Effect of PO_4^{3-} and PO_4^{3-}–SO_4^{2-} modification of TiO_2 on its photocatalytic properties

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Abstract

In this paper, novel photocatalysts were prepared by PO_4^{3-} and PO_4^{3-}/SO_4^{2-} surface modification of TiO_2. Photocatalytic activities of these photocatalysts as affected by preparation conditions were studied by examining the degradation of aqueous methylthionine chloride solution. Their properties were measured and compared by XRD, IR and UV. The experimental results indicate that the modification of TiO_2 by PO_4^{3-} and PO_4^{3-}–SO_4^{2-} enhance distinctly its photocatalytic activity, especially the PO_4^{3-}–SO_4^{2-}/TiO_2. The synergistic effect of photocatalytic decomposition and surface acidity of catalyst is observed by optimized the ratio of PO_4^{3-} and SO_4^{2-}. Super acidification of TiO_2 increases the absorbance of catalyst in ultraviolet region, and improves distinctly the photocatalytic activity on 365 nm light.
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1. Introduction

The study of heterogeneous photocatalysis attracts increasing interest because it has a great potential for the removal of organic pollutants from wastewater and air, especially the application of semiconductor photocatalyst. Titania has received great attention as a photocatalyst because of its long-term stability, low toxicity and good photocatalytic activity [1], and is widely used for air purification, deodorant, sterilization, anti-fouling, and demister [2].

Since the band gap of titania is about ∼3.2 eV, the irradiation of UV-light below 380 nm is necessary for the photocatalysis process of TiO_2. If the natural sunlight is used for the photoexcitation of titania, only about 5% of the incident radiation has enough energy for this process. In addition, the quantum efficiency of titania photocatalysis is lower as a result of quick recombination of photogenerated electron–hole pairs. Thus, how to improve sunlight utilization efficiency, and to enhance the photocatalytic quantum efficiency are important subjects for the exploitation and application of TiO_2 photocatalyst. In recent years, modifications of TiO_2 by changing the electrical properties [3,4] and inducing batho-chromic shift of the band gap [5] were widely studied in order to improve the utilization efficiency of visible light and the photocatalytic quantum efficiency of TiO_2. Asahi et al. [6] reported a nitrogen doped titania possesses viable light photocatalytic activity and hydrophilicity. Anpo et al. [7] doped a series of transition metal, such V, Cr and Ni into TiO_2 films with band gap shifting to visible light. Studies [8–10] demonstrate that dye (sensitizer) adsorbed on TiO_2 surface can effect charge injection into the conduction band of TiO_2 by absorbing visible light and the catalytic processes is followed through interfacial electron transfer. In addition, the complex of different semiconductors can not only extend the photoexcitation wavelength but also improve the stability of photocatalyst [11].

Sulfate promoted TiO_2 has been extensively used for the catalyst of organic reactions because of its superacidity. Recently sulfate promoted TiO_2 has been also proved as interesting photocatalyst [12–15]. However, the reasons for the photocatalytic optimization are still unclear. Mugli and Ding [13] suggested that the strong acid sites on TiO_2/SO_4^{2-} play an important role in photocatalytic oxidation reaction, and strong acid sites increase the adsorption strengths and coverages of different organics, which contribute to the improved photocatalytic activity. Fu et al. [12,16] concluded that the improved photocatalytic activity of sulfated titanium dioxide is due to a greater surface area as well as larger fraction of anatase phase, which is more active than

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rutile for the photocatalytic application. Nevertheless, Colón et al. [14] found that the presence of sulfate in TiO_2/SO_4^{2-} by calcinating at lower temperature (400 and 500 °C) seems to be a negative fact since photon efficiencies of sulfated TiO_2 are lower than non-sulfated one, and this better photocatalytic behaviour cannot be explained by terms of surface acidity. They suggested that the sulfation treatment of TiO_2 would affect to the TiO_2 crystallization by stabilizing the anatase phase at higher temperature and keeping at the same time a rather high specific surface area. In previous works, we investigated also photocatalytic performance of SO_4^{2-}/TiO_2 in aqueous solution and found that the overall photocatalytic activity of SO_4^{2-}/TiO_2 will be improved if its strong acidity and photocatalysis are ideally combined [15]. Therefore a synergistic effect of surface acidity and photocatalytic activity will be obtainable by super acidification modification to change the surface acidity of TiO_2.

Based on previous experimental results, our group expended interest to the surface modification of TiO_2 by the super acidification of PO_4^{3-} and PO_4^{3-}–SO_4^{2-}, emphasizing its effect on the structure and the photocatalysis properties of organic contaminant in wastewater. In this paper, the novel catalysts, modified by PO_4^{3-} and PO_4^{3-}/SO_4^{2-}, were prepared by the method of precipitation-dipping. The influences of preparation conditions on the photocatalytic performance were studied using methylthionine chloride as model reactant of aromatic contaminant in aqueous solution.

2. Experiments

2.1. Preparation of pure TiO_2, PO_4^{3-}/TiO_2 and SO_4^{2-}–PO_4^{3-}/TiO_2

The hydroxide of TiO_2 was obtained by hydrolization of $TiCl_4$. Firstly, 25 g of ammonium sulfate dissolved in 100 ml of 0.1 mol/l chlorhydric acid aqueous solution. In a ice-water bath, 12 ml $TiCl_4$ was diluted and hydrolyzed with above solution under vigorous stirring, and then the above solution was warmed to 95 °C for 1 h. In order to ensure its complete hydrolysis reaction, a diluted ammonium solution (10%) was added dropwise into $TiCl_4$ aqueous solution to obtain hydroxide precipitate, giving an ultimate suspension of pH 10. The precipitate solution was standing overnight at room temperature. Finally the precipitate was adequately washed with distilled water to removal Cl^- till the pH value of filtrated water was below 7.5, and dried at 120 °C for 24 h.

Modification of TiO_2 was performed typically by suspending the fresh powders in a 0.25 mol/l phosphoric acid or a mixed acid of 2 mol/l sulfuric and 0.25 mol/l phosphoric acid for 1 h. Then, the suspension was filtrated and power was dried at 120 °C overnight. Modified and non-modified TiO_2 samples were calcined at temperature 550 °C for 3 h. All chemicals used were of reagent grade.

2.2. Photocatalysis

The aqueous solution of methylthionine chloride with a concentration of 50 mg/l was used as the subject of photogradation.

0.1 g catalyst powder was added into 100 ml of the above solution, and agitated vigorously for 10 min under black box before irradiation of ultraviolet light (8 W, $\lambda_{max} = 254$ nm) in order to offset the influence of adsorption. A UV1100 UV–vis spectrometer was used to record the change of concentration of the methylthionine chloride in the centrifuged samples of the above suspension before photolysis.

2.3. Characterization

The phase composition of catalyst power was determined by a Rigaku D/Max-γA X-ray diffractormeter with Cu Kα radiation. The diffuse reflection spectra of catalysts were recorded by Lamda 900 UV/vis/NIR spectrometer. Fresh catalysts and used catalysts were characterized by IR spectra using a PE-Spectrum One IR spectrometer. The sample was mixed with KBr and mixture was pressed into a pellet. The spectra were recorded at room temperature.

The acid strength of catalyst was measured using Hammett indicators. The sample was heated under vacuum at 200 °C for 1 h, then connected with the vapor of Hammett indicators. The change in the color of the indicators with different pK_a was observed.

3. Results and discussion

3.1. Characterization of the modified catalysts

Fig. 1 shows the XRD patterns of three catalysts. Similar to the power of pure TiO_2, PO_4^{3-}/TiO_2 and SO_4^{2-}–PO_4^{3-}/TiO_2 exist in the form of anatase phase and the surface modification of PO_4^{3-} and PO_4^{3-}–SO_4^{2-} does not change the crystallographic texture of TiO_2.

The diffuse reflectance spectra of modified and pure TiO_2 photocatalysts are shown in Fig. 2. It is observed that the absorption edges of TiO_2 modified by PO_4^{3-} and PO_4^{3-}–SO_4^{2-} shift slightly towards a shorter wavelength compared to that of pure TiO_2. The blue shift of the absorption edge of PO_4^{3-}–SO_4^{2-}/TiO_2 is more than that of PO_4^{3-}/TiO_2. Moreover, absorbance of modified TiO_2 is greater than that of pure, especially that of TiO_2 modified by PO_4^{3-}–SO_4^{2-}. The mod-
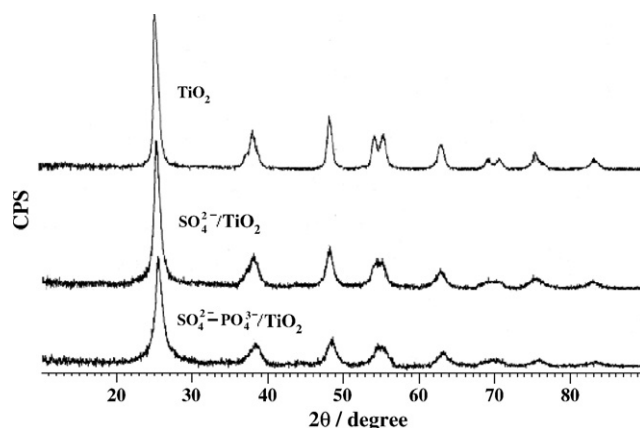

Fig. 1. XRD patterns of photocatalysts prepared on optimization conditions.
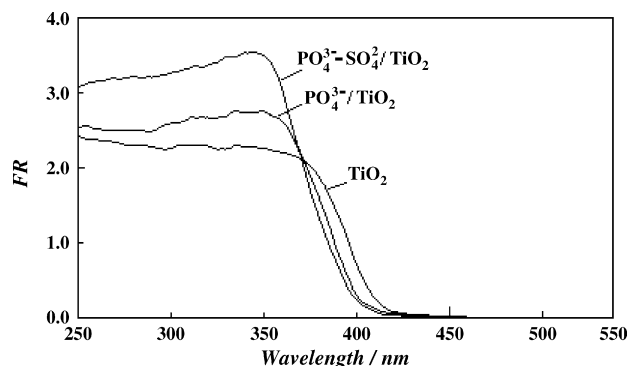
Fig. 2. The diffuse reflection spectra of photocatalysts.

ification of PO_4^{3-} and SO_4^{2-}–PO_4^{3-}, therefore, enhances the absorbance and changes the absorption characterization of TiO_2.

Fig. 3 shows the FTIR spectra of modified and used catalysts. Firstly, a wide and strong absorption band in the range of 900–1200 cm^{-1} is observed for the modified catalysts (spectrum a–d), which is attributed to the stretch vibration of double bond of PO_4^{3-}, but the absorption band of used PO_4^{3-}/TiO_2 (spectrum d) decreases and widens. Then two little absorption peaks present on the spectra of SO_4^{2-}–PO_4^{3-}/TiO_2 at 1382 and 1399 cm^{-1}, respectively, which are attributed to the stretch vibration of SO_4^{2-} with bidentate bond. It may be shielded by 900–1200 cm^{-1} absorption band of PO_4^{3-} that absorption band of SO_4^{2-} linked with ionic bond can not be observed. It was reported that the absorption band nearby 1400 cm^{-1} results in the super acidity of catalyst [17]. Above absorption characterizations do not exist in the TiO_2. Moreover, the absorption band of water exists in all samples because of the hygroscopicity of catalysts.

The modified catalysts by PO_4^{3-} and SO_4^{2-}–PO_4^{3-} possess super acidity, and their acid strength (H_0) are −13.16 and −13.75, respectively, measured using Hammett indictors. Therefore, PO_4^{3-}/TiO_2 and SO_4^{2-}–PO_4^{3-}/TiO_2 both show super acidity.
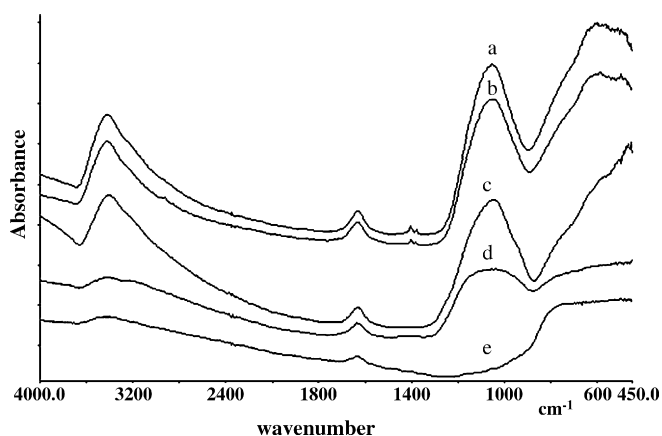
Fig. 3. FTIR spectra of samples: (a) fresh PO_4^{3-}/TiO_2; (b) used PO_4^{3-}/TiO_2; (c) fresh SO_4^{2-}–PO_4^{3-}/TiO_2; (d) used SO_4^{2-}–PO_4^{3-}/TiO_2; (e) fresh TiO_2.

3.2. Photocatalytic properties of PO_4^{3-}/TiO_2

It has been found that the photocatalytic activity of TiO_2 is phase dependent and the anatase phase shows the highest photocatalytic activity among the three crystalline forms of TiO_2 [18,19]. Since the anatase phase of TiO_2 is metastable phase, it is prepared by calcinations at certain temperature. From Fig. 4(a), it is shown that the degradation of methylthionine chloride increases along with the increase of calcinations temperature of catalyst. Meanwhile, the absorption experiments under non-light irradiation also shows that the absorption yields of methylthionine chloride on the surface of catalysts calcinated at temperature from 400 to 600 °C are respectively 41.5, 39.5, 31.5, 16.0 and 55.0%, and the methylthionine chloride absorbed on the surface of catalysts, which show stronger absorption, can not been degraded ultimately after 2 h irradiation. Compared with the absorption of methylthionine chloride on the surface of catalysts, it can be included that the photocatalytic activity of PO_4^{3-}/TiO_2 increases with the increase of calcinate temperature up to 550 °C. Although the degradation of catalysts calcinated at 600 °C is the highest, its absorption also is the strongest due to its strong acidity. However, over-absorption depresses the photocatalysis of catalyst by decreased the absorption of light on the photocatalytic center of catalyst and accelerates the deactivation of catalyst, and results in the present of methylthionine chloride on the surface of catalyst after 2 h irradiation. Therefore 550 °C is selected as the calcinations temperature of PO_4^{3-}/TiO_2.

Fig. 4(b) shows the influence of calcinations time on the degradation of methylthionine chloride. While calcinations time is within 4 h, the degradation increases with calcinations time of catalyst. But the catalyst calcinated for 5 h has lower photocatalytic activity than that calcinated for 4 h. It is likely that the time is necessary for the transform of TiO_2 from aormphism to anatase, but over-long calcinations time results in the aggregation and the decrease of the specific area of TiO_2. The influence of calcinations time on the absorption of catalysts is also similar to calcinations temperature, and the absorption on the surface of catalyst calcinated for 4 h is the lowest. Therefore, 4 h is optimal calcinations time under 550 °C.

The effect of concentration of maceration solution is shown in Fig. 4(c). From the changes of degradation with irradiation time, the catalysts show similar and good photocatalysis activity while the concentration of PO_4^{3-} is under 0.4 mol/l, but higher concentration of PO_4^{3-} is not favorable to enhance the efficiency of degradation. Though absorption of catalysts decreases with the decrease concentration of PO_4^{3-}, adsorbate on the catalysts surface is degraded ultimately except for catalysts dipped by 0.4 and 0.5 mol/l PO_4^{3-} after 2 h irradiation. Thus, compared with the degradation of TiO_2 shown in Fig. 4(d), the modification using lower concentration PO_4^{3-} improves the photocatalytic efficiency of TiO_2.

To study photocatalytic performance of modified catalysts under different wavelength of irradiation light, λ_{max} 365 nm ultraviolet light (8 W) is used to replace λ_{max} 254 nm ultraviolet light to photocatalyze by same procedure. The changes of degradation with time are shown in Fig. 4(d). Compared with
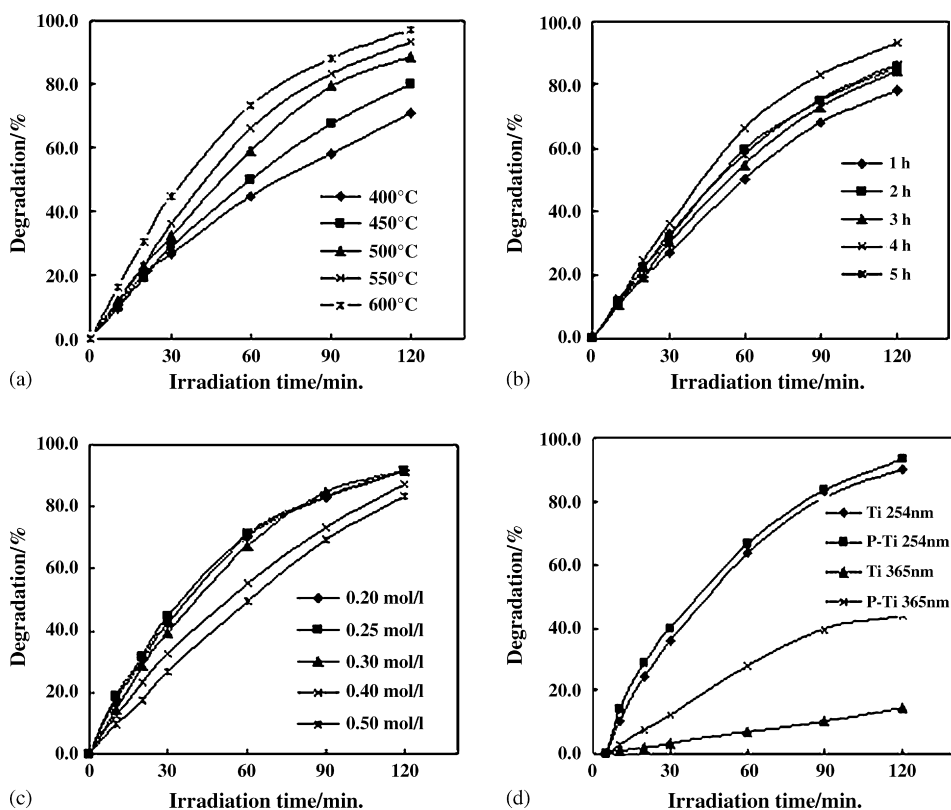
Fig. 4. Effect of preparation conditions and the wavelength of irradiation on the degradation of methylthionine chloride: (a) calcinations temperature of catalyst; (b) calcination time of catalyst; (c) concentration of PO_4^{3-}; (d) wavelength of light.

TiO_2, the modification of PO_4^{3-} not only advance the photocatalytic activity under 254 nm ultraviolet light irradiation but enhance evidently the activity under 365 nm light irradiation. It may be relative to the UV–vis absorption characterization as shown in Fig. 2 because the modification of PO_4^{3-} improves the absorbance of catalyst, especially at nearby 350 nm.

3.3. Photocatalytic properties of SO_4^{2-}–PO_4^{3-}/TiO_2

The changes of degradation of methylthionine chloride with irradiation time for the catalysts prepared at different calcinations temperature are shown in Fig. 5(a). The catalysts calcinated between 550 and 500 °C show the highest degradation rate and degradation of methylthionine chloride. According to the experiment of methylthionine chloride adsorption, the adsorption yield are, respectively, 1.5, 6.4, 21, 16 and 16% with the increase of calcinations temperature. Compared to PO_4^{3-}/TiO_2, the presence of SO_4^{2-} not only reduce slightly the calcinations temperature of catalyst but also decrease the adsorption of catalyst. As a result of high electron negativity of sulfur, sulfate ion induces higher polarization than phosphate ion and SO_4^{2-}–PO_4^{3-}/TiO_2 catalyst shows stronger acidity than PO_4^{3-}/TiO_2 catalyst. The highly polarized state of surface acidity would favor the trapping of electrons on the UV-excited TiO_2, resulting in an improved quantum efficiency of photocatalysis [20,21]. It also is in according with the diffuse reflectance spectra shown in Fig. 2 in which SO_4^{2-}–PO_4^{3-}/TiO_2 shows the strongest absorbance. Moreover, the decrease of the photocat-

alytic activity of SO_4^{2-}–PO_4^{3-}/TiO_2 calcinated at 600 °C may result from the transform of TiO_2 from anatase phase to rutile. So, the range of 500–550 °C might be the optimal calcinations temperature of SO_4^{2-}–PO_4^{3-}/TiO_2.

Fig. 5(b) shows the influence of calcinations time on the photocatalytic degradation of methylthionine chloride. Similar to PO_4^{3-}/TiO_2, 3 and 4 h are the optimal calcinations time for SO_4^{2-}–PO_4^{3-}/TiO_2. The amorphous TiO_2 cannot transform ultimately to anatase phase before 3 h, so that the photocatalytic activity increases with the increase of calcinations time. Since the specific surface area of SO_4^{2-}–PO_4^{3-}/TiO_2 decreases sharply after 4 h of calcinations, resulting in the decrease of total number of photocatalytic centers, the photocatalysis of catalyst calcinated 5 h is lower than that of catalyst calcinated 4 h. Moreover, the effect of calcinations time on the absorption of catalyst is not obvious as that of PO_4^{3-}/TiO_2. Thus SO_4^{2-} promotes the forming of anatase phase TiO_2 and restrains the absorption of catalyst.

Fig. 5(c) shows the effects of SO_4^{2-} concentrations in 0.25 mol/l PO_4^{3-} maceration solution on the photocatalytic performance of SO_4^{2-}–PO_4^{3-}/TiO_2. The concentration of SO_4^{2-} in the range of 1–3 mol/l improves the photocatalytic activity of SO_4^{2-}–PO_4^{3-}/TiO_2, and 2 mol/l SO_4^{2-} in 0.25 mol/l PO_4^{3-} solution gives the highest photocatalytic activity. Compared with PO_4^{3-} (0.25 mol/l)/TiO_2, as shown in Fig. 4(c), 0.5 and 4 mol/l SO_4^{2-} cannot improve the photocatalytic property of SO_4^{2-}–PO_4^{3-}/TiO_2. Because of stronger induction of SO_4^{2-} than PO_4^{3-}, the acidity of SO_4^{2-}–PO_4^{3-}/TiO_2 increases
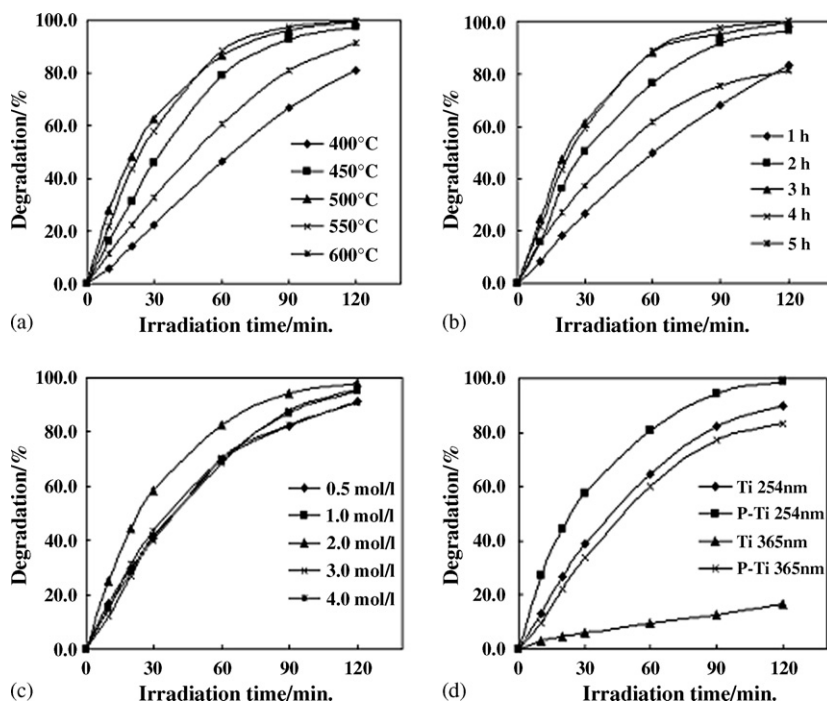
Fig. 5. Effect of preparation conditions and the wavelength of irradiation on the degradation of methylthionine chloride: (a) calcination temperature of catalyst; (b) calcination time of catalyst; (c) concentration of SO_4^{2-}; (d) wavelength of light.

with the increase of SO_4^{2-} content. However, Lewandowski et al. did not observed a synergistic effect of photocatalytic decomposition and strong acidity of sulfated TiO_2 because its acidity exceeds its photocatalytic activity [22]. Thus, it may suggest that a proper ratio of surface acidity and photocatalytic activity can obtain by optimized the ratio of SO_4^{2-} and PO_4^{3-}.

From the degradation of methylthionine chloride under different wavelength light irradiation as shown in Fig. 5(d), it is surprising to find that the modification using mixed acid of sulfuric acid and phosphoric acid not only increase the degradation under 254 nm light irradiation but also improve the degradation effect under 365 nm remarkably, which is closed to the degradation of TiO_2 under 254 nm light irradiation. Based on the diffuse reflectance spectra of catalysts, it is concluded that the improved absorbance intensity of SO_4^{2-}–PO_4^{3-}/TiO_2 is one of the reasons of outstanding photocatalytic performance.

4. Conclusion

In this paper, we have investigated the modification of PO_4^{3-} and SO_4^{2-}–PO_4^{3-} on TiO_2 by characterization of catalysts and the photocatalytic experiments using methylthionine chloride as model compound in aqueous. The modification of PO_4^{3-} and SO_4^{2-}–PO_4^{3-} improve the photocatalytic properties of TiO_2, especially SO_4^{2-}–PO_4^{3-}/TiO_2. The synergistic effect of photocatalytic decomposition and strong acidity of modified is only observed on the proper ratio of surface acidity and photocatalytic activity, which can be obtained by changed the ratio of SO_4^{2-} and PO_4^{3-} in maceration solution. In addition, the modifica-

tion of SO_4^{2-}–PO_4^{3-} also improves the UV–vis absorbance of SO_4^{2-}–PO_4^{3-}/TiO_2 and results in excellent the photocatalytic activity under 365 nm light irradiation.

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