# Detection of reactive oxygen species (ROS) generated by $TiO_2(R)$, $TiO_2(R/A)$ and $TiO_2(A)$ under ultrasonic and solar light irradiation and application in degradation of organic dyes

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## ARTICLE INFO

## ABSTRACT

In the present work, the rutile, anatase and mixed (rutile and anatase) crystal phase $TiO_2$ powders were irradiated by ultrasound and solar light, respectively, and the generation of reactive oxygen species (ROS) were detected through the oxidation reaction from 1,5-diphenyl carbazide (DPCI) to 1,5-diphenyl carbazone (DPCO). The DPCO can be extracted by the mixed solvent of benzene and carbon tetrachloride and the extract liquors display an obvious absorption peak around 563 nm. In addition, the influences of (ultrasonic or solar light) irradiation time, $TiO_2$ addition amount and DPCI concentration on the quantities of generated ROS were also reviewed. The kinds of generated ROS were determined by using several radical scavengers. At last, the researches on the sonocatalytic and photocatalytic degradation of several organic dyes were also performed. It is wished that this paper might offer some important subjects for broadening the applications of sonocatalytic and photocatalytic technologies.

## 1. Introduction

Since the beginning of the twenty-first century, the application of photocatalytic technology using semiconductors to solve the environmental problems has been received much attention [1–5]. Many studies showed that the heterogeneous photocatalysis through light illumination on a semiconductor surface was an attractive Advanced Oxidation Processes (AOPs) [6–9]. During this process, the generation of powerful reactive oxygen species (ROS) like superoxide radical anion ($^\bullet O_2{}^-$), hydroxyl radical ($^\bullet OH$), hydrogen peroxide ($H_2O_2$) and singlet oxygen ($^1O_2$) and so on takes place markedly [10–14]. These oxidizing substances with higher reaction activity than common oxygen molecules can completely destroy various organic pollutants in wastewaters [15–17]. However, for the sewage with high concentration and low- or non-transparency, the photocatalytic technology generally cannot do anything. Fortunately, the application of sonocatalytic technology has been proposed in recent years. That is, titanium dioxide ($TiO_2$) or zinc oxide (ZnO) as a sonocatalyst irradiated by ultrasound as an excited source has been successfully used in the degradation of

toxic organic compounds [8,18] and dye pollutants [19,20]. Nevertheless, as a new AOPs, the reaction mechanism of sonocatalytic degradation as well as the relevant generation of ROS that bears the degradation of organic pollutants have not been studied yet in detail. In order to enhance the sonocatalytic degradation efficiency and search new high active sonocatalysts, it is necessary to study the sonocatalytic degradation process and determine the kind of generated ROS under ultrasonic irradiation.

In recent years, the electron spin resonance, chromatography, chemiluminescent method and some other technologies have been used in the study on the generation and identification of ROS [21–24]. These detecting techniques exhibited high precision, but factually their applications were limited by some drawbacks such as the need for expensive laboratory equipment, the complexity of the experiment, heavy detection workload and too many limiting factors. Besides, due to the short half-life of ROS and dynamic experiments conducted under ultrasonic and light irradiation, it is certainly difficult and inconvenient to directly trace and detect the ROS. Recently, it was reported that the existence of various oxidizing substances could be detected through the oxidation of some capturing reagents (for example: 1,5-diphenyl carbazide (DPCI)) and subsequent spectrophotometric analysis, namely, Oxidation-Extraction Photometry (OEP) method [25,26]. That is, the DPCI can be oxidized by oxidizing substances into 1,5-diphenyl carbazone (DPCO), which can be extracted by organic solvents and

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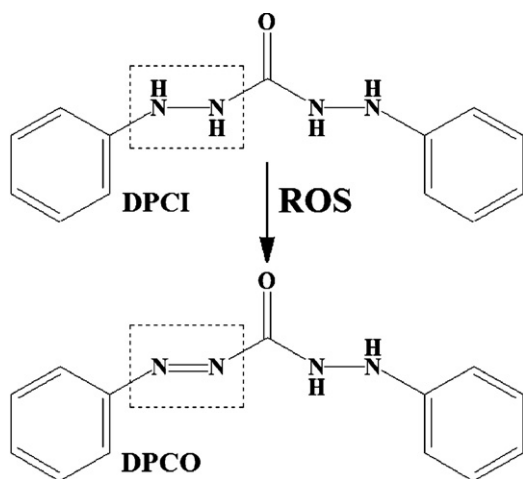
**Fig. 1.** Molecular structures of 1,5-diphenyl carbazide (DPCI) and 1,5-diphenyl carbazone (DPCO).

display an obvious absorbance in a certain range of wavelength. As well known, the ROS has a very strong oxidability. Similarly, the DPCI should be oxidized by various ROS. Because of fast and accurate detection, simple equipment requirements, low-cost reagent, wide detection range and simple requirements for sample, the OEP method could be widely applied in the biological and chemical systems. Theoretically, the quantities and kinds of generated ROS should be evaluated by the quantities of oxidized DPCI and the adding of different radical scavengers. For example, L-histidine (His) can quench $^1O_2$, dimethylsulfoxide (DMSO) and thiourea (TU) can do $\bullet$OH. And that the Vitamin C (VC) can quench almost all kinds of ROS [27,28]. If the absorbance of DPCO extract liquors decreases after adding some kind of radical scavengers, it will demonstrate that there is a kind of corresponding ROS in the system.

In the present work, the rutile phase $TiO_2$ ($TiO_2(R)$) and anatase phase $TiO_2$ ($TiO_2(A)$) powders were used for preparing the mixed (rutile and anatase) crystal phase $TiO_2$ ($TiO_2(R/A)$) powder. Acting as the sonocatalyst and photocatalyst, the ($TiO_2(R/A)$) powder was irradiated by ultrasound or solar light, and then the generated ROS was estimated by the OEP method. In addition, some influencing factors, such as (ultrasonic or solar light) irradiation time and $TiO_2$ addition amount, on the generation of ROS were reviewed. The effect of DPCI concentrations on the determined quantities of generated ROS was also considered. Meanwhile, several radical scavengers were used to determine the kinds of generated ROS. At last, the sonocatalytic and photocatalytic degradation of some organic dyes in aqueous solution under ultrasonic and solar light irradiation combined with nano-sized $TiO_2$ powder was carried out [29–32]. The molecular structures of DPCI and DPCO and the transformation process are given in Fig. 1.

## 2. Experimental

### 2.1. Materials

The nano-sized rutile phase $TiO_2$ ($TiO_2(R)$) powder (grain size: 20–30 nm and BET: 90–100 m²/g) and anatase phase $TiO_2$ ($TiO_2(A)$) powder (grain size: 20–30 nm and BET: 45–50 m²/g) (Veking Company, China) were used as the raw materials for preparing the mixed crystal phase $TiO_2$ ($TiO_2(R/A)$) as a sonocatalyst or photocatalyst. The preparing process is as follows. The 5.00 g equivalent molar rutile and anatase phase nano-sized $TiO_2$ powders were added into 100 mL de-ionized water, and then were scattered by ultrasound and heated to boiling state for 30 min. The mixture was separated by filter and washed three times. After heat-treatment

at 500 °C for 30 min, the equably mixed (rutile and anatase) crystal phase $TiO_2$ ($TiO_2(R/A)$) powders were obtained. For comparison, the nano-sized rutile $TiO_2$ ($TiO_2(R)$) and anatase phase $TiO_2$ ($TiO_2(A)$) powders were also treated under the same condition. 1,5-Diphenyl carbazide (DPCI, purity > 99.0%), L-histidine (His, purity > 99.0%), Vitamin C (VC, purity > 99.0%), dimethylsulfoxide (DMSO, purity > 99.0%) and thiourea (TU, purity > 99.0%) (Sinopharm Chemical Reagent Co., Ltd., China) were purchased commercially. Benzene (purity > 99.0%) and carbon tetrachloride (purity > 99.0%) (Shenyang Dongxing Reagent Factory, China) were as the extractant. Methyl orange, Acid red B, Methylene blue, Acid orange II and Azo fuchsine (AR, Tianjin Kaiyuan Reagent Corporation, China) were used as model organic pollutants to estimate the catalytic activity of $TiO_2$. The other chemical reagents were all of analytical reagent grade, and double distilled water was used for solution preparation. Water purified by a Milli-Q water system (Millipore Company, USA) was used throughout.

### 2.2. Apparatus

Muffle furnace (SX2-4-10, Great Wall Furnace Company, China) and electric oven (101-1, Shanghai Experiment Apparatus Company, China) were used to prepare mixed (rutile and anatase) crystal phase $TiO_2$ ($TiO_2(R/A)$) powder. X-ray diffractometer (XRD, Rigaku Rint-2500, Rigaku Corporation, Japan) was used to confirm the crystal phases of prepared $TiO_2$. The determined results are shown in Fig. 2. The Controllable Serial-Ultrasonics apparatus (SG3200HE, Shanghai GuTel Ultrasonic Instrument Company, China) was used as the irradiation sources, operating at ultrasonic frequency of 40 kHz and output power of 50 W through manual adjusting. Solar light irradiation apparatus consisted of a magnetic stirring and several open conical flasks directly utilized the natural solar light (0.12 W/cm² irradiation power, 123°24′ east longitude and 41°50′ north latitude and 20–22 °C temperature during the daytime in Shenyang city). The UV–vis spectrophotometer (Cary 50, Varian Company, USA) was used to estimate the generation of ROS and the degradation of organic dyes.

### 2.3. Evaluation of reactive oxygen species (ROS)

Experiments were performed according to the reported method in Refs. [25,26]. Firstly, six 10.00 mL DPCI stock solutions ($1.00 \times 10^{-2}$ mol/L) were added into six 100 mL volumetric flasks, respectively. And then two 100 mg $TiO_2(R)$ powers, two 100 mg $TiO_2(R/A)$ powers and two 100 mg $TiO_2(A)$ powers were added to above DPCI solutions, respectively. All of the six solutions were diluted to 100 mL with double distilled water. For all six solutions, the final DPCI concentration and $TiO_2$ amount were $1.00 \times 10^{-3}$ mol/L and 1.00 g/L, respectively. Among them, three solutions, containing $TiO_2(R)$, $TiO_2(R/A)$ and $TiO_2(A)$ powers, respectively, were put into an ultrasonic apparatus away from light directly under ultrasonic irradiation. And the other three corresponding solutions were directly put into solar light irradiation apparatus. Under solar light irradiation, the same experiments were performed from 11:00 a.m. to 14:00 p.m. every day as this time period corresponds to the maximum incident solar light. For all samples, the solution temperature was controlled at $22.00 \pm 0.02$ °C. After 60 min irradiation, from each sample 10.00 mL solution was taken exactly and extracted with mixed solvent of benzene and carbon tetrachloride (volume ratio = 1:1). And then, all extracted solutions were diluted to 10.00 mL with the same mixed benzene-carbon tetrachloride solvent and their UV–vis spectra were determined. Each experiment was repeated three times and the average values were taken as the result. The obtained results were given in Fig. 3.
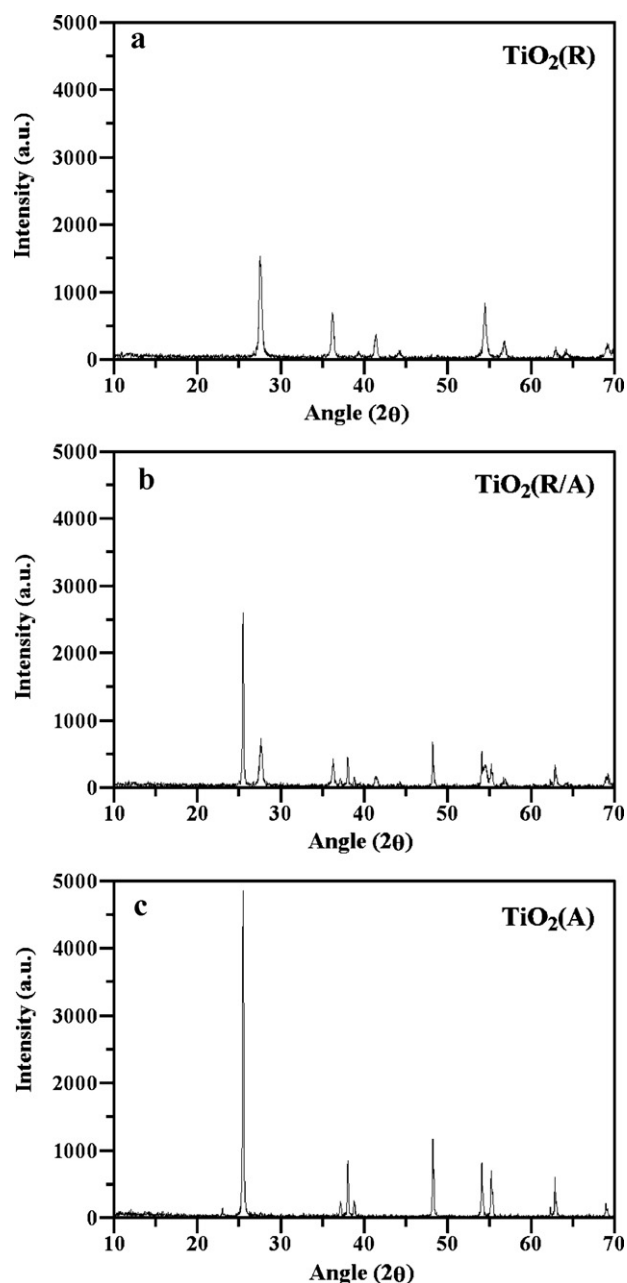
**Fig. 2.** XRD of rutile phase TiO₂ (TiO$_2$(R)) (a), mixed (rutile and anatase) phase TiO$_2$ ((TiO$_2$(R/A)) (b) and anatase phase TiO$_2$ (TiO$_2$(A)) (c) powders.



**Fig. 3.** UV–vis spectra of DPCO extract liquors in the presence of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) under (a) ultrasonic (US) and (b) solar light (SL) irradiation ([DPCI] = 1.00 × 10$^{-3}$ mol/L, [TiO$_2$] = 1.00 g/L, $T$ = 295 K and $t$ = 60 min).

## 2.4. Influence factors on the generation of reactive oxygen species (ROS)

Currently, TiO$_2$ amount and DPCI concentration were fixed as 1.00 g/L and 1.00 × 10$^{-3}$ mol/L, respectively. The other experimental conditions such as 22.00 ± 0.02 °C solution temperature, 100 mL total volume and 60 min ultrasonic or solar light irradiation time were adopted except the special statement. Firstly, the ultrasonic and solar light irradiation time from 0 min to 100 min at 20 min intervals and the TiO$_2$ amount from 0.00 g/L to 1.25 g/L at 0.25 g/L intervals were changed and the influences on the generation of ROS were investigated. The corresponding results were shown in Figs. 4 and 5, respectively. And then, the DPCI concentration was changed from within 2.50 × 10$^{-3}$ mol/L at 0.50 × 10$^{-3}$ mol/L intervals and the influence on the determined quality of generated ROS was reviewed. Each experiment was repeated three times with the
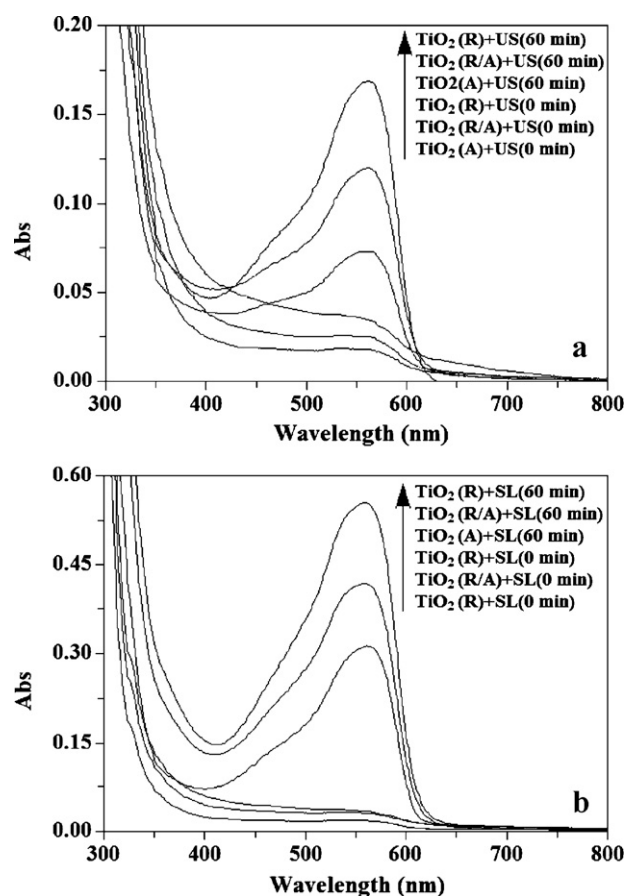
same conditions. And the average of the three values was taken as the result. The result was offered in Fig. 6.

## 2.5. Determination of the kind of reactive oxygen species (ROS)

In order to detect the kind of ROS generated during sonocatalytic and photocatalytic reactions, several radical scavengers were used to quench the different ROS. In general, His can quench the singlet state molecular oxygen ($^1$O$_2$), while DMSO and TU can do the hydroxyl radicals (•OH). As a strong reducing agent the VC can quench almost all kinds of ROS [33–35]. Firstly, five 2.50 mL DPCI stock solutions (1.00 × 10$^{-2}$ mol/L) and five 25 mg TiO$_2$ powder (1.00 g/L) (two shares for every kind of TiO$_2$) were added into five 25.00 mL volumetric flasks, respectively. 2.50 mL His, VC, DMSO and TU stock solutions (0.05 mol/L) were added into above four volumetric flasks. All five solutions were diluted to 25.00 mL with double distilled water. For all samples the final DPCI concentration and TiO$_2$ amount were 1.00 × 10$^{-3}$ mol/L and 1.00 g/L, respectively. The final His, VC, DMSO and TU concentrations are all 5.00 × 10$^{-3}$ mol/L. All of the solutions were averagely transferred into two conical flasks. Then one group of the conical flasks was placed away from light under direct ultrasonic irradiation. After 60 min, from each sample 10.00 mL solution was taken exactly and extracted by the mixed solvent of benzene and carbon tetrachloride (volume ratio = 1:1). And then, they were diluted to 10.00 mL with the same mixed benzene-carbon tetrachloride solvent. The UV–vis spectra of all the solutions were determined. For another group of the conical flask, under solar light irradiation the same experiments were carried out. Each experiment was repeated three
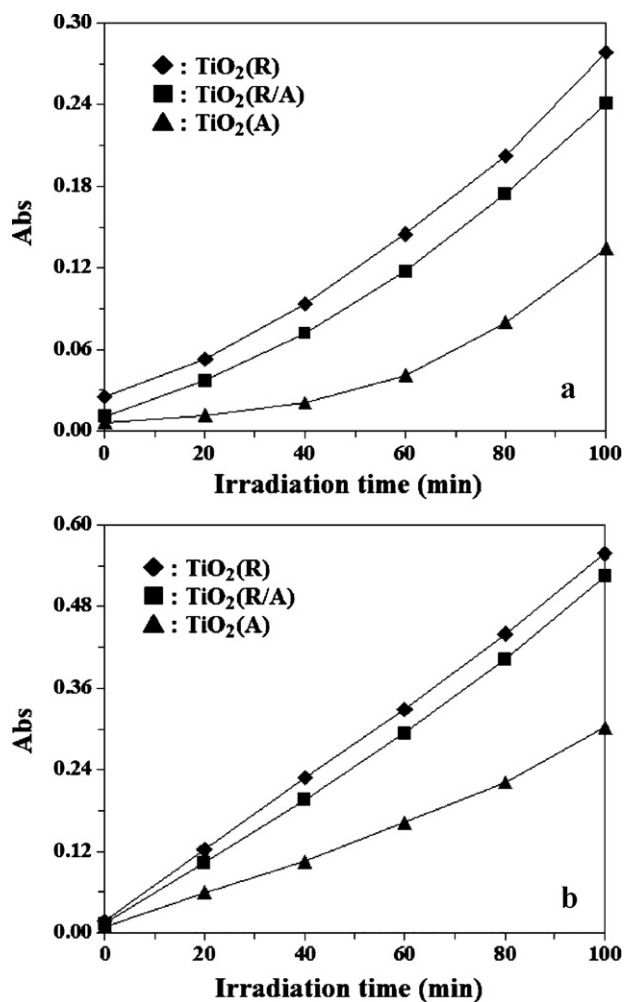
**Fig. 4.** Absorbance changes of DPCO extract liquors in the presence of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) with (a) ultrasonic and (b) solar light irradiation time ([DPCI] = 1.00 × 10$^{-3}$ mol/L, [TiO$_2$] = 1.00 g/L and T = 295 K).

times and the average values were taken as the result. All results were provided in Fig. 7.

### 2.6. Sonocatalytic and photocatalytic degradation of some dyes

In order to evaluate the feasibility of sonocatalytic and photocatalytic degradation using mixed (rutile and anatase) crystal phase TiO$_2$ (TiO$_2$(R/A)) powder under ultrasonic and solar light irradiation, some organic dyes with different chemical compositions and molecular structures, such as Methyl orange, Acid red B, Methylene blue, Acid orange II and Azo fuchsine, are selected as the model organic pollutants. The manipulative experiments were performed with 1.00 g/L TiO$_2$(R/A) amount for different dye solutions with 10.00 mg/L concentration. Under ultrasonic or solar light irradiation, within 180 min at 30 min intervals for any treated dye solution a small amount volume of dye solution was taken and the UV–vis spectrum was determined to evaluate the degradation. For TiO$_2$(A) or TiO$_2$(R), the same process was also carried out by the above method. Each experiment was repeated three times and the average values were taken as the result. The obtained results were given in Fig. 8.
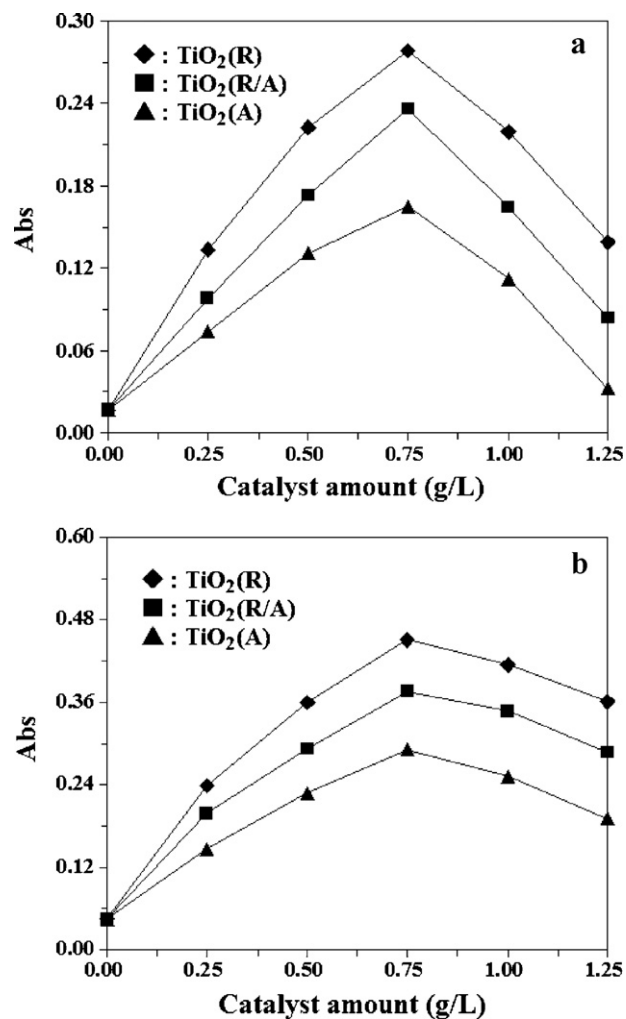


**Fig. 5.** Absorbance changes of DPCO extract liquors under (a) ultrasonic and (b) solar light irradiation with TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) amount ([DPCI] = 1.00 × 10$^{-3}$ mol/L, T = 295 K and t = 60 min).

## 3. Results and discussion

### 3.1. XRD of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) powders

Fig. 2 shows the X-ray diffraction (XRD) patterns of heat-treated nano-sized rutile phase TiO$_2$ (TiO$_2$(R)), mixed (rutile and anatase) crystal phase TiO$_2$ (TiO$_2$(R/A)) and anatase phase TiO$_2$ (TiO$_2$(A)) powders. From corresponding characteristic 2$\theta$ values (2$\theta$ = 27.50° in Fig. 2a and 2$\theta$ = 25.00° in Fig. 2c) of the diffraction peaks, it can be confirmed that the nano-sized TiO$_2$(R) and TiO$_2$(A) powders are mainly identified as rutile and anatase phases, respectively. That is, the main sharp peaks belong to rutile phase and anatase phase, respectively, for heat-treated TiO$_2$(R) and TiO$_2$(A). The average crystallite size of nano-sized TiO$_2$(R) and TiO$_2$(A) particles are about 33 nm and 27 nm, respectively, estimated according to the Scherrer's equation: $D = k(\lambda/\beta \cos \theta)$ (where $k$ is a constant equal to 0.89, $\lambda$ is the X-ray wavelength equal to 0.154 nm, $\beta$ is the full width at half maximum and $\theta$ is the half diffraction angle (18.14°)).

For TiO$_2$(R/A), Fig. 2b synchronously gives the characteristic 2$\theta$ values (2$\theta$ = 27.50° and 2$\theta$ = 25.00°) of rutile and anatase phases. It indicates that the prepared TiO$_2$(R/A) indeed contains rutile phase TiO$_2$ (TiO$_2$(R)) and anatase phase TiO$_2$ (TiO$_2$(A)). According to the quantitative equation: $\beta_R$ (%) = 1/[1 + 0.8($I_A$/$I_R$)] and $\beta_A$ (%) = 1/[1 + 1.26($I_R$/$I_A$)] ($I_A$: diffraction intensity of anatase phase; $I_R$: diffraction intensity of rutile phase), the TiO$_2$(R/A) powder con-
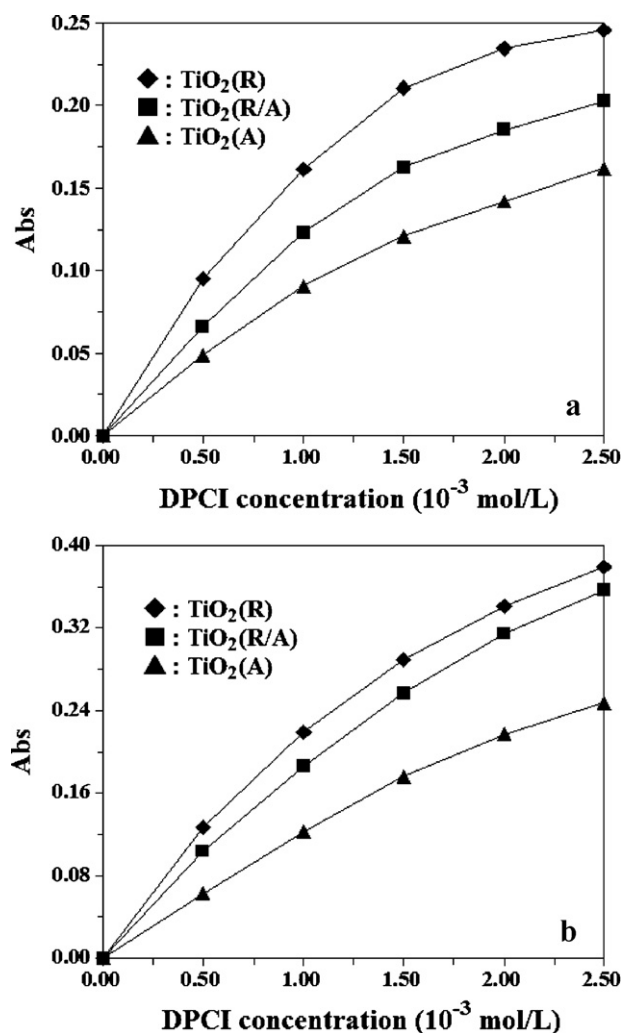
**Fig. 6.** Absorbance changes of DPCO extract liquors in the presence of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) under (a) ultrasonic and (b) solar light irradiation with DPCI concentration ([TiO$_2$] = 1.00 g/L, T = 295 K and t = 60 min).



**Fig. 7.** Absorbance changes of DPCO extract liquors in the presence of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) under (a) ultrasonic and (b) solar light irradiation with various quenching reagents ([DPCI] = 1.00 × 10$^{-3}$ mol/L, [TiO$_2$] = 1.00 g/L, [His] = [VC] = [DMSO] = [TU] = 5.00 × 10$^{-3}$ mol/L, T = 295 K and t = 60 min).

tains approximately 26.13% rutile phase and 73.71% phase anatase. Otherwise, in TiO$_2$(R/A) powder the calculated average crystallite sizes of rutile phase TiO$_2$ and anatase phase TiO$_2$ are about 31 nm and 25 nm, respectively, based on the Scherrer's equation.

### 3.2. UV–vis spectra of DPCI solutions in the presences of TiO$_2$(R), TiO$_2$(R/A) and TiO$_2$(A) under ultrasonic and solar light irradiation

The ROS could be detected by UV–vis absorption spectrum according to the method of Oxidation-Extraction Photometry (OEP) [25,26]. Under ultrasonic or solar light irradiation, as a semiconductor material the TiO$_2$ turns into the excited state. That is, some electrons are transited from valence band (VB) to conduction band (CB). Simultaneity, the electron–hole pairs form on the surface or in the inner of TiO$_2$ particles. The electrons and holes react with the molecular oxygen (O$_2$) dissolved in aqueous solution and water molecules (H$_2$O) absorbed on the surface of TiO$_2$ particles, respectively, producing the superoxygen radical anions ($^{\bullet}$O$_2{}^-$) and hydroxyl radicals ($^{\bullet}$OH). At last, the unstable $^{\bullet}$O$_2{}^-$ also becomes $^{\bullet}$OH through a series of chemical reactions. Owing to the strong oxidation ability, these $^{\bullet}$OH can oxidize 1,5-diphenyl carbazide (DPCI) into 1,5-diphenyl carbazone (DPCO). The DPCO can be extracted by the mixed extraction solvent of benzene and carbon tetrachloride
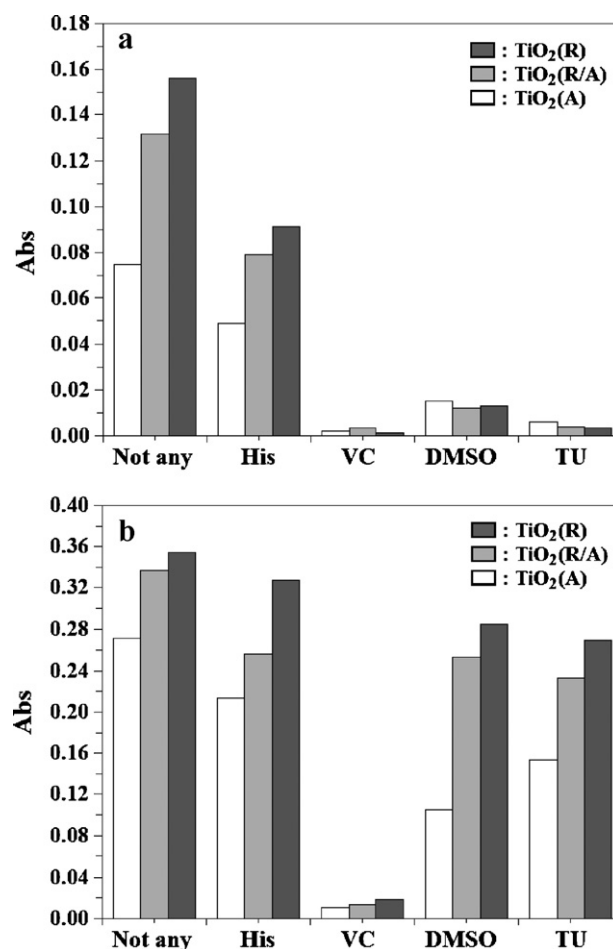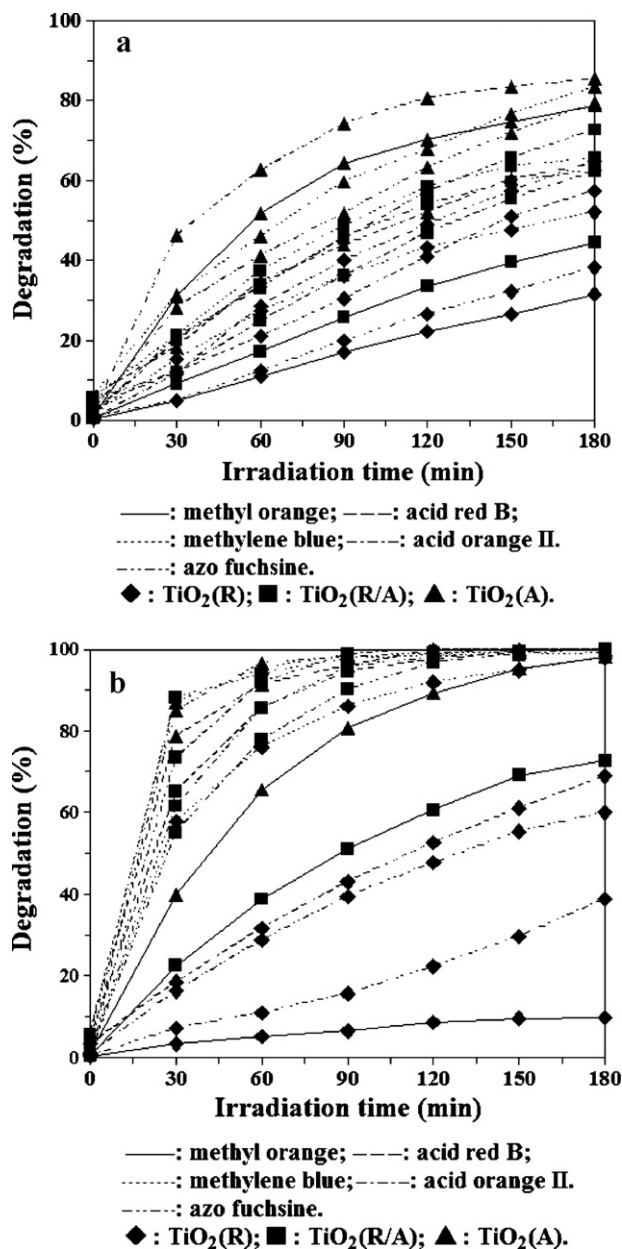
and show an obvious absorbance at 563 nm wavelength. Sequentially, the produce and output of $^{\bullet}$OH can be easily detected.

In Fig. 3 it can be seen that, under ultrasonic or solar light irradiation, the absorption peaks of DPCO extract liquors around 563 nm show an obvious increase compared with the corresponding ones without any irradiation. And that, for any crystal phase TiO$_2$ under solar light irradiation the DPCI solution exhibits more obvious absorbance than corresponding that under ultrasonic irradiation. It indicates that the solar light can directly excite the semiconductor TiO$_2$ to carry out photocatalytic oxidation reaction with high efficiency. Moreover, for two cases the absorption peaks of DPCO extract liquors irradiated both increase as the order of TiO$_2$(A) < TiO$_2$(R/A) < TiO$_2$(R). It indicates that the DPCI are mainly oxidized by generated $^{\bullet}$OH in sonocatalytic or photocatalytic reactions.

### 3.3. Influence of ultrasonic and solar light irradiation time on the generation of ROS

It can be seen from Fig. 4 that for two courses, the absorbance of DPCO extract liquors at 563 nm both increases with the increase of ultrasonic and solar light irradiation time. It indicates that more and more DPCI are oxidized to DPCO by generated ROS. However, at any irradiation time the absorbance under solar light irradiation in the presence of any crystal phase TiO$_2$ is much higher than corresponding that under ultrasonic irradiation. This proves again that the solar light can excite various TiO$_2$ to generate the ROS more

**Fig. 8.** Effects of (a) ultrasonic and (b) solar light irradiation time on the degradation of several organic dyes in the presence of $TiO_2(R)$, $TiO_2(R/A)$ and $TiO_2(A)$ ([$TiO_2$] = 1.00 g/L, [dye] = 10 mg/L and $T$ = 295 K).

erated. Nevertheless, when the $TiO_2$ amount is added more than 0.75 g/L, owing to the obstruction to the transmission of ultrasound or solar light the quantity of generated ROS begins to decrease along with the further increase of $TiO_2$ amount. Thus, it causes the decrease of the absorbance of DPCO extract liquors.

### 3.5. Influence of DPCI concentration on the determination of ROS

It is observed from Fig. 6 that, without adding DPCI, even under ultrasonic or solar light irradiation there is not absorbance at 563 nm. It demonstrates that the absorption peak around 563 nm only comes from the oxidation of DPCI. Under ultrasonic or solar light irradiation, the absorbance of DPCO extract liquors fleetly increases along with the increase of DPCI concentration. It indicates that more and more DPCO are generated with the increase of DPCI concentration. Apparently, the DPCO concentration relates to the quantity of generated ROS. That is, the DPCO concentration can express the real quantity of generated ROS.

### 3.6. Kind of generated ROS under ultrasonic and solar light irradiation

To understand the mechanism of the sonocatalytic and photocatalytic reactions, it is necessary to determine the kind of generated ROS. Here, several radical scavengers are used for this purpose. According to the reports, L-histidine (His) can quench singlet molecular oxygen ($^1O_2$), while dimethylsulfoxide (DMSO) and thiourea (TU) can do hydroxyl radicals ($^\bullet OH$). Owing to the strong reduction characteristic the Vitamin C (VC) can quench almost all kinds of ROS [33–35]. Based on the quenching resulted from different radical scavengers the kinds of ROS could be judged.

It is observed from Fig. 7 that, for both ultrasonic and solar light irradiation, in the absence of any radical scavenger the relatively high absorbances of DPCO extract liquors at 563 nm can be found for all three kinds of $TiO_2$ powders ($TiO_2(R)$, $TiO_2(R/A)$ and $TiO_2(A)$). It indicates that a great amount of ROS are generated and then a certain amount of DPCI molecules are oxidized to DPCO. Of course, for any kind of $TiO_2$ the absorbance under solar light irradiation is slightly higher than corresponding that under ultrasonic irradiation. Moreover, as a sensitive compound to ROS, the DPCI more easily becomes DPCO in the presence of $TiO_2(R)$ than in the presences of $TiO_2(R/A)$ and $TiO_2(A)$. That is, under ultrasonic or solar light irradiation, the $TiO_2(R)$ can generate more ROS than the $TiO_2(R/A)$ or $TiO_2(A)$ does.

Nevertheless, after adding radical scavengers, the absorbances of DPCO extract liquors are weakened more or less. Particularly, under ultrasonic irradiation the absorbances obviously decrease after adding DMSO and TU. It illustrates that the $^\bullet OH$ are largely consumed by the used radical scavengers (DMSO and TU). Moreover, it also indicates that, under ultrasonic irradiation, the $TiO_2(R)$ can generate more $^\bullet OH$. Whereas, after adding radical scavengers, under solar light irradiation the absorbance of DPCO extract liquors at 563 nm only slightly decreases for all three kinds of $TiO_2$ powders ($TiO_2(R)$, $TiO_2(R/A)$ and $TiO_2(A)$). It also demonstrates that, under solar light irradiation, the $TiO_2$ oxidizes the DPCI mainly through hole oxidation mechanism.

### 3.7. Degradation of organic dyes in the presence of $TiO_2$ under ultrasonic and solar light irradiation

Under ultrasonic and solar light irradiation, the sonocatalytic and photocatalytic degradations of several organic dyes with different chemical compositions and molecular structures were also performed [36,37]. In Fig. 8 it is observed that, under ultrasonic or solar light irradiation, the degradation ratios of five dyes all increase gradually with the increase of irradiation time. It indi-

effectively than ultrasonic irradiation. Otherwise, from Fig. 4 it also estimates that the rutile phase $TiO_2$ ($TiO_2(R)$) irradiated by ultrasound or solar light can generate more ROS than the anatase $TiO_2$ ($TiO_2(A)$) and mixed crystal phase $TiO_2$ ($TiO_2(R/A)$). Of course, for any phase $TiO_2$ the quantities of generated ROS both increase with the increase of ultrasonic or solar light irradiation time.

### 3.4. Influence of $TiO_2$ amount on the sonocatalytic and photocatalytic generation of ROS

It is apparent in Fig. 5 that, under ultrasonic or solar light irradiation, for any phase $TiO_2$ the absorbance of DPCO extract liquors rapidly increases at beginning. And then, it decreases with increasing of the $TiO_2$ amount. It indicates that the ultrasonic or solar light irradiation only can generate limited ROS in the absence of any phase $TiO_2$. That is, under ultrasonic or solar light irradiation, below 0.75 g/L as the $TiO_2$ amount increases, more and more ROS are gen-

cates that more and more dye molecules have been decomposed. However, for any organic dye, the degradation ratios under ultrasonic irradiation are slightly lower than corresponding ones under solar light irradiation. It indicates that again, under the same conditions, the direct solar light irradiation can effectively excite the $TiO_2$ particles as photocatalyst to degradate any organic dye. For ultrasonic irradiation, the degradation ratios array as the order 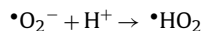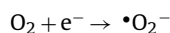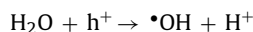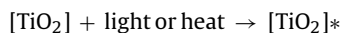of $TiO_2(A) > TiO_2(R/A) > TiO_2(R)$. And that for solar light irradiation, the degradation ratios array in the main as the order of $TiO_2(R/A) > TiO_2(A) > TiO_2(R)$. It means that for both ultrasonic and solar light irradiation the degradation of organic dyes are degradated mainly through hole oxidation mechanism. Particularly, with regard to the photocatalytic degradation the mixed (rutile and anatase) crystal phase enhances the photocatalytic activity of $TiO_2$. Of course, because of different chemical compositions and molecular structures, these dyes give a series of different degradation ratios.

### 3.8. Possible mechanism on the generation of ROS in the presence of $TiO_2$ under ultrasonic and solar light irradiation

The method of ultrasonic and solar light irradiation combined with semiconductor oxides (such as $TiO_2$ and ZnO) can generate reactive oxygen species (ROS) to degrade various organic pollutants. Therefore, as novel Advanced Oxidation Processes (AOPs) they are called as sonocatalytic and photocatalytic degradation process, respectively. In principle, the sonocatalytic process is based on the ultrasonic cavitation effect. As well known, under ultrasonic irradiation, the adiabatic expansion of the gas or vapor in the micro-bubbles happens. And then, the micro-bubbles implode after reaching the limit. This process will generate high temperatures and high pressures in their surroundings and inners, which usually results in the short and local sonoluminescence and hot-spots [38]. These energies are sufficient to activate the semiconductors which selectively accumulate in aqueous phase. The sonoluminescence caused by ultrasonic cavitation generates the lights with wide wavelength range. And the hot-spots also produced by ultrasonic cavitation effect in water medium can generally reach 5000–10,000 °C.

Under the excitation of such light or hot-spots, some electrons could be transited from valence band (VB) of semiconductor oxides (for example: $TiO_2$) to conduction band (CB). At the same time, the electron–hole pairs could be formed. Being similar to the photocatalytic process, these electrons and holes react with the molecular oxygen ($O_2$) dissolved in aqueous solution and the water molecules ($H_2O$) absorbed on the surface of $TiO_2$ particles, respectively, and produce the superoxygen radical anions ($^\bullet O_2{}^-$) and hydroxyl radicals ($^\bullet OH$) with strong oxidation ability. Eventually, the $^\bullet O_2{}^-$ can also become the $^\bullet OH$ through a series of chemical reactions. Moreover, the excited $TiO_2$ particles can also transfer the appropriate energy to the ground (triplet) state molecular oxygen ($^3O_2$) to give birth to excited (singlet) state molecular oxygen ($^1O_2$) [18,25,39]. Hence, in view of the comparability of sonocatalytic and photocatalytic reactions, the semiconductors excited by ultrasonic cavitation could also lead to the generation of the ROS. These ROS at least including $^\bullet OH$ and $^1O_2$ will oxidize a wide range of organic compounds, like dye, pesticide and surfactant and so on. Apparently, the effective generation of ROS is based on the combination of ultrasonic irradiation and semiconductor. The possible process is thought as following.

Ultrasonic irradiation (cavitation effect) → light + heat

$$[TiO_2] + \text{light or heat} \rightarrow [TiO_2]*$$

$$[TiO_2]* \rightarrow [TiO_2] + h^+ + e^-$$

$$H_2O + h^+ \rightarrow {}^\bullet OH + H^+$$

$$O_2 + e^- \rightarrow {}^\bullet O_2{}^-$$

$$^\bullet O_2{}^- + H^+ \rightarrow {}^\bullet HO_2$$

$$^\bullet HO_2 + H_2O \rightarrow H_2O_2 + {}^\bullet OH$$

$$H_2O_2 + \text{light or heat} \rightarrow 2{}^\bullet OH$$

$$[TiO_2]* + {}^3O_2 \rightarrow [TiO_2] + {}^1O_2$$
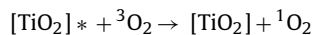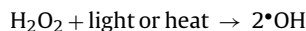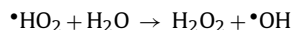
In fact, it includes the photocatalytic reaction process. Of course, because of the direct excitation, under solar light irradiation the $TiO_2$ displays slightly higher activity than that under ultrasonic irradiation.

## 4. Conclusions

This study reveals that the reactive oxygen species (ROS) including not less than singlet state molecular oxygen ($^1O_2$) and hydroxyl radicals ($^\bullet OH$) can be generated, when the $TiO_2$ powders were irradiated by ultrasound and solar light, respectively. The quantities of generated ROS increase with the increase of ultrasonic or solar light irradiation time and $TiO_2$ addition amount. Meanwhile, the determined quantity of generated ROS is also related to the 1,5-diphenyl carbazide (DPCI) concentration. In addition, several conventional dyes as the model organic pollutants can effectively be degraded by using nano-sized $TiO_2$ powder under ultrasonic or visible light irradiation. Particularly, the research results offered some important proofs about sonocatalytic and photocatalytic degradation process and mechanism of organic pollutants in wastewater. For both sonocatalytic and photocatalytic degradation, the rutile $TiO_2$ ($TiO_2(R)$) is inclined to radical oxidation, while the anatase $TiO_2$ ($TiO_2(A)$) does hole oxidation. The combination of rutile and anatase phase $TiO_2$ contributes to the enhancement of photocatalytic and sonocatalytic activity. Moreover, it proves that the $TiO_2$ not only absorbs the solar energy to operate the photocatalytic reaction, but also utilizes the heat energy and sonoluminescence to perform the sonocatalytic reaction. It is expected that this work could offer some valuable references for studying the reaction mechanism of sonocatalytic and photocatalytic degradation and promoting their applications in environment treatment and energy exploitation.

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