombination of photogenerated electrons and holes was accompanied by the generation of fluorescence. The stronger the fluorescence intensity was, the higher the recombination rate of photogenerated electrons and holes was, and the shorter the lifetime of photogenerated carriers was. On the contrary, the weaker the fluorescence intensity was, the higher the separation efficiency of photogenerated electrons and holes was, and the longer the lifetime of photogenerated carriers was [46,47]. In Fig. 9, the fluorescence intensity of

ZnO/graphene was lower than that of pure ZnO both in the UV and visible regions from photoluminescence spectrum of ZnO and ZnO/graphene. Because of the presence of graphene, the photogenerated electrons not only could be easily transferred to the surface of ZnO accelerating the separation efficiency of photogenerated electrons and holes, but also they could enabled to combine with O_2 on the surface forming hydroxyl radical which reduced the recombination of electrons and holes, so that the photocatalytic property of ZnO/graphene enhanced.

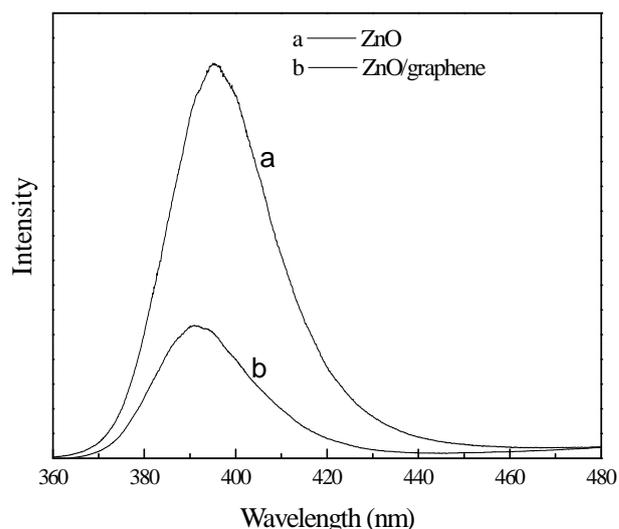


Fig. 9. Photoluminescence spectra of ZnO/graphene and ZnO

In addition, the transient response of ZnO/graphene electrode to the photocurrent was found by Xu [21]. The photocurrent of the ZnO/graphene electrode was about 3.5 times than that of the ZnO electrode, and ZnO and ZnO/graphene flat band potentials were -0.36 and -0.29 V, respectively. Besides, ZnO/graphene electrode electrochemical impedance spectrum EIS Nyquist radius was much smaller than that of the ZnO electrode. All that demonstrated the existence of graphene could effectively accelerate the separation of electrons and holes. The hole could be combined with water molecules or OH^- to form a hydroxyl radical with strong oxidation ability, and then methyl orange (MO) was oxidized to produce H_2O and CO_2 .

5. Conclusions

In this study, the existence of graphene could significantly increase the photocatalytic efficiency of ZnO under different pH conditions. When $\text{pH}=3-5$, ZnO/graphene had better photocatalytic degradation effect on methyl orange. The results of cyclic degradation experiment under various pH conditions and scanning electron microscope of recycling samplings after cyclic

degradation indicated that the presence of graphene had a protective effect on ZnO, which could improve the stability of its reuse. And in the experiment of photoluminescence spectra of ZnO/graphene and ZnO, the existence of graphene could also accelerate the effective separation efficiency of photogenerated electrons and holes, thus improved the photocatalytic degradation efficiency of ZnO / graphene and ZnO which provides theories for ZnO / graphene in the treatment of dye wastewater under various pH conditions particularly in acidic condition.

Acknowledgments

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References

- [1] F. Xu, L. Sun, *Energy & Environmental Science* **4**(3), 818 (2011).
- [2] J. Huang, Z. Yin, Q. Zheng. *Energy & Environmental Science* **4**(10), 3861 (2011).
- [3] I. Gonzalez-Valls, M. Lira-Cantu, *Energy & Environmental Science* **2**(1), 19 (2009).
- [4] W. Yu, J. Zhang, T. Peng, *Applied Catalysis B: Environmental* **181**(12), 220 (2016).
- [5] Q. B. Zhang, Z. F. Feng, N. N. Han, L. L. Lin, J. Z. Zhou, Z. H. Lin, *Chinese Journal of Physical Chemistry* **26**(11), 2927 (2010).
- [6] X. Wang, L. Yin, G. Liu, L. Wang, R. Saito, G. Q. Lu, *Energy & Environmental Science* **4**(10), 3976 (2011).
- [7] F. U. Tianhua, Q. Gao, F. Liu, H. Dai, *Chinese Journal of Catalysis* **31**(7), 797 (2010).
- [8] C. A. Gouvea, F. Wypych, S. G. Moraes, N. N. Durã, N. Nagata, *Chemosphere* **40**(4), 433 (2000).
- [9] C. G. Silva, M. J. Sampaio, S. A. C. Carabineiro, J. W. L. Oliveira, D. L. Baptista, R. Bacsa, *Journal of Catalysis* **316**(3), 182 (2014).
- [10] K. M. Parida, S. Parija, *Solar Energy* **80**(8), 1048 (2006).
- [11] S. K. Pardeshi, A. B. Patil, *Solar Energy* **82**(8), 700 (2008).
- [12] A. Senthilraja, B. Krishnakumar, B. Subash, A. J. F. N. Sobral, M. Swaminathan, M. Shanthi, *Journal of Industrial and Engineering Chemistry* **33**, 51 (2016).
- [13] M. A. Behnajady, N. Modirshahla, R. Hamzavi, *Journal of Hazardous Materials* **133**(1-3), 226 (2006).
- [14] A. Franco, M. C. Neves, M. M. L. R. Carrott, M. H. Mendonca, M. I. Pereira, O. C. Monteiro, *Journal of Hazardous Materials* **161**(1), 545 (2009).
- [15] R. Lamba, A. Umar, S. K. Mehta, S. K. Kansal, *Journal of Alloys and Compounds* **653**(25), 327 (2015).
- [16] S. Balachandran, M. Swaminathan, *The Journal of Physical Chemistry C* **116**(50), 26306 (2012).
- [17] H. Zhu, R. Jiang, Y. Fu, Y. Guan, J. Yao, L. Xiao, *Desalination* **286**(1), 41 (2012).
- [18] I. Lightcap, T. Kosel, P. Kamat, *Nano Letters* **10**(2), 577 (2010).
- [19] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, et al., *Nature* **438**(7065), 197 (2011).
- [20] W. Bei, W. Ying, J. Park, H. Ahn, G. Wang, *Journal of Alloys and Compounds* **509**(29), 7778 (2011).
- [21] T. Xu, L. Zhang, H. Cheng, Y. Zhu, *Applied Catalysis B: Environmental* **101**(3), 382 (2011).
- [22] B. Li, H. Cao, *Journal of Materials Chemistry* **21**(10), 3346 (2011).
- [23] X. J. Liu, L. K. Pan, T. Lv, T. Lu, G. Zhu, Z. Sun, *Catalysis Science & Technology* **1**(7), 1189 (2011).
- [24] E. Gao, W. Wang, M. Shang, J. Xu, *Physical Chemistry Chemical Physics* **13**(7), 2887 (2011).
- [25] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, *ACS Nano* **4**(1), 380 (2009).
- [26] D. Fu, G. Han, Y. Chang, J. Dong, *Materials Chemistry and Physics* **132**(2), 673 (2012).
- [27] X. Y. Zhang, H. P. Li, X. L. Cui, Y. Lin, *Journal of Materials Chemistry* **20**(14), 2801 (2010).
- [28] J. Wu, X. Shen, J. Lei, K. Wang, K. Chen, *Applied Surface Science* **256**(9), 2826 (2010).
- [29] J. Li, T. Pham, R. Abdelmoula, F. Song, C. P. Jiang, *International Journal of Solids and Structures* **48**(24), 3346 (2011).
- [30] N. Yang, J. Zhai, D. Wang, Y. Chen, L. Jiang, *ACS Nano* **4**(2), 887 (2010).
- [31] S. N. Alam, N. Sharma, L. Kumar, *Graphene* **6**(1), 1 (2017).
- [32] D. A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, *Nature* **448**(7152), 457 (2007).
- [33] M. R. Rajan, J. Archana, R. Ramesh, V. Keerthika, *PARIPEX-Indian Journal of Research* **5**(10), (2017).
- [34] Y. Bu, Z. Chen, W. Li, B. Hou, *ACS Applied Materials & Interfaces* **5**(23), 12361 (2013).
- [35] Y. Shao, J. Wang, M. Engelhard, C. Wang, Y. Lin, *Journal of Materials Chemistry* **20**(4), 743 (2010).
- [36] Q. Xiang, J. Yu, M. Jaroniec, *Chemical Society Reviews* **41**(2), 782 (2012).
- [37] I. Lightcap, T. Kosel, P. Kamat, *Nano Letters* **10**(2), 577 (2010).
- [38] S. Lathasree, A. N. Rao, B. Siva Sankar, V. Sadasivam, K. Rengaraj, *Journal of Molecular Catalysis A Chemical* **223**(1), 101 (2000).
- [39] J. Wang, B. Guo, X. Zhang, Z. Zhang, J. Han, J. Wu, *Ultrasonics Sonochemistry* **12**(5), 331 (2005).
- [40] H. S. Goh, R. Adnan, M. A. Farrukh, *Turkish Journal of Chemistry* **35**(3), 375 (2011).

- [41] L. H. Gan, X. L. Wang, Z. X. Hao, Y. D. Wang, *Journal of Tongji University (Natural Science)* **33**(8), 107 (2005).
- [42] T. Xu, L. Zhang, H. Cheng, Y. Zhu, *Applied Catalysis B: Environmental* **101**(3), 382 (2011).
- [43] B. Li, H. Cao, *Journal of Materials Chemistry* **21**(10), 3346 (2011).
- [44] G. Williams, P. V. Kamat, *Langmuir* **25**(24), 13869 (2009).
- [45] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, A. K. Geim, *Reviews of Modern Physics* **81**(1), 109 (2009).
- [46] W. Li, F. Chang, S. Dai, J. Yue, F. Hua, H. Hao, *Applied Catalysis B: Environmental* **168-169**, 465 (2015).
- [47] Y. Bu, Z. Chen, *Electrochimica Acta* **144**(144), 42 (2014).

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