

# Investigation on degradation of dyestuff wastewater using visible light in the presence of a novel nano TiO<sub>2</sub> catalyst doped with upconversion luminescence agent

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## Abstract

A new upconversion luminescence agent, 40CdF<sub>2</sub>·60BaF<sub>2</sub>·1.0Er<sub>2</sub>O<sub>3</sub>, was synthesized and its fluorescent spectrum was determined. This upconversion luminescence agent can emit five upconversion fluorescent peaks shown in the fluorescent spectrum whose wavelengths are all below 387 nm under the excitation of 488 nm visible light. This upconversion luminescence agent was mixed into nano rutile TiO<sub>2</sub> powder by ultrasonic and boiling dispersion and then a novel doped nano TiO<sub>2</sub> photocatalyst utilizing visible light was firstly prepared. The doped nano TiO<sub>2</sub> powder was characterized by XRD and TEM and its photocatalytic activity was checked through the photocatalytic degradation reaction of azo fuchsine as a model compound under the visible light irradiation emitted by 6 three basic color lamps. Otherwise, in order to compare the photocatalytic activities the same experiment was carried out for undoped TiO<sub>2</sub> powder. The degradation ratio of azo fuchsine in the presence of doped nano TiO<sub>2</sub> powder reached 95% under visible light irradiation within 24 h, which was obviously higher than the corresponding degradation ratio of 21% in the presence of undoped nano rutile TiO<sub>2</sub> powder. It indicates that the upconversion luminescence agent prepared as dopant can effectively turn visible lights to ultraviolet lights that are absorbed by nano TiO<sub>2</sub> particles to produce the electron–cavity pairs. All the results show that the nano rutile TiO<sub>2</sub> powder doped with upconversion luminescence agent is a promising photocatalyst using sunlight for treating the industry dye wastewater in great force.

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**Keywords:** Upconversion luminescence agent; Nano rutile TiO<sub>2</sub>; Photocatalytic degradation; Visible light; Azo fuchsine

## 1. Introduction

Every year, large numbers of wastewaters containing high concentration poisonous organic compounds are brought from dyeing processes and dye production [1,2]. If these wastewaters were not treated properly and betimes, they would seriously contaminate our environments. Knowing the ponderance of these problems, people have already begun to treat these toxic wastewaters adopting all kinds of methods [3–5]. However, such organic pollutants cannot be decomposed easily and completely using ordinary chemical and biological methods, since the

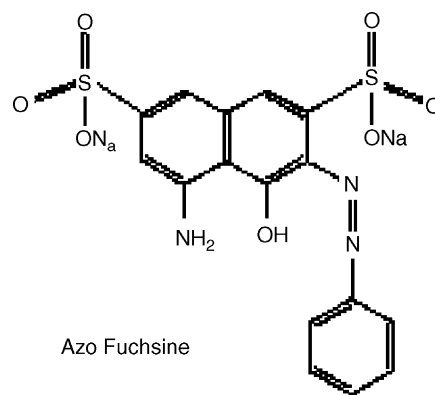
structures of these organic dye compounds in wastewaters usually contain one or several benzene rings. In recent years, many attentions have been paid to the method of semiconductor-based photocatalytic degradation to treat these dye wastewaters [6,7]. In these semiconductor materials, titanium dioxide (TiO<sub>2</sub>) as photocatalyst is widely used to photodegrade many organic pollutants for its relatively high catalytic reactivity, physical and chemical stability, avirulence and cheapness and so on [8–10]. Even so, only under irradiation of ultraviolet light ( $\lambda < 387$  nm) TiO<sub>2</sub> catalyst can effectively destroy the organic pollutants in wastewaters because of its broad band-gap ( $E_g = 3.2$ – $4.5$  eV). In general, the sunlight only contains 3–4% ultraviolet light, so it is impossible to utilize sunlight directly for activating TiO<sub>2</sub> photocatalyst effectively. Hence, the photocatalytic degradation method treating wastewaters needs costly equipments and

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large numbers of energies as light source. This is a big burden for many countries, especially for those developing countries.

For long time, many scholars and experts being engaged on the synthesis and preparation of inorganic materials have been interested in extending the range of absorption wavelength of TiO<sub>2</sub> catalysts, namely making TiO<sub>2</sub> particles as photocatalysts absorb the visible light at full steam. Many reformative methods were adopted such as the doping of transition-metal ions [11,12], combination of narrow band-gap semiconductors [13,14] and aggradation of noble metals [15,16] as well as some other special treatment methods, for example: ultraviolet light irradiation and ultrasonic dispersion during the preparation of TiO<sub>2</sub> catalysts, H<sub>2</sub>O<sub>2</sub> dipping and so on [17–20]. Whereas, we have not thought that these methods can really improve the photocatalytic activity of TiO<sub>2</sub> catalyst all through. We are insisting all the while that the electron–cavity pairs generated by excitation of various wavelength lights are different, that is to say, their oxidation–reduction potentials are different. The oxidation potentials of the cavities from ultraviolet lights must be higher than those from visible lights. Only those cavities from the excitation of ultraviolet lights should possess the strong oxidative ability to decompose the stable organic pollutants directly which contain benzene rings and aliphatic chains or indirectly to degrade them through oxidizing the H<sub>2</sub>O molecule in wastewaters to generate the hydroxyl radicals ( $\bullet$ OH) also having high oxidative ability. Even though the excitation wavelength range of TiO<sub>2</sub> photocatalysts is extended to visible lights unilaterally and blindly, it is difficult to obtain the better degradation effect.

To sum up, in all the reformative methods mentioned above, the light source used for exciting TiO<sub>2</sub> catalyst is visible light which possess low energy, so the oxidative ability of these cavities generated on the surface of TiO<sub>2</sub> particle by the excitation of visible light source must be very low. Beyond all doubt, such cavities cannot bring large numbers of  $\bullet$ OH radicals effectively and then destroy the stable organic pollutants completely. In order to get the cavities possessing high oxidative ability, it is necessary to use ultraviolet lights to excite TiO<sub>2</sub> particles as photocatalysts. For this purpose, we have considered whether there are some substances those can turn visible lights into the ultraviolet lights to satisfy the requirement of TiO<sub>2</sub> photocatalysts. Fortunately, the upconversion luminescence materials containing rare earth metals are just what we want to adulterate to general TiO<sub>2</sub> photocatalysts. In this work, a new upconversion luminescence agent containing Erbium (Er) element was synthesized and then mixed into the nano rutile TiO<sub>2</sub> powder by ultrasonic dispersion. Lastly, an unreported doped nano TiO<sub>2</sub> photocatalyst that can utilize visible lights was firstly prepared and its photocatalytic degradation activity was tested simultaneously. It was found that this novel doped nano TiO<sub>2</sub> photocatalyst could effectively decompose the azo fuchsine dye in solution under the irradiation of visible light. It can be forecasted that the nano TiO<sub>2</sub> catalyst doped with upconversion luminescence agent is a promising photocatalyst utilizing sunlight, which will widely be used to treat various dye wastewaters.



## 2. Experimental

### 2.1. Apparatus and materials

Three basic color lamp (FL40T8EXD/36, Toshiba Company, Japan) as light source was used to irradiate the reaction system and the light intensity is 964347 lx. The degradation process was tracked adopting UV–vis Spectrometer (LAMBDA-17, Perkin-Elmer Company, USA). The luminescence capability of upconversion luminescence agent was affirmed by Fluorescent Spectrometer (F-4500, 150 W Xe lamp, Hitachi Company, Japan). Azo fuchsine (98% purity), nano TiO<sub>2</sub> (rutile), Er<sub>2</sub>O<sub>3</sub> (99.999% purity), CdF<sub>2</sub> (analytical pure), BaF<sub>2</sub> (analytical pure) and H<sub>2</sub>O<sub>2</sub> (30%, analytical pure) were all purchased from Aldrich Company (USA). The solutions were prepared with water from a Millipore Waters Milli-Q water purification system.

### 2.2. Preparation of upconversion luminescence agent

The optimal composition of upconversion luminescence agent was gotten by comparing the emission intensities of upconversion luminescence agent with different Er<sub>2</sub>O<sub>3</sub> adding amount. In these samples, the molar ratio of CdF<sub>2</sub> and BaF<sub>2</sub> was approximately fixed at 40:60 throughout, and the molar ratio of Er<sub>2</sub>O<sub>3</sub> was changed from 0.2 to 1.2. The results show that the highest emission intensity is attained when the molar ratio of Er<sub>2</sub>O<sub>3</sub> is about 1.0. Hence, in this work the molar ratio of 40CdF<sub>2</sub>·60BaF<sub>2</sub>·1.0Er<sub>2</sub>O<sub>3</sub> was adopted. The preparation process of the upconversion luminescence agent is as follows: the 10.0 g mixed powders as total amount of CdF<sub>2</sub>, BaF<sub>2</sub> and Er<sub>2</sub>O<sub>3</sub> with molar ratio of 40:60:1.0 were weighed out and whetted adequately for 1.0 h, and then put into a crucible and calcined at 1000 °C for 20 min. The melted mixtures were cooled down naturally to 800 °C and fleetly poured into a copper crucible. After cooling at a gallop the non-crystalline transparent sample was obtained and then shattered drastically for the determination of luminescence and preparation of doped TiO<sub>2</sub> photocatalyst. The upconversion luminescence property was detected by spectrofluorimeter under excitation of 488 nm wavelength visible light. The upconversion fluorescence emission and excitation spectra were shown in Figs. 1 and 2, respectively.

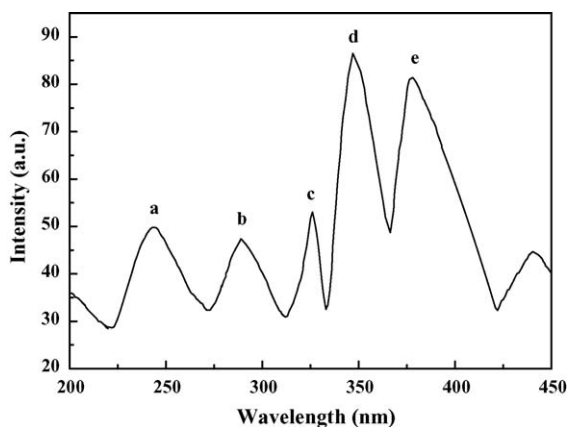


Fig. 1. Emission spectra of upconversion luminescence agent under excitation of 488 nm wavelength light: (a)  ${}^2I_{11/2} \rightarrow {}^4I_{15/2}$  (243 nm), (b)  ${}^2I_{11/2} \rightarrow {}^4I_{13/2}$  (291 nm), (c)  ${}^2I_{11/2} \rightarrow {}^4I_{11/2}$  (324 nm), (d)  ${}^2I_{11/2} \rightarrow {}^4I_{9/2}$  (351 nm) and (e)  ${}^4G_{11/2} \rightarrow {}^4I_{15/2}$  (378 nm).

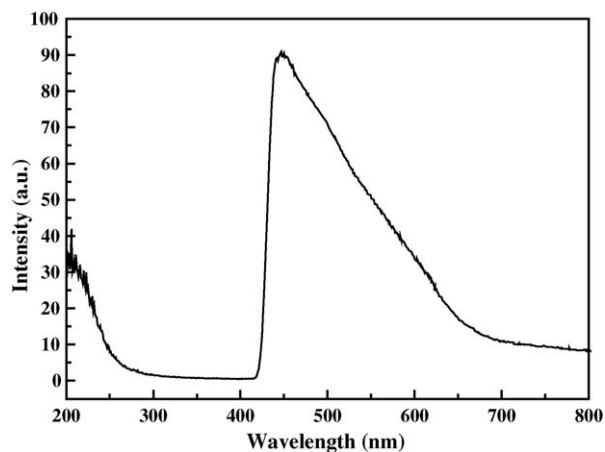


Fig. 2. Excitation spectra for upconversion luminescence agent.

### 2.3. Preparation of nano $TiO_2$ catalyst doped with upconversion luminescence agent

Both rutile and anatase  $TiO_2$  were doped with the upconversion luminescence agent in the experiments, and both of them were characterized by XRD and TEM, but the results showed that a majority of anatase  $TiO_2$  changed to rutile crystalline form

$TiO_2$  due to the high treatment temperature ( $\geq 500^\circ C$ ) during the preparation process. In order to avoid the conglomeration of the upconversion luminescence agent during the process of crystal form transition, the rutile  $TiO_2$  was chosen as the main component of the photocatalyst. The mixture of 0.2 g upconversion luminescence agent and 9.8 g nano rutile  $TiO_2$  powder were added into 100 mL beaker containing 50 mL distilled water and adequately dispersed by ultrasound of 80 kHz frequency and 50 W output power for 15 min. The suspended liquid was

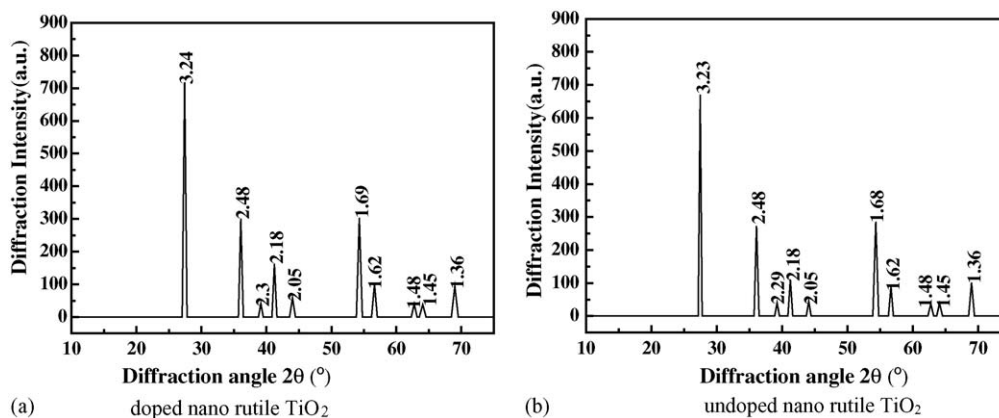


Fig. 3. XRD of doped and undoped nano  $TiO_2$  powders: (a) doped nano rutile  $TiO_2$  and (b) undoped nano rutile  $TiO_2$ .

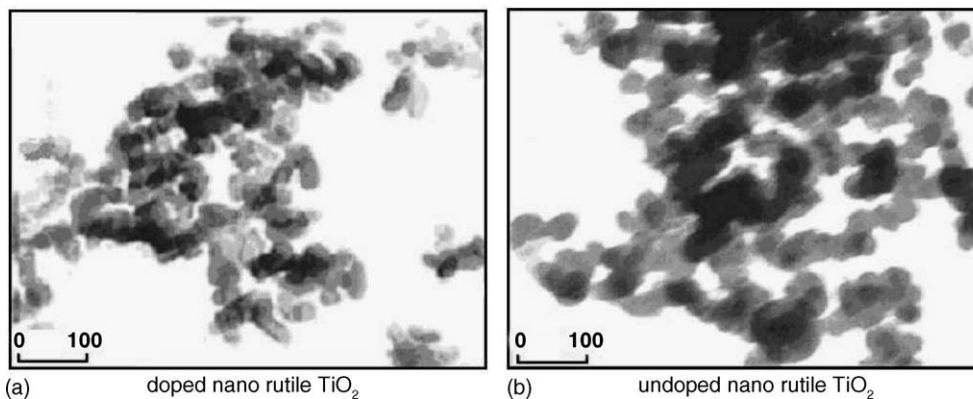


Fig. 4. TEM of doped and undoped nano  $TiO_2$  powders: (a) doped nano rutile  $TiO_2$  and (b) undoped nano rutile  $TiO_2$ .

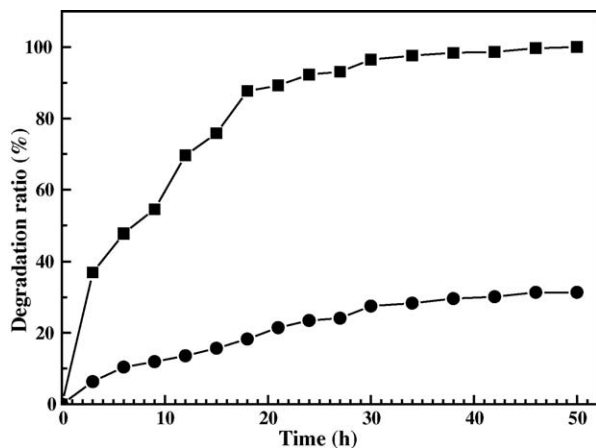


Fig. 5. Influence of irradiation time on degradation ratio of azo fuchsine: (■) irradiation + doped nano TiO<sub>2</sub> and (●) irradiation + undoped nano TiO<sub>2</sub>.

heated to boiling point and kept constant temperature for 30 min. After filtration and lotion the separated powder was put into a crucible and heated in a muffle furnace at the calefactive rate of 2.0 °C/min and then the temperature was maintained at 500 °C for 3.0 h and the doped nano TiO<sub>2</sub> photocatalyst was attained. For comparison, the original nano TiO<sub>2</sub> powder was also treated by the same procedure. The X-ray diffraction (XRD) and transmission-electron microscope (TEM) of doped and undoped nano TiO<sub>2</sub> powders were determined as shown in Figs. 3 and 4, respectively.

#### 2.4. Analysis method

The UV–vis spectra of the original and degradative azo fuchsine solutions were determined by UV–vis spectrophotometer in the wavelength range from 190 to 700 nm. The maximal absorbency of azo fuchsine solution below the concentration 30.0 mg/L abides by Lambert-Beers's law and the standard calibration curve of azo fuchsine solutions is used to estimate the degradation ratio.

#### 2.5. Measurement of photocatalytic activity of doped nano TiO<sub>2</sub> catalyst

Fifty milliliter azo fuchsine solution (10 mg/L) prepared and 50 mg nano TiO<sub>2</sub> powder doped with upconversion luminescence agent were put into a conical flask, and the mixed solution was stirred for 3.0 h without any irradiation for the purpose to attain the balance between absorption and desorption. Then the definite amount of mixed solution was taken out and centrifuged. The separated upper pellucid solution was used for determining UV–vis spectra. After that, 6 three basic color lamps around the conical flask were used as irradiation source and the mixed solution was sampled at definite interval time for tracking the degradation process of azo fuchsine solution until 50.0 h. For comparison, the photocatalytic activity of undoped nano TiO<sub>2</sub> powder was also measured following the same procedure and all the results were shown in Fig. 5. Otherwise, the corresponding kinetics result was shown in Fig. 6. The systemic temperatures

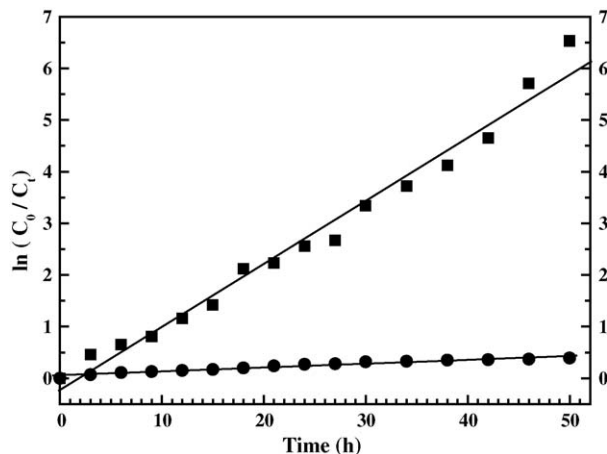


Fig. 6. Reaction kinetics on photocatalytic degradation of azo fuchsine: (■) irradiation + doped nano TiO<sub>2</sub> and (●) irradiation + undoped nano TiO<sub>2</sub>.

were controlled within  $25.0 \pm 0.2$  °C throughout whole experiments.

### 3. Results and discussion

#### 3.1. Fluorescence spectrum of upconversion luminescence agent

When the prepared upconversion luminescence agent, 40CdF<sub>2</sub>·60BaF<sub>2</sub>·1.0Er<sub>2</sub>O<sub>3</sub>, was excited with visible light of 488 nm wavelength, five emission peaks in the region of 200–450 nm (Fig. 1) were detected. All these signals exhibited quadratic dependence on pump power, suggesting that only two photons are involved in the upconversion process. These signals were thought to correspond with <sup>2</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> (a: 243 nm), <sup>2</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>13/2</sub> (b: 291 nm), <sup>2</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>11/2</sub> (c: 324 nm), <sup>2</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>9/2</sub> (d: 351 nm) and <sup>4</sup>G<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> (e: 378 nm), respectively. The wavelengths of these emission peaks are all shorter than 378 nm that effectively exciting TiO<sub>2</sub> catalyst, which shows that this upconversion luminescence agent can supply the ultraviolet light that the nano TiO<sub>2</sub> photocatalyst needs. The upconversion emission efficiency for the signal at 378 nm (<sup>4</sup>G<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>) is calculated as follows: Judd-Ofelt intensity parameters were derived here using the standard procedure [21] from the absorption spectrum as  $\Omega_2 = 2.96 \pm 0.15 \times 10^{-20}$ ,  $\Omega_4 = 1.49 \pm 0.18 \times 10^{-20}$  and  $\Omega_6 = 1.10 \pm 0.12 \times 10^{-20}$  cm<sup>2</sup>. Using these parameters, we could successfully estimate the absorption cross sections of several transitions. The electric dipole transition probabilities were also calculated for various transitions using Eq. (1)

$$A(J, J') = \frac{64\pi^4 e^2}{(2J+1) 3h} \frac{\eta (\eta^2 + 2)^2}{9} \frac{1}{\lambda^3} \times \sum_{t=2,4,6} \Omega_t |\langle \alpha S L J | U^{(t)} | \alpha' S' L' J' \rangle|^2 \quad (1)$$

where  $U^{(t)}$  are the reduced matrix elements and rest of the symbols have their usual meanings. The magnetic dipole transition

Table 1  
Predicted probabilities and lifetimes for radiative transition of  ${}^4G_{11/2} \rightarrow {}^4I_{15/2}$

Transition	${}^4G_{11/2} \rightarrow {}^4I_{15/2}$
Wavelength (nm)	378
Transition probability	
Electric dipole ( $s^{-1}$ )	7862.5
Magnetic dipole ( $s^{-1}$ )	
Total lifetime	
Radiative (ms)	0.156
Experimental (ms)	0.014

rate between two states is estimated using Eq. (2)

$$A(J, J') = \frac{64\pi^4\eta^3}{3h\lambda^3(2J+1)} \left| \sum \langle \alpha SLJ || M || \alpha' S' L' J' \rangle \right|^2 \quad (2)$$

where  $J$  is the angular momentum of the initial state,  $\lambda$  the transition wavelength and the rest of the symbols have their usual meaning. The magnetic dipole operator is given by Eq. (3)

$$M = \left( \frac{-e}{2mc} \right) (L + 2S) \quad (3)$$

where  $L$  is the orbital angular momentum and  $S$  is the spin. The matrix elements of  $M$  between the different states are calculated using the standard formula given elsewhere [21]. The radiative lifetime is calculated by Eq. (4)

$$\tau_r = \frac{1}{\sum_j A_{ij}} \quad (4)$$

where  $j$  is the summation to all the lower levels, and the transition rate includes both electric and magnetic dipole transitions. So the predicted probabilities and lifetimes of the  ${}^4G_{11/2}$  state is listed in Table 1, and therefore the quantum efficiency of level  ${}^4G_{11/2}$  is estimated by Eq. (5)

$$\eta = \frac{\tau_m}{\tau_r} = \frac{0.014}{0.156} = 0.0897 \quad (5)$$

Upconversion efficiency = 100 × number of photons emitted/number of photons absorbed. The absorbed photons at 488 nm are estimated from the absorption coefficient, sample length and incident power. Experimentally, the emission line area is measured. To convert this area into photons, we compared the signal area obtained under 488 nm laser excitation with that obtained by direct pumping of the  ${}^4G_{11/2} \rightarrow {}^4I_{15/2}$  states. Under direct pumping the quantum efficiency = number of photons emitted/number of photons absorbed =  $\tau_m/\tau_r = 0.0897$  for  ${}^4G_{11/2}$ . Therefore, under direct excitation, the number of photons emitted =  $A \times 0.0897 \times$  number of photons absorbed, where  $A$  is the branching ratio for the emission of photons. The emitted 378 nm signal area is directly proportional to the number of emitted photons. With this method the upconversion efficiency of 378 nm emission was estimated at 0.78%. The quantum efficiency of other emission was also calculated follow the same procedure, and the detail process will be shown in another article.

### 3.2. The XRD and TEM of doped nano TiO<sub>2</sub> catalyst

The XRD (shown in Fig. 3) shows that the doped TiO<sub>2</sub> powder basically retains the rutile crystal form because the positions and intensities of some diffraction peaks change slightly comparing with the original rutile TiO<sub>2</sub> powder, which indicates that the Cd<sup>2+</sup>, Ba<sup>2+</sup> and Er<sup>3+</sup> ions do not enter the crystal lattice of rutile TiO<sub>2</sub> particle but the upconversion luminescence agent, 40CdF<sub>2</sub>·60BaF<sub>2</sub>·1.0Er<sub>2</sub>O<sub>3</sub>, is adsorbed onto the surface of TiO<sub>2</sub> particles. The upconversion luminescence agent is combined together with rutile TiO<sub>2</sub> particle through some weak interaction. In addition, in order to maintain the high photocatalytic activity, the proper doping amount of upconversion luminescence agent is necessary, because the large amount of upconversion luminescence agents decrease the surface area of TiO<sub>2</sub> particles which results in low adsorption amount of organic pollutants. However, it is noteworthy that some diffraction peaks (Fig. 3a) of doped TiO<sub>2</sub> powder appreciably broaden comparing with ones (Fig. 3b) of undoped TiO<sub>2</sub> powder, which indicates that the granularities of doped TiO<sub>2</sub> particles become thin in a way because of ultrasonic dispersion and boiling function. The TEM further proves the inference mentioned above. Fig. 4 shows that the granularities of undoped TiO<sub>2</sub> particles spread at about range of 50–70 nm (Fig. 4b), while the doped TiO<sub>2</sub> particles become smaller than undoped TiO<sub>2</sub> particles and their granularities are only 20–30 nm (Fig. 4a).

### 3.3. The Influences of irradiation time on the degradation ratio of azo fuchsine

Fig. 5 shows the comparison of photocatalytic degradation ratio of azo fuchsine solution (of 10 mg/L initial concentration) between in the presences of doped and undoped nano TiO<sub>2</sub> powders (of 1000 mg/L addition amount) under the visible light irradiation at different moment. It can be seen that the photocatalytic activity of doped nano TiO<sub>2</sub> powder is obviously better than that of undoped nano TiO<sub>2</sub> powder. The degradation ratio in the presence of doped nano TiO<sub>2</sub> powder increases fleetly with the irradiation time and attains about 95% at 24 h, while the degradation ratio in the presence of undoped nano TiO<sub>2</sub> powder is only 21% at the same time. Finally, the azo fuchsine in solution are decomposed completely within 45 h, but the highest degradation ratio in the presence of undoped nano TiO<sub>2</sub> powder is only about 30% beyond 50 h.

In addition, Fig. 6 indicate that the reactions of photocatalytic degradation of azo fuchsine in the presence of both doped and undoped TiO<sub>2</sub> powders accord with the first order kinetics. The rate constant ( $0.133 \text{ h}^{-1}$ ) catalyzed by doped TiO<sub>2</sub> powder is head and shoulders above that ( $0.009 \text{ h}^{-1}$ ) by undoped TiO<sub>2</sub> powder.

### 3.4. 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 fuch-

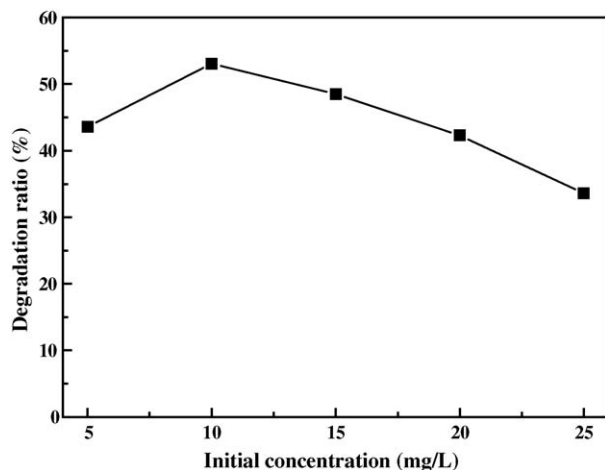


Fig. 7. Influence of initial concentration on degradation ratio of azo fuchsine.

sine on the photocatalytic degradation ratio was investigated over the concentration range of 5.0–25.0 mg/L and the adding amount of photocatalyst is 1000 mg/L. It can be seen from Fig. 7 that within the certain time period (10 h), as the increase of azo fuchsine initial concentration, the degradation ratio firstly ascend until up to the maximum whose corresponding concentration is about 10 mg/L, and then decline following the unceasingly increase of initial concentration. This is just the ordinary law of photocatalytic degradation reaction using TiO<sub>2</sub> powder as photocatalyst. The increase of initial concentration is bound to weaken the transmission ability of various lights for the solution and also subsequently decrease the light intensity that arrive at the surface of doped nano TiO<sub>2</sub> catalyst. In this case, the doped nano TiO<sub>2</sub> powder in solution cannot operate adequately, which is just the reason why degradation ratio decline for high concentration dye wastewater. Therefore, a proper initial concentration should be chosen in order to get an ideal degradation ratio.

### 3.5. The influences of addition amount of TiO<sub>2</sub> catalyst on the degradation ratio of azo fuchsine

The effect of adding amount of doped nano TiO<sub>2</sub> catalyst on the photocatalytic degradation of azo fuchsine solution (10 mg/L) was studied by varying the adding amount of doped TiO<sub>2</sub> powder from 500 to 2000 mg/L. Fig. 8 shows the changes of degradation ratios along with various catalyst adding amount by visible irradiation for 10 h. It can be seen that the adding amount of TiO<sub>2</sub> catalyst has a significant effect on the degradation ratio. At beginning the adding of doped nano TiO<sub>2</sub> catalyst can enhance the degradation ratio at a large extent compared with one-fold visible irradiation. After adding amount of 1000 mg/L the degradation ratio begin to decline slightly with the increase of TiO<sub>2</sub> catalyst. It indicates that an optimized adding amount of TiO<sub>2</sub> catalysts is necessary for enhancing the degradation ratio. The redundant nano TiO<sub>2</sub> catalysts mutually defilade among TiO<sub>2</sub> particle and then weaken the transmission ability of light.

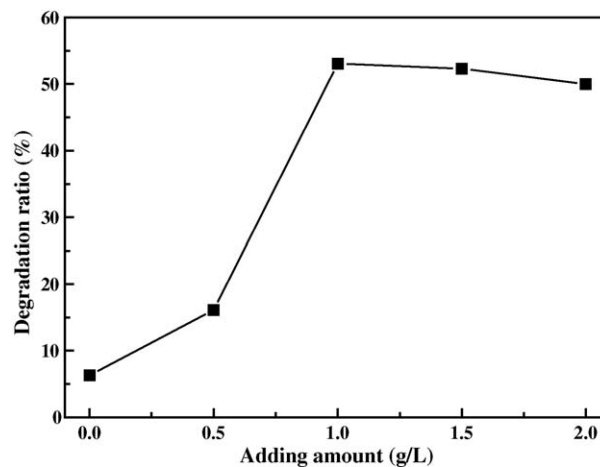


Fig. 8. Influence of addition amount of photocatalyst on degradation ratio of azo fuchsine.

### 3.6. Photocatalytic principle of nano doped TiO<sub>2</sub> catalyst

In the last decade, many researches have been bound up in extending the absorption range of TiO<sub>2</sub> photocatalysts for light adopting manifold methods, but we think it is unadvisable somewhat. Theoretically, in order to fill the role of the photocatalyst effectively, the TiO<sub>2</sub> powder must absorb the ultraviolet light ( $\lambda < 387$  nm). In general, the various wavelength lights can all excite the TiO<sub>2</sub> photocatalyst to produce the free electrons and cavities on the surface or in the interior of the TiO<sub>2</sub> particles. All free electrons should be identical in the energy or reductive ability, but the cavities from the excitation of different wavelength lights are different, namely they should have different oxidative ability along with different light irradiation. Hence, the cavities excited by long wavelength lights (for example, visible light) have low oxidative abilities and then easily recombine with other free electrons, while the cavities excited by short wavelength lights (for example, ultraviolet lights) have high oxidative abilities. According to our design as shown in Fig. 9, firstly, the upconversion luminescence agent doped in the nano rutile TiO<sub>2</sub> powder absorbs the visible lights and then turn them into ultraviolet lights those can effectively excite the nano TiO<sub>2</sub> particles to generate the high active cavities. These cavities having high

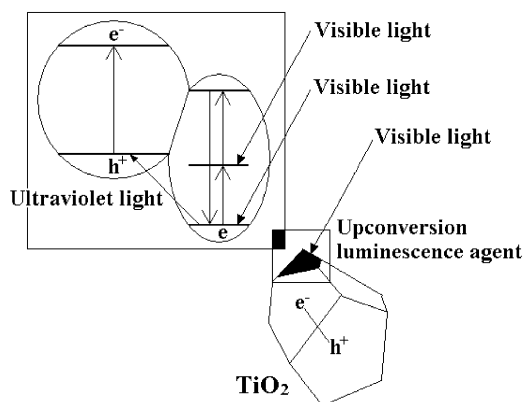


Fig. 9. Principle on excitation of nano TiO<sub>2</sub> doped upconversion luminescence agent by visible light.

oxidative ability not only can directly decompose the organic pollutants in wastewaters around them, but also can degrade the organic pollutants indirectly through oxidating H<sub>2</sub>O molecular to get •OH radicals that also possess strong oxidative ability.

#### 4. Conclusion

- (1) A new upconversion luminescence agent, 40CdF<sub>2</sub>·60BaF<sub>2</sub>·1.0Er<sub>2</sub>O<sub>3</sub>, was synthesized and its upconversion luminescence character was also determined by fluorescent spectrometer. The fluorescent spectrum shows that this upconversion luminescence agent can emit five upconversion luminescence peaks whose wavelengths are all below 387 nm in the range of 200–450 nm under the excitation of 488 nm visible light. The new upconversion luminescence agent including erbium possess following advantages compared with other hitherto upconversion luminescence agents: prepared method is more easily, conversion efficiency is higher and ultraviolet emission intensity is also higher.
- (2) This upconversion luminescence agent was mixed into nano rutile TiO<sub>2</sub> powder by ultrasonic and boiling dispersal and a novel doped nano TiO<sub>2</sub> photocatalyst having high photocatalytic activity under visible light irradiation was obtained firstly.
- (3) The degradation ratio of azo fuchsine in the mixed solution in the presence of nano TiO<sub>2</sub> doped with upconversion luminescence agent can attain about 70% within 12 h under visible light irradiation, while the corresponding degradation ratio in the presence of undoped nano TiO<sub>2</sub> powder is only 13% at the same time. Finally, the azo fuchsine can completely be decomposed in the presence of nano doped TiO<sub>2</sub> within about 45 h, but the corresponding degradation ratio in the presence of undoped nano TiO<sub>2</sub> powder is only 25% even above 55 h.

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