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Investigation on degradation of azo fuchsine using visible light in the presence of heat-treated anatase TiO_2 powder

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Abstract

The phase transformation of TiO_2 powder from anatase phase to rutile phase was attempted by heat-treatment, and a new TiO_2 photocatalyst was obtained which could be excitated by visible light. The heat-treated TiO_2 powder at different transition stage was characterized by XRD, FT-IR and TEM methods. The test of photocatalytic activities of the heat-treated TiO_2 powders were carried out through the photocatalytic degradation of azo fuchsine dye in aqueous solution under the irradiation of visible light. The results indicate that the TiO_2 photocatalyst heat-treated at 400 °C within 60 min shows the highest photocatalytic activity which can effectively degrade the azo fuchsine under the irradiation of visible light. The remarkable improvement of photocatalytic activity of heat-treated TiO_2 powders at 400 °C was mainly illustrated by the special interphase formed between rutile and anatase phases which not only restrains the recombination of photogenerated electron–hole pairs, but also reduces the adsorbability of anatase TiO_2 powders at a certain extent. The degradation ratio of azo fuchsine in the presence of the heat-treated TiO_2 catalyst surpassed 84.36% at 3 h visible light irradiation, while the degradation ratios are only 44.2% and 64.84% for ordinary rutile and anatase TiO_2 catalysts, respectively, under the same experimental conditions. The total degradation process of azo fuchsine has been monitored by UV–vis spectra and ion chromatography. At last, the azo fuchsine molecules in aqueous solution are completely degraded and become some simple inorganic ions such as NO_3^- and SO_4^{2-}, etc. In this paper, the research on photocatalytic degradation kinetics was also performed and proved to be a first-order reaction.

Keywords: Heat-treated; Anatase TiO_2; Photocatalytic degradation; Visible light; Azo fuchsine

1. Introduction

Photocatalytic degradation of organic pollutants in water and air is attracting much attention for application to environmental problems [1,2]. Therefore, TiO_2 powder is currently believed to be the most promising known semiconductor material, due to its superior photoreactivity, nontoxicity, and long-term stability. In general, the photocatalytic activity of the TiO_2 powder depends on various parameters, including crystallinity, purity, surface area and density. Furthermore, the most significant factor is the crystal form of TiO_2 powder [3,4]. The TiO_2 powders generally exist in two crystal forms, namely, anatase and rutile phases. It is well known that the anatase TiO_2 powder is usually used as a photocatalyst to treat various wastewaters because of the high photocatalytic activity [5]. However, because of the broad energy gap ($E_g = +3.20–4.50$ eV), the anatase TiO_2 powder must absorb the ultraviolet light ($\lambda \leq 387$ nm) to bring photocatalytic activity into play more functionally. Although the rutile TiO_2 powder is provided with narrow energy gap ($E_g = +3.00–3.80$ eV), it is unfit for

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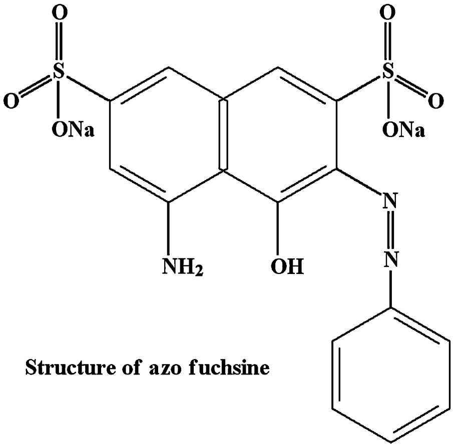
the photocatalytic degradation of organic pollutants. Two main reasons as follows can explain this phenomenon. On the one hand, the photogenerated electrons and holes produced on the surface or in the inner of rutile TiO_2 particles by irradiation of ultraviolet or visible light recombine very easily. On the other hand, the holes produced under the irradiation of visible light have no strong oxidation ability. Therefore, in order to improve the photocatalytic activity and to enhance the absorption ability for visible light, many reformative methods for anatase TiO_2 powder were adopted such as doping transition-metal ions [6,7], combination of other narrow band-gap semiconductor material [8,9] and aggradation of noble metals [10]. These methods make anatase TiO_2 powder to extend the range of absorption wavelength for irradiation light, indeed, whereas, they suffer from thermal instability, costly equipments, expensive raw materials and complicated treatment processes [11]. Some researchers have also studied the partial phase transformation through heat-treatment to enhance the photocatalytic activity of anatase TiO_2 powder [12–14]. It is known that the heat-treatment method not only causes the phase transformation of TiO_2 powder from anatase phase to rutile phase, but also produces the intermediate or transitional state between anatase and rutile phases [15]. Based upon these changes, the specific surface and active centers should appear [3]. However, the relationship between the crystal phase and photocatalytic activity is very complicated. How to control the proper heat-treated temperature and the extent of phase transformation for obtaining high photocatalytic activity is still a troubled project.

In this paper, the relationship between the phase transformation of the anatase TiO_2 powders and their photocatalytic activities was especially investigated. In contrast to the traditional ideas extending the range of absorption wavelength, with the purpose of converting their shortcomings into advantages and bringing their respective traits into play, an effective photocatalyst at special transition stage through heat-treating anatase TiO_2 powders was prepared. It was found, during the degradation of azo fuchsine as a model compound by visible light irradiation, that the highest photocatalytic activity of anatase TiO_2 powders emerged just when the rutile phase TiO_2 was on the point of appearance as a quasi-sovereign phase or yielded a small folium on the surface of primary anatase TiO_2 particles along with increasing heat-treated temperatures. The coupled rutile and anatase stage contributes to the enhancing effects of using visible lights. In addition, it was found that once the rutile phase TiO_2 appears as an absolute crystal form, the photocatalytic activity begins to decrease rapidly. Hague et al. have presented a model for illuminating the process of phase transformation and crystal growth of anatase TiO_2 [16]. In this paper, it is thought that the phase transformation is a slow process, which takes place at approximately 500 °C. This process can be controlled through enhancing the heat-treated temperature slowly and adjusting the heat-treated time exactly. During heat-treatment, the crystal interphase between anatase and rutile phases forms originally, and then the rutile phase appears independently and grows gradually. The intermediate product or transitional state formed initially on the surface of primary anatase TiO_2 particles are of significance for this experimental research. Such heat-treated TiO_2 powders can be excited by visible light and then the photogenerated electrons further transfer from rutile phase to anatase phase, thus the recombination chance of photogenerated electron–hole pairs reduces greatly. Additionally, it is well known that the proper adsorption, to a certain extent, is of advantage to the photocatalytic degradation of organic pollutants, while the excessive adsorption usually prohibits the TiO_2 particles from absorbing both ultraviolet and visible lights, which makes the part surface of the TiO_2 photocatalyst probably become unavailable for photon absorption, thus bringing little stimulation to the catalytic reaction. Anyhow, the existence of coupled rutile–anatase phase on the surface of the anatase TiO_2 particles can not only extend the range of absorption wavelength but also properly reduce the adsorbability of the anatase TiO_2 particles. Therefore, through controlling the heat-treated temperature and heat-treated time appropriately, the TiO_2 photocatalyst which can be excited by visible light and also which possesses appropriate adsorbability can easily be obtained.



Structure of azo fuchsine

2. Experimental section

2.1. Heat-treatment of anatase TiO_2 powders

A series of anatase TiO_2 powders (purchased from Aldrich Company, USA) were heated in muffle furnace at different temperatures (300–800 °C) for 60 min. Another series of anatase TiO_2 powders were heated at different time (20–100 min) at 400 °C in muffle furnace. All the heat-treated anatase TiO_2 powders were cooled to room temperature naturally and then the characterization and photocatalytic activities were carried out.

2.2. Characterization of heat-treated TiO_2 powders

The XRD patterns were determined by powder X-ray diffraction measurements (XRD-Rigaku, RINT 2500, Japan) using Ni-filtered Cu Kα radiation in the range of 2θ from 10° to 70° for confirming the change of crystal phases of heat-treated

TiO_2 powders. The TEM observations were carried out using a transmission electron microscope (JEOL, JEM-3010, Japan) for observing the sizes of heat-treated TiO_2 particles. Otherwise, the infrared absorptions were studied adopting FT-IR spectrometer (Perkin–Elmer 2000, USA) for judging the phase transformation of anatase TiO_2 particles and the formation of rutile phase TiO_2. The samples were mixed with potassium bromide (KBr) and the content of the samples were kept around 1.0%.

2.3. Photocatalytic activities of heat-treated TiO_2 powders

The experiments of the photocatalytic degradation of azo fuchsine were carried out for affirming the photocatalytic activities of heat-treated TiO_2 powders. The experimental conditions such as 10 mg/L azo fuchsine concentration, 1000 mg/L TiO_2 addition amount, 50 mL total volume, 144 W irradiation power and 20.0 ± 0.2 °C systematic temperature were kept throughout this work. The heat-treated TiO_2 powder was first mixed into azo fuchsine solution well and the equilibrated suspension was obtained by adequate agitation, and then placed in the dark for 30 min. After the balance of adsorption and desorption, the suspension was irradiated by four triphosphor lamps (FL40T8EXD/36, Toshiba Company, Japan; color temperature 4000 K and light intensity 964,347 lux). The triphosphor blend is a combination of three narrow-band rare phosphors that reproduce three primary colors of the spectra, each with a very narrow bandwidth, so there is no ultraviolet region involved. The suspensions at specific intervals were sampled to monitor the changes of the leftover azo fuchsine concentration. The sampled suspensions were centrifuged at 4000 rpm for 20 min to remove the TiO_2 powder and then analyzed by UV–vis spectrophotometer. Ion chromatography (ICS-90, USA) was used to observe the mineralized anion produced during degradation process in the solution.

3. Results and discussions

3.1. XRD and TEM of heat-treated TiO_2 powders

Fig. 1 shows that the changes of the XRD patterns of the anatase TiO_2 powders take place along with increasing heat-treated temperature from 300 °C to 800 °C. It is found that the diffraction peak at 27.5° (2θ) as the characteristic peak of rutile phase TiO_2 begins to appear when the heat-treated temperature reaches to 500 °C, which indicates the formation of rutile phase on the surface or in the inner of anatase TiO_2 particles. The characteristic diffraction peak of rutile phase at 27.5° becomes higher and higher with increasing heat-treated temperatures. Finally, all diffraction peaks of anatase TiO_2 powders disappear almost at 800 °C, while all characteristic diffraction peaks of rutile phase appear synchronously, which represents that all unstable anatase phase have already become stable rutile phase. In addition, it can be seen that the diffraction peaks of anatase TiO_2 powders become thinner and thinner as increasing the heat-treated temperature. It indicates that the increasing granularity of anatase TiO_2 powders may be the fundamental point of phase transformation from anatase phase to rutile phase under heat-treatment.

The TEM image proved the inference mentioned above. Fig. 2 shows that the granularity of anatase TiO_2 particles before heat-treatment spread at range of 100 nm (as shown in Fig. 2a), but it is 150–160 nm and slightly become larger than primary anatase TiO_2 particles after heat-treatment (as shown in Fig. 2b). In general, the 400 °C heat-treated

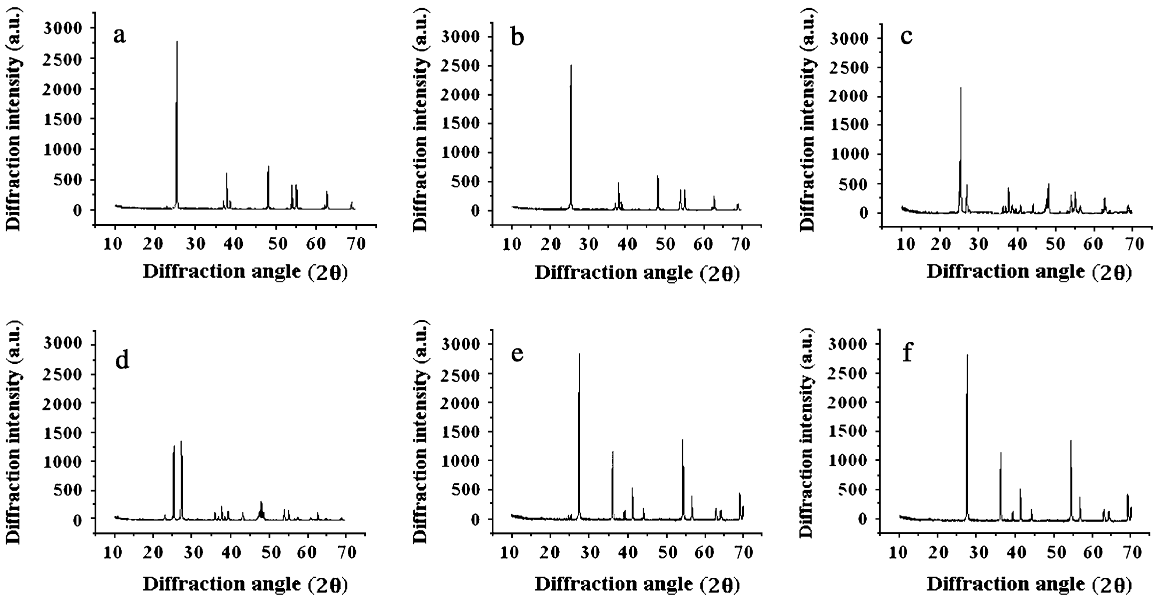
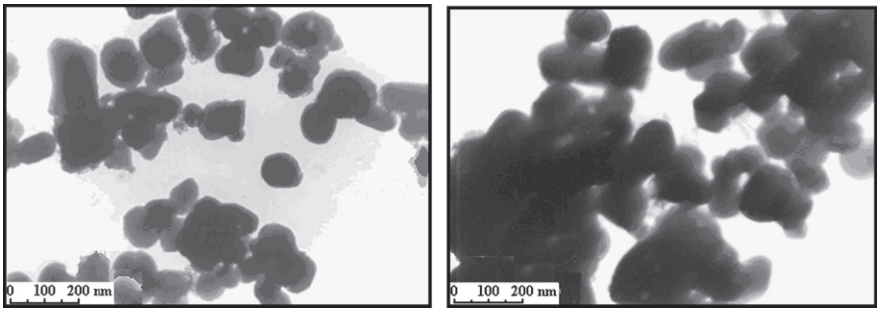


Fig. 1. XRD of TiO_2 powders at different heat-treated temperatures (60 min). a: 300 °C; b: 400 °C; c: 500 °C; d: 600 °C; e: 700 °C; f: 800 °C.



a: before heat-treatment (original anatase TiO_2 powder) b: after heat-treatment (400 °C and 60 min)

Fig. 2. TEM of TiO_2 powders before and after heat-treatment.

temperature is unable to result in the obvious aggregation of anatase TiO_2 particles. Hence, the changes of the surface or inner of anatase TiO_2 particles must be the reason that the anatase TiO_2 particles bulge.

3.2. FT-IR spectra of heat-treated TiO_2 powders

FT-IR analyses were conducted to study the surface changes of anatase TiO_2 particles at different heat-treated temperatures as shown in Fig. 3. In general, the anatase TiO_2 powder gives only one absorption peak (curve c) at around 500 cm^{-1} between 450 cm^{-1} and 750 cm^{-1} in FT-IR spectra, while the rutile TiO_2 powder gives two absorption peaks (curve b) at 510 cm^{-1} and 640 cm^{-1}, respectively. And they are all ascribed to the stretching vibrations of Ti–O bond [15]. In fact, these absorption peaks are regarded to be the characters identifying anatase and rutile TiO_2 powders. According to the changes of absorption peaks of anatase TiO_2 powder, the process of phase transformation of TiO_2 particles from anatase phase to rutile phase can be found clearly. As the heat-treated temperature reaches to 400 °C, one broad absorption band (curve a) appears at 500–650 cm^{-1}, which indicates the formation of partial rutile phase on the surface of anatase TiO_2 particles. Along with continuously raising heat-treated temperatures, more and more anatase phase transform to rutile phase. It suggests that all anatase TiO_2 particles have already become rutile TiO_2 particles at this time.

In addition, for anatase and rutile TiO_2 powders, the FT-IR spectra show two broad absorption bands (curves b and c) around 3450 cm^{-1} and 1630 cm^{-1}. It has been reported that the water molecules adsorbed on the surface of TiO_2 particles reveal such absorption bands [17]. However, the spectrum of heat-treated (400 °C and 60 min) TiO_2 powder gives the red-shifted broad absorption band around 3400 cm^{-1} and spiculate absorption peak at 1650 cm^{-1} (curve a) compared with above two cases. In fact, these new absorption band and peak of the heat-treated (400 °C and 60 min) TiO_2 powder belong to the vibration absorption of hydroxyl groups of Ti–OH bonds on the surface of the TiO_2 particles. Perhaps, this is one possible reason why the heat-treated TiO_2 powder at 400 °C has high photocatalytic activity under irradiation of visible light referred subsequently [18].

3.3. Photocatalytic activities of heat-treated TiO_2 powders

The photocatalytic activities of a series of heat-treated TiO_2 powders at different heat-treated temperatures are shown in Fig. 4. As mentioned above, the rutile phase appears when the heat-treated temperature reaches to 500 °C according to the XRD determination, and then the content of rutile TiO_2 increases gradually as with increasing heat-treated temperature. However, it was found, under the irradiation of visible light, in the presence of the heat-treated TiO_2 powder at 400 °C within 60 min, the best degradation ratio of azo fuchsine in aqueous solution could be obtained. Only when the rutile phase is about to appear or a small folium forms on the surface of anatase TiO_2 particles between 400 °C and 500 °C, the photocatalytic activities of heat-treated TiO_2 powder are the highest in all heat-treated temperature range. After 500 °C, the photocatalytic activities of heat-treated TiO_2 powders fleetly decline along with increasing heat-treated temperatures. Perhaps, these phenomena should be explained through the effects of the special combination of anatase and rutile phases. In general, the anatase TiO_2 powders must exclusively absorb the ultraviolet light, and then the photocatalytic degradation of

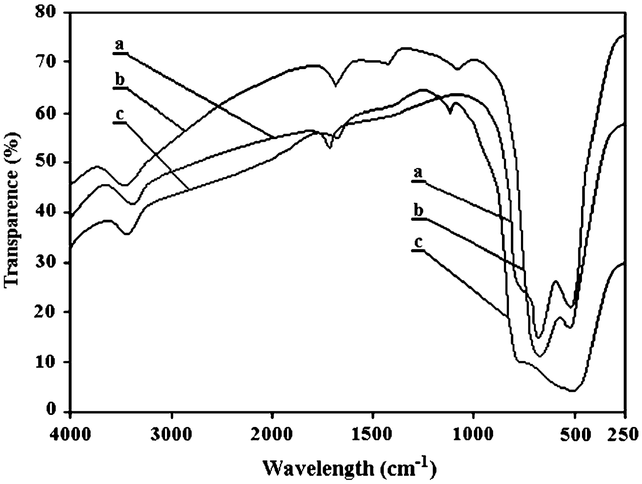


Fig. 3. FT-IR of different TiO_2 powders. a: Heat-treated TiO_2 (400 °C and 60 min); b: rutile TiO_2; c: anatase TiO_2.

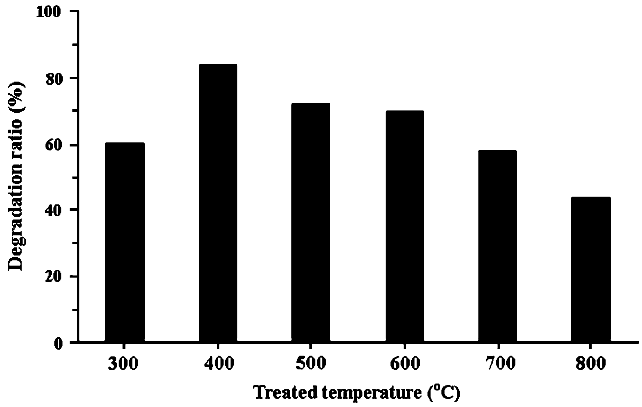


Fig. 4. Photocatalytic activities of heat-treated TiO_2 at different heat-treated temperatures (60 min) during the degradation of azo fuchsine (3 h irradiation).

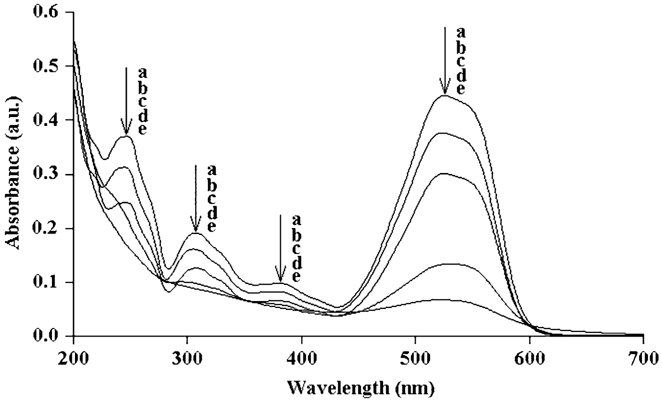


Fig. 6. UV–vis spectra of azo fuchsine solutions under different conditions. a: Original solution; b: heat-treated TiO_2 (without irradiation); c: rutile TiO_2 (with irradiation); d: anatase TiO_2 (with irradiation); e: heat-treated TiO_2 (with irradiation).

organic pollutants could occur. The rutile TiO_2 powders hardly show the photocatalytic activities, because the electrons and holes photogenerated by the irradiation of ultraviolet or visible light are easily recombined. Hence, when the heat-treated temperature is lower than 400 °C, just like the pure anatase TiO_2 powders, such heat-treated TiO_2 powders do not have high photocatalytic activities under the irradiation of visible light. Whereas, when the heat-treated temperature is higher than 500 °C, large numbers of rutile TiO_2 particles present as a self-existent phase so that such heat-treated TiO_2 powders also cannot have high photocatalytic activities either. In addition, for the large rutile TiO_2 particles resulted from heat-treatment, the photogenerated electrons mainly enter the interior of rutile phase TiO_2 particles and instantly produce the Ti^{3+} ions. Subsequently, these Ti^{3+} ions react with the photogenerated holes, which thus must bring side-effect in the photocatalytic reaction [19].

For this sensitive heat-treated temperature (400 °C), that is, the critical temperature of the phase transformation from anatase phase to rutile phase, the content of rutile phase also depends on the heat-treated time. In general, the longer the heat-treated time, the more is the content of rutile phase TiO_2 on the surface of the anatase TiO_2 particles becomes for this critical temperature. Hence, the photocatalytic activities of heat-treated TiO_2 powders also relate to the heat-treated time. Fig. 5 shows the effects of heat-treated time on the degradation ratio of azo fuchsine in the presence of heat-treated (400 °C) TiO_2 powder. It indicates that the best degradation is obtained when the heat-treated time is 60 min, and that both short and long heat-treated time cannot bring better photocatalytic effect.

In addition, Fig. 6 obviously shows the comparison of photocatalytic activities of different crystal phase TiO_2 powders. The absorption peaks (curve b) of azo fuchsine in aqueous solution in the presence of heat-treated (400 °C and 60 min) TiO_2 powder without irradiation of any light after 3 h slightly decrease when compared with original solution (curve a), which indicates that the azo fuchsine molecules were scarcely decomposed except for slight adsorption. The anatase TiO_2 and rutile TiO_2 powders both represent the photocatalytic activities to a certain extent for the degradation of azo fuchsine under the irradiation of visible light. The degradation effects of azo fuchsine in the presence of anatase and rutile TiO_2 powders can be estimated from the changes of absorption

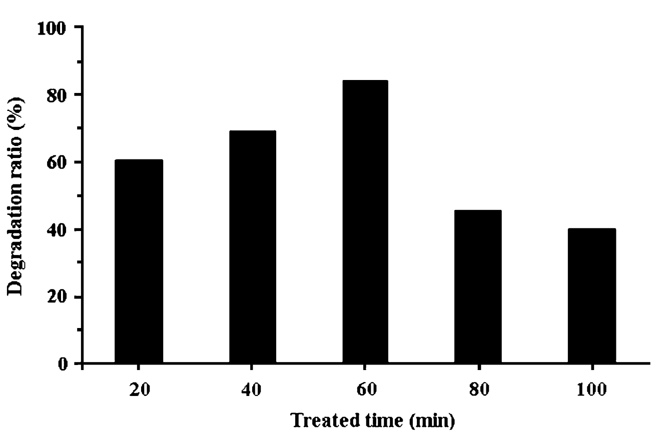


Fig. 5. Photocatalytic activities of heat-treated TiO_2 at different heat-treated time (400 °C) during the degradation of azo fuchsine (3 h irradiation).

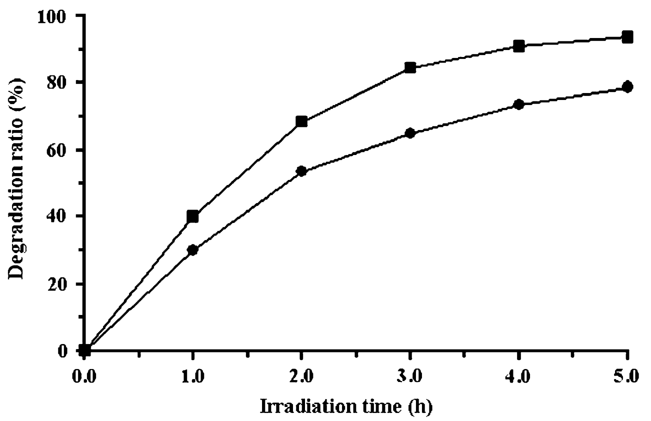


Fig. 7. Influence of irradiation time on degradation ratio of azo fuchsine. ■: Irradiation + heat-treated (400 °C and 60 min) TiO_2; ●: irradiation + anatase TiO_2.

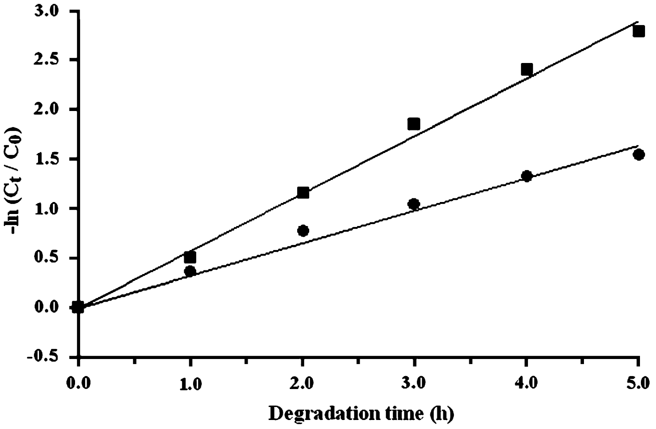


Fig. 8. Reaction kinetics on the photocatalytic degradation of azo fuchsine. ■: Irradiation + heat-treated (400 °C and 60 min) TiO_2; ●: irradiation + anatase TiO_2.

peaks (curves c and d). Comparatively, the heat-treated (400 °C and 60 min) TiO_2 powder exhibits the obvious photocatalytic activities for the degradation of azo fuchsine under the irradiation of visible light. At the same irradiation time, the degradation ratio of azo fuchsine is close to 86.84%, while about 70.1% and 32.47%, respectively, correspond to the anatase and rutile TiO_2 powders. Moreover, in any case the order of photocatalytic activities is rutile $TiO_2 <$ anatase $TiO_2 <$ heat-treated TiO_2 (400 °C and 60 min). Evidently, the photocatalytic activities of heat-treated TiO_2 powders largely depend on the heat-treated temperature and heat-treated time, and this phenomenon may be explained through the effects of the special interphase between rutile and anatase phases.

3.4. The influences of irradiation time on the degradation ratio of azo fuchsine

Fig. 7 shows the comparison of photocatalytic degradation ratios of azo fuchsine in aqueous solution in the presence of heat-treated (400 °C and 60 min) and anatase TiO_2 powders under the visible light irradiation at different moments. In this study, the initial concentration of azo fuchsine and addition amount of TiO_2 catalyst are 10 mg/L and 1000 mg/L, respectively. It can be seen that the photocatalytic activity of heat-treated (400 °C and 60 min) TiO_2 powder is obviously better than that of anatase TiO_2 powder. The degradation ratio in the presence of heat-treated (400 °C and 60 min) TiO_2 powder increases fleetly along with the irradiation time and attains about 84.36% within 3 h irradiation, while the degradation ratio in the presence of anatase TiO_2 powder is only 64.84% at the same irradiation time. Finally, the azo fuchsine in aqueous solution is decomposed completely within 5 h, while within 13 h in the presence of anatase TiO_2 powder.

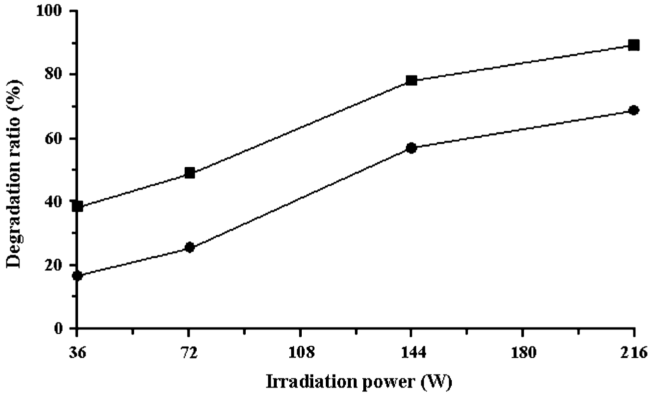


Fig. 9. Influence of power of lamp on the degradation ratio of azo fuchsine. ■: Irradiation + heat-treated (400 °C and 60 min) TiO_2; ●: irradiation + anatase TiO_2.

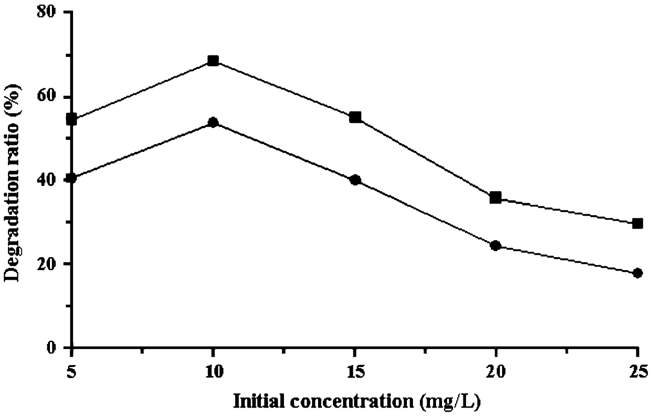


Fig. 10. Influence of initial concentration on the degradation ratio of azo fuchsine. ■: Irradiation + heat-treated (400 °C and 60 min) TiO_2; ●: irradiation + anatase TiO_2.

In addition, Fig. 8 indicates that the photocatalytic degradation reactions of azo fuchsine in the presence of heat-treated (400 °C and 60 min) and anatase TiO_2 powders both accord with the first-order kinetics. The rate constant (0.582 h^{-1}) for heat-treated (400 °C and 60 min) TiO_2 powder is head and shoulders above that (0.3295 h^{-1}) for anatase TiO_2 powder.

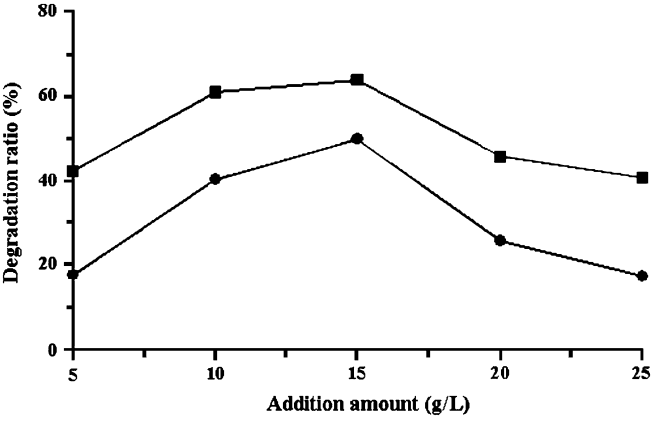


Fig. 11. Influence of addition amount on the degradation ratio of azo fuchsine. ■: Irradiation + heat-treated (400 °C and 60 min) TiO_2; ●: irradiation + anatase TiO_2.

3.5. The influences of power of irradiation lamps on the degradation ratio of azo fuchsine

As shown in Fig. 9, the power of irradiation lamps can bring the considerable influence on the photocatalytic degradation ratio of azo fuchsine. The effect of power on the photocatalytic degradation of azo fuchsine in aqueous solution (10 mg/L) within 100 min was studied by varying the power of irradiation lamps ranging from 36 W to 216 W, and the addition amount of heat-treated (400 °C and 60 min) TiO_2 catalyst is 1000 mg/L. It can be seen from Fig. 9 that within 100 min, along with the increase in the power of irradiation lamps, the degeneration rate is distinctly enhanced. Apparently, the bigger the power of irradiation lamps, the stronger is the light intensity, and therefore, the degeneration ratio is higher.

3.6. The influences of initial concentration of azo fuchsine on the degradation ratio

Since the pollutant concentration is an important parameter in water treatment, the effect of initial concentration of azo fuchsine on the photocatalytic degradation ratio was investigated over the concentration range of 5.0–25.0 mg/L. It can be seen from Fig. 10 that within 2 h, as with the increase of azo fuchsine's initial concentration, the degradation ratio first ascends until up to the maximum whose corresponding concentration is about 10 mg/L, and then declines with the unceasingly increase of initial concentration. This is just the ordinary law of photocatalytic degradation reaction using TiO_2 powder as photocatalyst. The increase of initial concentration weakens the transmission ability of various lights for the solution, and also decreases the light intensity that arrives at the surface of heat-treated (400 °C and 60 min) TiO_2 catalyst. In this case, the heat-treated (400 °C and 60 min) TiO_2 powder in solution cannot operate adequately, which is just the reason why the degradation ratio declines for high concentration of dye wastewater. Therefore, a proper initial concentration should be chosen in order to get an ideal degradation ratio.

3.7. The influences of addition amount of TiO_2 catalyst on the degradation ratio of azo fuchsine

The effect of addition amount of heat-treated (400 °C and 60 min) TiO_2 catalyst on the photocatalytic degradation of azo fuchsine in aqueous solution (10 mg/L) was studied by varying the addition amount from 5.0 to 25.0 g/L. Fig. 11 shows the changes of degradation ratios along with the addition amount of various TiO_2 catalysts under visible light irradiation for 100 min. It can be seen that the addition amount of TiO_2 catalyst has a significant effect on the degradation ratio. At the beginning the increasing addition amount of heat-treated (400 °C and 60 min) TiO_2 catalyst can enhance the degradation ratio. After the addition amount of 10.0 g/L the degradation ratio begins to decline slightly with the increase of TiO_2 catalyst. It indicates that an optimized addition amount of TiO_2 catalysts is necessary for obtaining high degradation ratio. The redundant TiO_2 particles in azo fuchsine solution mutually defilade one another, which weakens their own photocatalytic ability.

3.8. The ion chromatograms of the azo fuchsine

The ion chromatograms of the azo fuchsine solution during degradation are shown in Fig. 12. They clearly prove that the sulphur and nitrogen heteroatoms in the azo fuchsine molecule are converted into the simple inorganic SO_4^{2-}, NO_3^- and NO_2^- anions dissolved in aqueous solution. However, the peaks of NO_3^- and NO_2^- anions seem to be much lower compared with the theoretic content of nitrogen in azo fuchsine molecule. Two reasons can be used to explain this phenomenon. Firstly, during the photocatalytic degradation, at the beginning the azo bond of azo fuchsine molecule is decomposed and then reduced to some NH_4^+ cations which do not appear in the ion chromatograms. Secondly, as the azo fuchsine in aqueous solution is gradually degraded, a series of nitrogen oxides (NO_x) and nitrogen gas (N_2) are also produced. Some volatile nitrogen oxides and nitrogen gas escape from the reaction system, which results in the low peak of the NO_3^- and NO_2^- anions [20].

3.9. Possible principle on exciting heat-treated TiO_2 photocatalyst

A smaller folium of rutile phase TiO_2 appeared on the surface of primary anatase TiO_2 particles can absorb the visible light as shown in Fig. 13, and then be excitated firstly because of the narrow energy gap. The photogenerated electrons' transfer from valence-band to conduction-band of thin rutile phase

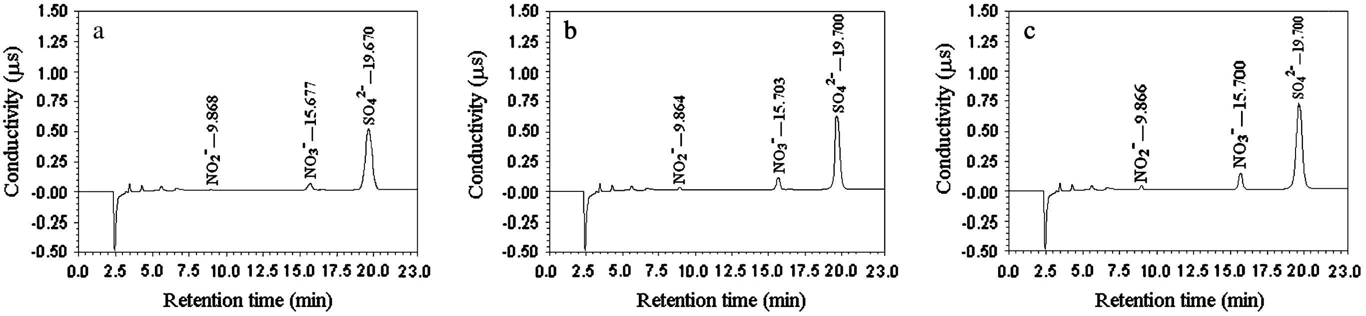


Fig. 12. Ion chromatography of azo fuchsine at different irradiation time. a: 1 h; b: 3 h; c: 5 h.

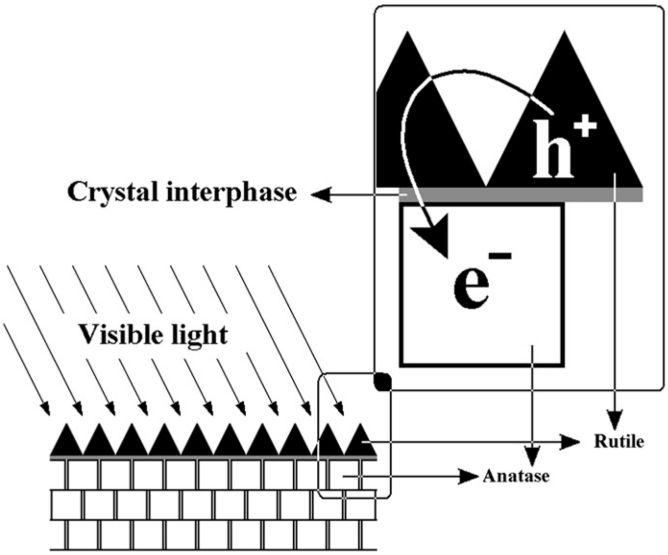


Fig. 13. Possible principle of exciting heat-treated TiO_2 (400 °C and 60 min).

TiO_2 folium and thus the electron–hole (e− and h+) pairs are yielded at the same time. Afterwards, the photogenerated electrons are continuously excited by visible light and further transferred to the conduction-band of anatase TiO_2 particles. In fact, this process can result in the separation of electrons and holes, and thus effectively avoids their recombination as shown in Fig. 14.

Necessarily speaking, the anticipatory rutile phase folium must form on the surface of anatase TiO_2 particles. If it locates in the inner of TiO_2 particles, heat-treated TiO_2 would not show the photocatalytic effects under visible light irradiation. This rutile phase folium is too thin to admit over many photogenerated electrons, so that these photogenerated electrons have to enter the anatase TiO_2 particles, that is, transit to the conduction-band of anatase TiO_2 particle, under the visible light irradiation. Once the thick rutile TiO_2 layer as self-existent phase forms, which can admit abundant photogenerated electrons, it must restrict the transfer of electrons to anatase TiO_2 particles. Consequently, these photogenerated electrons easily recombine with photogenerated holes.

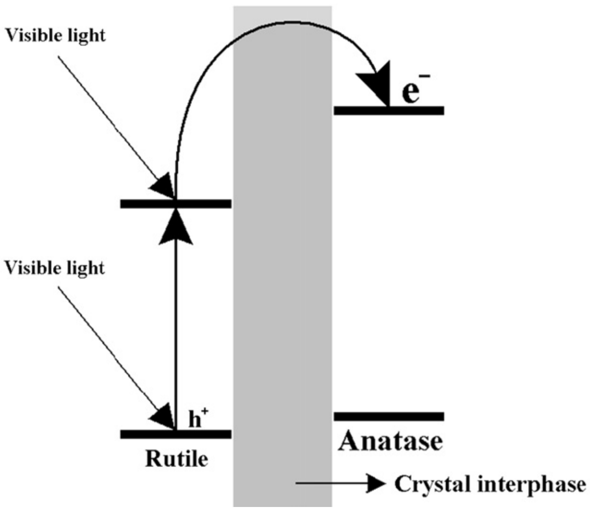


Fig. 14. Possible process of electron transfer in heat-treated TiO_2 (400 °C and 60 min).

4. Conclusions

The rutile–anatase coupled TiO_2 powders resulting from phase transformation have been prepared by changing the heat-treated temperature and heat-treated time. The results demonstrated that such combination between rutile and anatase phases could improve the photocatalytic activity of the anatase TiO_2 powders. That is, the photocatalyst with high photocatalytic activity utilizing the visible light has been obtained by controlling the coupled state of rutile-anatase phase. More importantly, the anticipatory interlaced energy level is convenient for capturing photons of low energy, and thus achieves the intention of using the visible light. The azo fuchsine in aqueous solution can be markedly decomposed by the photocatalytic reaction in the presence of the heat-treated TiO_2 catalysts. The photocatalytic performance of the heat-treated anatase TiO_2 powder is obviously better than those of the original anatase and rutile TiO_2 powders. Otherwise, the degradation of azo fuchsine is shown to depend on the addition amount of heat-treated TiO_2 catalyst, initial concentration of azo fuchsine solution, and irradiation power. Above all, the method of heat-treatment has many characteristics such as convenience, safety, credibility and high efficiency, so it is promising that this method is extended and applied in the treatment of wastewaters on the basis of more research work.

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