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# Transformation of Crystal Phase of Micron-sized Rutile $TiO_2$ and Investigation on its Sonocatalytic Activity

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**Abstract** The partial transformation of crystal phase of micron-sized $TiO_2$ powder from rutile to anatase was realized utilizing microwave irradiation in hydrogen peroxide solution. Afterwards, the ultrasound of low power was used as an irradiation source to induce the transition crystal $TiO_2$ powder to perform the sonocatalytic activity through the degradation of azo fuchsine in aqueous solution. The results show that the sonocatalytic activity of the transition crystal $TiO_2$ powder is obviously higher than that of pure micron-sized rutile and anatase $TiO_2$ powders. The degradation ratio of azo fuchsine in the presence of the transition crystal $TiO_2$ powder attains nearly 80% within 80 min ultrasonic irradiation.

**Keywords** Transition crystal $TiO_2$ powder · Microwave · Sonocatalytic activity · Azo fuchsine

## 1 Introduction

In recent years, a great deal of effort has been devoted to develop heterogeneous catalysts with high catalytic activities for solving environmental problems [1–3]. The $TiO_2$ powder has been believed to be the most promising semiconductor material for long time, due to its superior photoreactivity, nontoxicity and long-term stability. It is well known that 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 phase of $TiO_2$ powder [4, 5]. In general, the photocatalytic activity of anatase phase $TiO_2$ powder is better than that of rutile phase $TiO_2$ powder [6]. In addition, a recent study showed that a mixture of both micron-sized anatase and rutile $TiO_2$ powder exhibited higher photocatalytic activity as well as effective degradation ability compared with pure anatase or rutile $TiO_2$ powder [7]. However, the photocatalytic degradation must need ultraviolet light to induce $TiO_2$ powder, which costs lots of electric energy. Moreover, in any case, this method is not suitable for the treatment of non- or low-transparent organic wastewaters. In fact, it can avoid these disadvantages to utilize ultrasonic irradiation. The penetrating ability of ultrasound is very strong for any water medium and its penetrating depth can ordinarily attain to 20–30 cm [8]. Besides, the ultrasound can usually be competent for catalyzing those chemical reactions as the ultraviolet and visible lights catalyzing [9, 10]. Hence, the ultrasound has been used as irradiation source instead of ultraviolet and visible lights and many studies on the sonocatalytic degradation of various organic pollutants in the presence of $TiO_2$ powder have been reported recently [11–14].

Be similar to the photocatalytic degradation, the sonocatalytic activity of $TiO_2$ powder also needs to be improved for high degradation efficiency. In this paper, the transformation of crystal phase of micron-sized rutile $TiO_2$ powder was performed by microwave hydrothermal method in hydrogen peroxide solution and the high sonocatalytic activity of transition crystal $TiO_2$ powder was probed [15, 16]. Fortunately, a novel and simple method for preparing transition crystal $TiO_2$ powder with high

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sonocatalytic activity has been realized in this paper. The experimental results show that such treated $TiO_2$ powder behaves high catalytic activity during the sonocatalytic degradation of some pesticides [17]. In this work, we choose the azo fuchsine to investigate the sonocatalytic activity of this transition crystal $TiO_2$. The molecular structure of azo fuchsine is shown in Scheme 1.

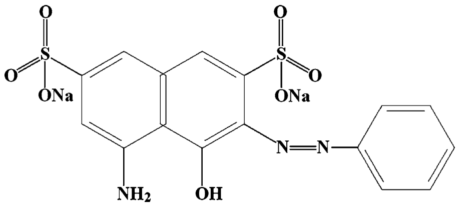
## 2 Experimental Section

### 2.1 Materials and Apparatus

Micron-sized $TiO_2$ powder (rutile and anatase, Harbin Chemistry Reagent Company, China); Hydrogen peroxide solution (AR, 30% content, Beijing Chemistry Reagent Corporation, China); Azo fuchsine (AR, Shanghai Xinzhong Chemistry Reagent Corporation, China). Muffle furnace (SX2-4-10, Great Wall Furnace Company, China); Micro-wave oven (WD750B, 2450 MHz, 800 W, Galanz Company, China); Controllable Serial-Ultrasonics apparatus (KQ-100, 40 kHz, 50 W, Kunshan Apparatus Company, China); X-ray diffractometer (Rint-2700, Rigaku Company, Japan); UV-vis spectrometer (LAMBDA-17, Perkin–Elmer Company, USA); Ion chromatogram (ICS-90, DIONEX Company, USA).

### 2.2 Preparation of Transition Crystal $TiO_2$ Sonocatalyst

The micron-sized rutile $TiO_2$ powder was used as the titanium source and the preparation of transition crystal $TiO_2$ powder was carried out as follows. First, the micron-sized rutile $TiO_2$ powder (2.0 g) and 30% hydrogen peroxide solution (20 mL) were put into a reaction kettle, and then this mixed solution was adjusted to pH = 5.0 and treated under microwave irradiation for 5.0 min. The produced pale yellow slurry was filtrated and washed three times using purified water. Afterwards, these precipitates were dried at 100 °C for 60 min in oven in order to vaporize water and ground adequately to a fine powder to obtain dried samples. Last, the dried samples were heated in muffle furnace maintained at 673 K for 30 min to obtain the new transition crystal $TiO_2$ catalysts.



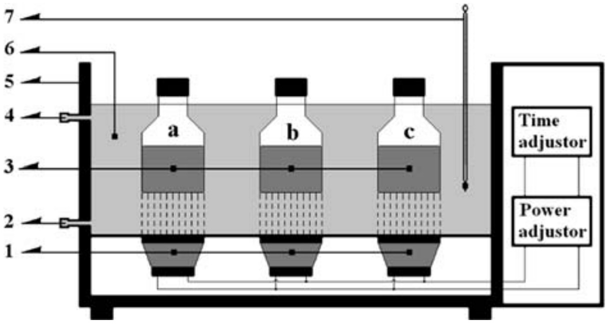
**Scheme 1** The structure of azo fuchsine molecule

### 2.3 Characterization of Transition Crystal $TiO_2$ Powder

In order to confirm the appearance of the anatase phase $TiO_2$, the X-ray diffraction (XRD) patterns of the transition crystal $TiO_2$ and original micron-sized rutile $TiO_2$ powders were determined. The particle size ($\alpha$) is approximately counted by the Scherrer equation: $\alpha = 0.89\lambda/B_{1/2}\cos\theta$ ($\lambda$: wavelength of incident X-ray; $B_{1/2}$ = width of half high peak; $\theta$ = diffraction angle). The proportion ($\beta$) of the rutile and anatase phase in the transition crystal $TiO_2$ powder was obtained according to the quantitative equation [18]: $\beta_R = [1 + 0.8(I_A/I_R)]^{-1}$ and $\beta_A = [1 + 1.26(I_R/I_A)]^{-1}$ ($I_A$: diffraction intensity of anatase phase; $I_R$: diffraction intensity of rutile phase).

### 2.4 Measurement of Sonocatalytic Degradation Activity of the Transition Crystal $TiO_2$ Powder

About 100 mL azo fuchsine solution and 100 mg transition crystal $TiO_2$ powder were put into a conical flask, and the mixed solution was stirred for 60 min without any irradiation for attaining the balance of absorption and desorption. Afterwards, small amount of mixed solution was taken out and centrifuged. The supernatant fluid was used for determining UV-vis spectra. It was found to be unchanged almost compared with that of original azo fuchsine solution. After that, the conical flask was placed inside an ultrasonic apparatus as irradiation source as shown in Scheme 2, and then, at regular intervals the mixed solution was sampled for tracking the degradation of azo fuchsine until to 120 min. In this work, the ultrasound of 50 W output power and 40 kHz frequency have been used. For comparison, the sonocatalytic activities of original micron-sized rutile and anatase



**Scheme 2** Illustration of experimental apparatus. (1) ultrasonic transducer, (2) water entrance, (3) reactor, (4) water exit, (5) flume, (6) water, (7) thermometer. (a) with transition crystal $TiO_2$, (b) with rutile $TiO_2$, (c) without any $TiO_2$

$TiO_2$ powders were also measured following the same procedure. The changes of degradation ratios in the presence of transition crystal and original micron-sized rutile $TiO_2$ and in the absence of any $TiO_2$ catalyst along with irradiation time were also reviewed. The solution temperature was controlled within 25.0 ± 0.2 °C throughout. The UV-vis spectra of the azo fuchsine solutions during degradation were determined in the wavelength ranging from 200 to 700 nm. The maximal absorbency (at 524 nm) of azo fuchsine solution below 20 mg/L concentration abides by Lambert–Beers's law and the standard calibration curve is used to estimate the degradation ratio of azo fuchsine. Hence, the conditions such as 50 mL total volume, 20 mg/L azo fuchsine concentration, 1,000 mg/L $TiO_2$ addition amount and 80 min ultrasonic irradiation were adopted without special statement.

In order to check up the mineralized degree of azo fuchsine, the ion chromatography analyses were performed. The degradation products of azo fuchsine contain plentiful nitrogen and sulphur atoms, so the formation of $NO_2^-$, $NO_3^-$ and $SO_4^{2-}$ anions can express the degradation of azo fuchsine.

In addition, the various influencing factors on the sonocatalytic activity of transition crystal $TiO_2$ powder, such as microwave irradiation time, heat-treated temperature, heat-treated time and treated solution acidity, were also reviewed.

## 3 Results and Discussions

### 3.1 XRD of Transition Crystal $TiO_2$ Powder

Figure 1 represents the XRD patterns of the treated and original micron-sized rutile $TiO_2$ powders, respectively. It is obviously observed that some new diffraction peaks belonging to anatase phase appear, which indicates that a small quantity of rutile phase $TiO_2$ have transformed to anatase phase $TiO_2$ on the surface of micron-sized rutile $TiO_2$ particles. As shown Table 1, the content of anatase phase in transition crystal $TiO_2$ powder is about 6.9%, which approximately corresponds to 1.649 nm anatase phase folium on the surface of micron-sized rutile $TiO_2$ particles.

### 3.2 Sonocatalytic Activities of Transition Crystal $TiO_2$ Powder

Figure 2 shows the UV-vis spectra of azo fuchsine solution under different conditions. In general, the azo fuchsine solution gives four absorption peaks at 250, 305, 375 and 525 nm, respectively, within the range of 200–700 nm corresponding to the benzene ring and azo bond in azo fuchsine molecule with adjusting any pH values.

It is found that, compared with the original azo fuchsine solution, under ultrasonic irradiation in the presence of micron-sized antase, rutile and transition crystal $TiO_2$ powders as well as in the absence of any $TiO_2$ catalyst, all absorption peaks decline more or less, which indicate that the benzene ring and azo bond in azo fuchsine molecule are partly destroyed simultaneously. Nevertheless, the results

**Table 1** The change of micron-sized rutile $TiO_2$ powder after treating

| Sample | Rutile particle (diameter/nm) | Anatase phase (thickness/nm) | Proportion of rutile and anatase |
|---|---|---|---|
| Transition crystal $TiO_2$ | 130–150 | 1.649 | 93.1% (rutile), 6.9% (anatase) |
| Original micron-sized rutile $TiO_2$ | 100–110 | 0 | 100% (rutile), 0% (anatase) |

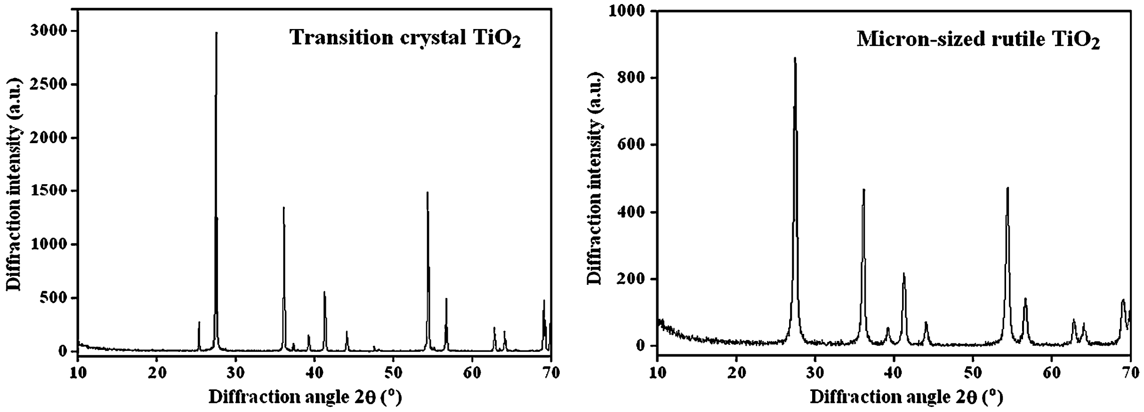


**Fig. 1** XRD patterns of transition crystal and micron-sized rutile TiO2 powders

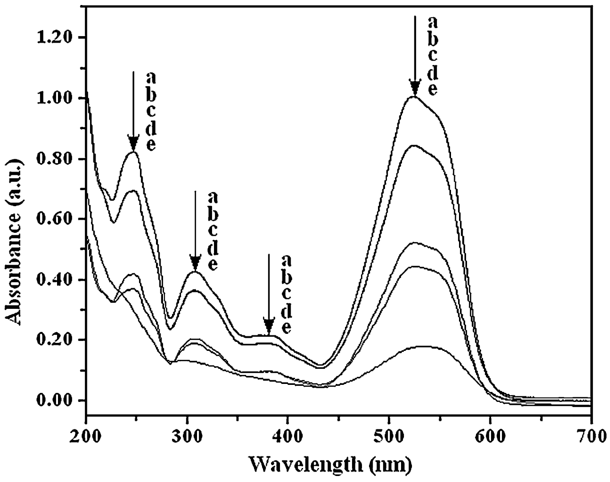


**Fig. 2** UV-vis spectra of azo fuchsine solutions under different conditions. (a) Original solution; (b) Only ultrasound (120 min); (c) Ultrasound + micron-sized antase $TiO_2$ (120 min); (d) Ultrasound + micron-sized rutile $TiO_2$ (120 min); (e) Ultrasound + transition crystal $TiO_2$ (120 min)

show that the sonocatalytic degradation effects are obviously higher than that of only ultrasonic degradation. Whereas, for three cases, the highest sonocatalytic activity is obtained in the presence of transition crystal $TiO_2$ powder and the activity order is as follows: transition crystal $TiO_2$ > micron-sized rutile $TiO_2$ > micron-sized anatase $TiO_2$. These results proved that the partial phase transformation from rutile to anatase indeed could improve the sonocatalytic activity of micron-sized rutile $TiO_2$ powder.

### 3.3 Influence of Ultrasonic Irradiation Time on the Degradation Ratio of Azo Fuchsine

Figure 3 shows the comparison of degradation ratios of azo fuchsine in the presence of the transition crystal and original micron-sized rutile $TiO_2$ powders as well as in the absence of any $TiO_2$ catalyst, respectively, under ultrasonic irradiation at different moments. It can be seen that the degradation ratios of azo fuchsine in the presence of the transition crystal and original micron-sized rutile $TiO_2$ powders increase fleetly and attain 94.59 and 67.39% within 120 min, respectively, while it is only 14.53% under only ultrasonic irradiation in the same ultrasonic irradiation time. These results indicate that the sonocatalytic activity of the transition crystal $TiO_2$ powder is obviously higher than that of original micron-sized rutile $TiO_2$ powder.

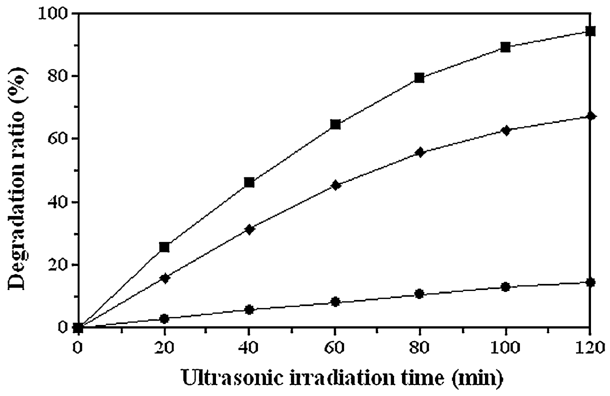


**Fig. 3** The change of degradation ratio (524 nm) of azo fuchsine with irradiation time. (■) Transition crystal $TiO_2$ + ultrasound; (◆) Micron-sized rutile $TiO_2$ + ultrasound; (●) Only ultrasound

Some ion chromatograms at different moments under ultrasonic irradiation in the presence of transition crystal $TiO_2$ powder were conducted as shown in Fig. 4. They clearly prove that the sulphur and nitrogen heteroatoms in azo fuchsine molecule, after sonocatalytic degradation, are converted into the simple and innocuous inorganic $NO_2^-$, $NO_3^-$ and $SO_4^{2-}$ anions. Especially, the peak corresponding to $SO_4^{2-}$ anion markedly becomes higher and higher, which represents the azo fuchsine molecule is decomposed gradually along with the ultrasonic irradiation.

As mentioned above, in any case, both UV-vis spectra and ion chromatograms determined revealed high sonocatalytic activity of transition crystal $TiO_2$ powder.

### 3.4 Influence of Microwave Irradiation Time on Sonocatalytic Activity of Transition Crystal $TiO_2$ Powder

Figure 5 shows the influence of different microwave irradiation time on the sonocatalytic activities of transition crystal $TiO_2$ powder. It could be seen that the amount of anatase phase in micron-sized rutile $TiO_2$ powder gradually rose along with increasing microwave irradiation time from 1.0 to 5.0 min, while it hardly changed from 5.0 to 7.0 min. Fortunately, the best sonocatalytic degradation ratio of azo fuchsine appears when the anatase phase $TiO_2$ attains to the highest amount between 5.0 and 7.0 min microwave irradiation. Apparently, the sonocatalytic activity of transition crystal $TiO_2$ powder relates to the amount of the formed anatase phase $TiO_2$. However, the amount of anatase phase in transition crystal $TiO_2$ powder depends on the microwave irradiation time. But after 5.0 min, longer microwave irradiation time is unable to increase the proportion of anatase phase in the transition crystal $TiO_2$ powder.

### 3.5 Influence of Heat-treated Temperature on Sonocatalytic Activity of Transition Crystal $TiO_2$ Powder

The temperature is one of the most important influence factors for the transformation of crystal phase. Figure 6 shows the influence of different heat-treated temperature

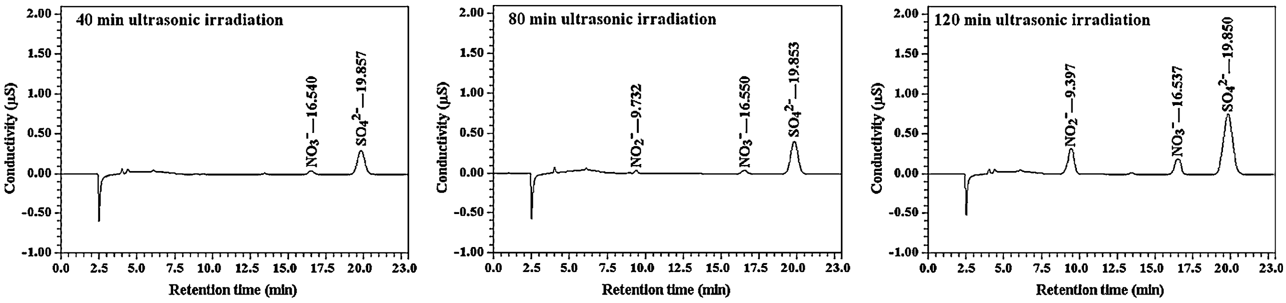


**Fig. 4** Ion chromatogram of azo fuchsine solution during ultrasonic irradiation in the presence of transition crystal $TiO_2$ powder

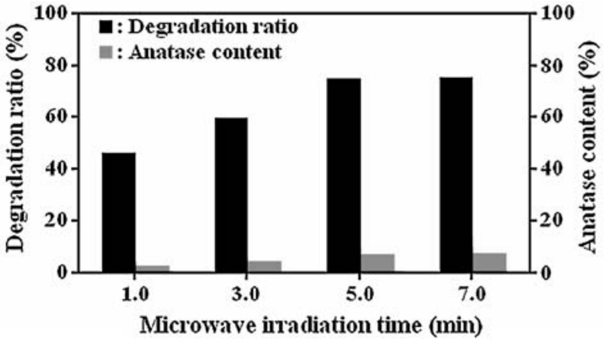


**Fig. 5** The influence of microwave irradiation time on the sonocatalytic degradation of azo fuchsine

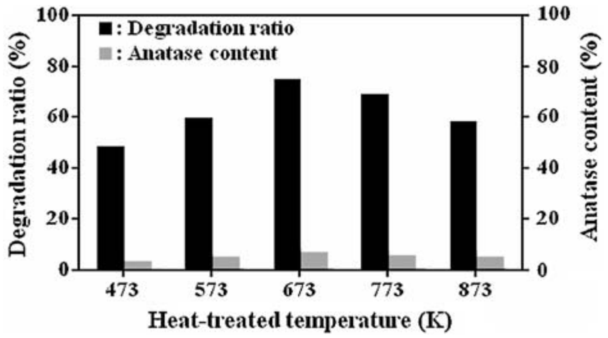


**Fig. 6** The influence of heat-treated temperature on the sonocatalytic degradation of azo fuchsine

on the sonocatalytic activities of transition crystal $TiO_2$ powder. It could be seen clearly that the amount of anatase phase $TiO_2$ increased along with increasing temperature from 473 to 673 K, and then it began to decline slowly. Hence, the most amount of anatase phase $TiO_2$ was obtained when the heat-treated temperature attained at 673 K. Finally, the anatase phase $TiO_2$ disappeared almost when the treated-temperature exceeded 873 K. At the same time, the sonocatalytic activity of transition crystal $TiO_2$ powder returned to the level of original micron-sized rutile $TiO_2$ powder. Here, the highest sonocatalytic activity also appeared at the greatest amount of anatase phase $TiO_2$ formed, which corresponded to 673 K heat-treated temperature. It was also proved that the sonocatalytic activity of transition crystal $TiO_2$ powder depended on the amount of anatase phase $TiO_2$.

## 3.6 Influence of Heat-treated Time on the Sonocatalytic Activity of Transition Crystal $TiO_2$ Powder

At 673 K, the different heat-treated time ranging from 10 to 50 min was used to review the sonocatalytic activity of transition crystal $TiO_2$ powder. As shown in Fig. 7, the most amount of anatase phase in transition crystal $TiO_2$ was obtained when the heat-treated time arrived to 30 min, and then it began to decline after 30 min. Similarly, the corresponding sonocatalytic activity fell along with the decrease of anatase phase $TiO_2$. Hence, the best sonocatalytic degradation also appeared at the highest amount of the anatase phase $TiO_2$, which corresponded to 30 min heat-treated time.

## 3.7 Influence of Treated Solution Acidity on Sonocatalytic Activity of Transition Crystal $TiO_2$ Powder

In general, any phase $TiO_2$ powder is soluble a little in both acidic and basic solutions and then becomes $TiO^{2+}$ and

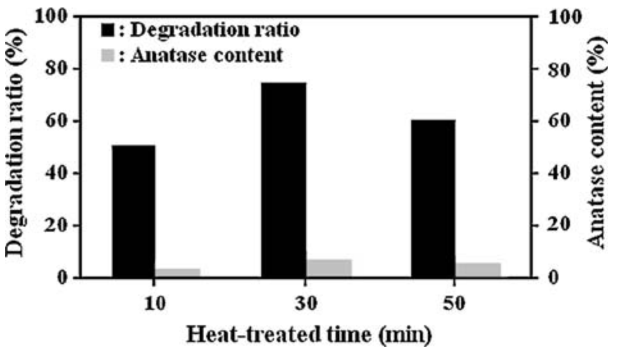


**Fig. 7** The influence of heat-treated time on the sonocatalytic degradation of azo fuchsine

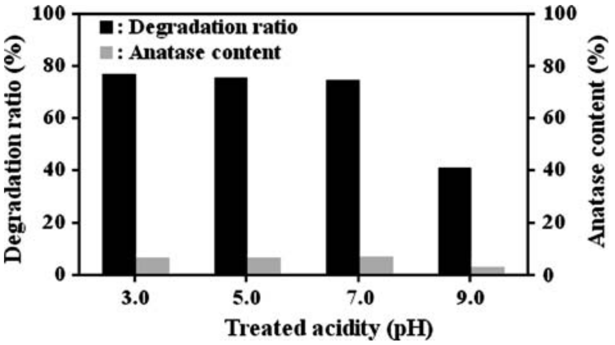


**Fig. 8** The influence of treated solution acidity on the sonocatalytic degradation of azo fuchsine

$TiO_3^{2-}$ ions, respectively. Perhaps, these ions may participate in the phase transformation of $TiO_2$ powder. Figure 8 shows the influence of treated solution acidity on the amount of anatase phase and sonocatalytic activities of transition crystal $TiO_2$ powder. It can be seen that the amount of anatase phase in transition crystal $TiO_2$ powder unchanged almost in the pH range from 3.0 to 7.0. The corresponding sonocatalytic activities decrease only slightly along with increasing pH values. Nevertheless, when the pH value excesses 7.0, the amount of anatase phase begins to decrease clearly. Accordingly, the sonocatalytic activity also decline markedly. It is well known that the point of zero charge (PZC) of micron-sized rutile $TiO_2$ powder is about pH = 4.5–6.0, which evidently leans to chemically acidity. Above this pH value, the surfaces of micron-sized rutile $TiO_2$ particles are negatively charged, while below this pH value they are positively charged. The $TiO^{2+}$ cations must be adsorbed by micron-sized rutile $TiO_2$ particles because of its negatively charged surface even though in acidic solution, which maybe administer to the phase transformation. Therefore, the transition crystal $TiO_2$ powder with high sonocatalytic activity containing high content of anatase phase $TiO_2$ was obtained in acidic solution. By contraries, in basic solution the formed $TiO_3^{2-}$ ions having negative charges can not be adsorbed on the same negatively charged surfaces. It must go against the phase transformation. Hence, the amount of anatase phase is very low, which results in low sonocatalytic activities.

### 3.8 The Possible Process of Transition Crystal of Micron-sized Rutile $TiO_2$ Powder

The possible process of transition crystal of micron-sized rutile $TiO_2$ powder is shown in Fig. 9. First, $H_2O_2$ and $H_2O$ molecules are decomposed into ·OH radicals, $H^+$ and $OH^-$ ions, respectively, under microwave irradiation. Second, the ·OH radicals attack the bridged oxygen atom of –Ti–O–Ti– on the surface of rutile phase $TiO_2$ particle. Third, the $H^+$ and $OH^-$ ions attack the terminated oxygen atom of O = Ti– and central titanium atom, respectively. Synchronously, the ·OH radicals depart from the surface of rutile phase $TiO_2$ particles. And then the $-[O-Ti^+(OH)-O-Ti(O^-)(OH)-]_n$ polymer is produced. The last, the amorphous polymer on the surface of rutile phase $TiO_2$ particles is dehydrated by heat-treatment at 300 °C, and the anatase $TiO_2$ phase folium is formed. Of course, the proper heat-treated temperature and heat-treated time are necessary in order to obtain high sonocatalytic activity.

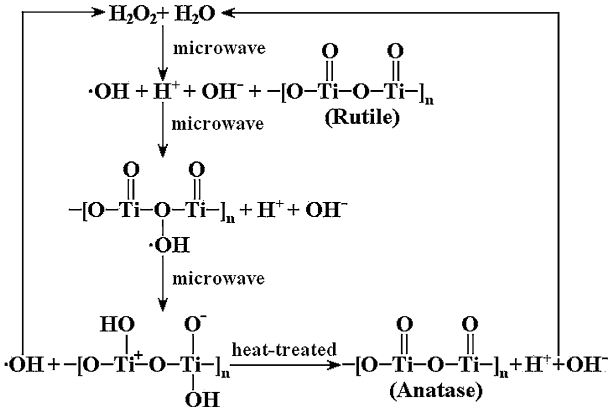


**Fig. 9** The possible process of transition crystal of micron-sized rutile $TiO_2$ powder

### 3.9 The Possible Degradation Mechanism of Azo Fuchsine in the Presence of Transition Crystal $TiO_2$ Powder

In general, the occurrence of sonocatalytic degradation of azo fuchsine and other organic pollutants in the presence of $TiO_2$ powder is thought to be based upon the following three points of view, namely, sonoluminescence, "hot spot" and oxygen atom escape. Firstly, it has been well known that the ultrasonic irradiation can result in the formation of the light with a comparatively wide wavelength range because of the ultrasonic cavitation. Those lights whose wavelengths are below 378 nm, beyond all doubt, can excite the $TiO_2$ particle acting as a photocatalyst and the holes with high oxidation activity will form on the surface of the $TiO_2$ particles. These holes can directly oxidate the azo fuchsine and other organic pollutants in aqueous solution, or form ·OH radicals through the reaction with $H_2O$ molecules, In fact, that is the familiar mechanism of photocatalytic degradation. Secondly, as well known, the temperature of "hot spot" also produced by ultrasonic cavitation can achieve $10^5$ and $10^6$ °C. And that so high temperature sufficiently brings many holes on the surface of $TiO_2$ particles, which can effectively produce ·OH radicals. Thirdly, the strong shock waves of ultrasound may induce some oxygen atoms on the surface of $TiO_2$ particles to escape from the crystal lattice and then the holes will be

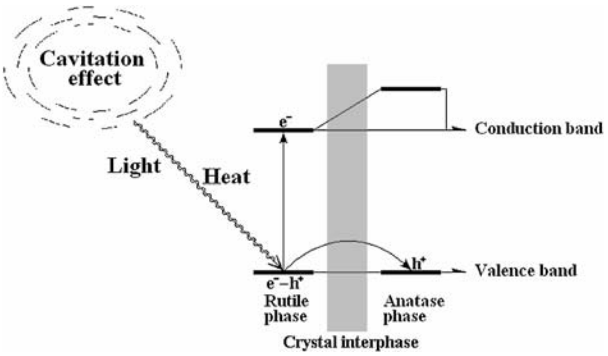


**Fig. 10** Possible process of exciting $TiO_2$ particle and separation of hole and electron

formed synchronously. Similarly, these holes can decompose the azo fuchsine adsorbed on the surface of $TiO_2$ particles directly or degrade them in aqueous solution indirectly through the ·OH radicals resulted from the reaction of holes and $H_2O$ molecules.

Like photocatalytic degradation, the sonocatalytic method also needs to restrain the recombination of electrons and holes for enhancing catalytic activity of $TiO_2$ powder. In this work, one way of restraining the recombination of electrons and holes was realized. The possible process was shown in Fig. 10. As mentioned above, under proper microwave irradiation in hydrogen peroxide solution, a part of anatase phase $TiO_2$ folium form on the surface of micron-sized rutile $TiO_2$ particle. Because of the narrow energy gap ( $\leq 3.2$ eV) the micron-sized rutile $TiO_2$ particles are firstly excited by the light and heat energy resulting from ultrasonic cavitation. The electrons jump to the conduction band and the corresponding holes leave on the valence band at the same time, so that the electron-hole pairs are produced on the surface of transition crystal $TiO_2$ particles. To heel the holes enter the anatase phase $TiO_2$ folium under the function of heat energy resulting from ultrasonic cavitation, which effectively results in the separation of electrons and holes. Otherwise, such separation that the electrons remain at rutile phase $TiO_2$ and the holes enter the anatase phase may redound to enhancing the sonocatalytic activity of micron-sized rutile $TiO_2$ powder. In general, the anatase $TiO_2$ particles have strong adsorbability to many organic pollutants, which is propitious to the holes oxidation. Contrarily, the rutile $TiO_2$ particles have weak adsorbability, which is propitious to the radical oxidation. Hence, that the electrons remain at rutile phase $TiO_2$ not only avoids the reduction of original or oxidated organic pollutants, but also promotes the formation of ·OH radicals resulting from the reactions of the electrons on the surface of the rutile phase $TiO_2$ with $H_2O$ molecules.

## 4 Conclusions

According to the results mentioned above, the sonocatalytic technique, as a novel degradation method of organic pollutants, under ultrasonic irradiation in the presence of transition crystal $TiO_2$ powder, can be used as a way of wastewater treatment. This transition crystal $TiO_2$ sonocatalyst can be prepared easily through microwave irradiation in hydrogen peroxide solution. Certainly, the detailed process of transformation of crystal phase of micron-sized rutile $TiO_2$ powder and the mechanism of sonocatalytic degradation of organic pollutants in aqueous solution needs to be further studied.

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