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Degradation of dyestuff wastewater using visible light in the presence of a novel nano TiO₂ catalyst doped with upconversion luminescence agent

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Abstract: A new upconversion luminescence agent, 40CdF₂ · 60BaF₂ · 0.8Er₂O₃, was synthesized and its fluorescent spectra were determined. This upconversion luminescence agent can emit five upconversion fluorescent peaks shown in the fluorescent spectra whose wavelengths are all below 387 nm under the excitation of 488 nm visible light. This upconversion luminescence agent was mixed into nano rutile TiO₂ powder by ultrasonic and boiling dispersion and the novel doped nano TiO₂ photocatalyst utilizing visible light was firstly prepared. The doped TiO₂ powder was characterized by XRD and TEM and its photocatalytic activity was tested through the photocatalytic degradation of methyl orange as a model compound under the visible light irradiation emitted by six three basic color lamps. In order to compare the photocatalytic activities, the same experiment was carried out for undoped TiO₂ powder. The degradation ratio of methyl orange in the presence of doped nano TiO₂ powder reached 32.5% under visible light irradiation at 20 h which was obviously higher than the corresponding 1.64% in the presence of undoped nano TiO₂ powder, which indicate the upconversion luminescence agent prepared as dopant can effectively turn visible lights to ultraviolet lights that are absorbed by nano TiO₂ particles to produce the electron-cavity pairs. All the results show that the nano rutile TiO₂ powder doped with upconversion luminescence agent is a promising photocatalyst using sunlight for treating the industry dye wastewater in great force.

Keywords: upconversion luminescence agent; nano TiO₂; photocatalytic degradation; visible light; methyl orange

Introduction

Every year, the dyeing processes and dye production bring large amounts of wastewaters containing high concentration poisonous organic compounds (Neppolian, 2002; An, 2002). If not being treated properly and betimes, the wastewaters will seriously contaminate the environments. Known the ponderance of these problems people have already begun to treat these toxic wastewaters adopting all kinds of methods (Juan, 1984; Moza, 1988; Shen, 1995). Because the structures of these organic dye compounds in wastewaters usually contain one or several benzene rings, these organic pollutants can not be decomposed easily and completely using ordinary chemical and biological methods. In recent years, many attentions have been paid to the method of semiconductor-based photocatalytic degradation to treat these dye wastewaters (Fox, 1993; Hoffmann, 1995). TiO₂ is widely used to photodegrade many organic pollutants for its relatively high catalytic reactivity, physical and chemical stability, avirulence and cheapness and so on (Heller, 1995; Linsebigler, 1995; Hadjiivanov, 1996). However, because of its broad band-gap ($E_g = 3.2-4.5$ eV), only under irradiation of ultraviolet light ($\lambda < 387$ nm) TiO₂ can effectively destroy the organic pollutants in wastewaters. In general, the sunlight only contains 3%—4% ultraviolet light, so it is impossible to utilize sunlight directly for activating TiO₂ photocatalyst effectively. Hence, the method of photocatalytic degradation needs costly equipments and large numbers of energies as light source, which is a big burden for many countries, especially for the 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 TiO₂ catalysts, namely, making the

TiO₂ powders as photocatalysts absorb the visible light at full steam. Many reformative methods were adopted such as doping of transition-metal ions (Diebold, 2003; Nagaoka, 2002), combination of narrow band-gap semiconductors (Kamat, 1993; Yu, 2003) and aggradation of noble metals (Shchukin, 2003; Moreau, 2004) as well as some other special treatments, for example: ultraviolet light irradiation and ultrasonic dispersion during preparation, H₂O₂ dipping and so on (D'Amore, 1999; Tokudome, 2004; Ooka, 2004; Yu, 2001). Whereas, we do not think these methods can really improve the photocatalytic activity of TiO₂ catalysts. 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 that from visible lights. Only the cavities those excited by 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 H₂O molecule in wastewaters to generate the hydroxyl(\cdot OH) radicals having high oxidative ability. Even though the excitation wavelength range of TiO₂ catalysts is extended to visible lights unilaterally and blindly, it is difficult to obtain the better degradation effect. This is the reason why the genuine photocatalysts fitting for visible lights have not been obtained up till now. Customarily, their catalytic activities are very low or the increased extent of absorption wavelength is comparatively small, which is only about 60 nm (from 387 nm to 450 nm). For this reason, we have considered whether there are some substances that can turn visible lights into ultraviolet lights to satisfy the requirement of TiO₂ catalysts. Fortunately, the upconversion luminescence materials are just what we want to adulterate to TiO₂ catalysts. In this work, a new upconversion

luminescence agent containing rare earth Er element was synthesized and then mixed into the nano rutile TiO₂ powders by ultrasonic dispersion. Lastly, an unreported doped nano TiO₂ 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 TiO₂ photocatalyst could effectively decompose the methyl orange in solution under visible light irradiation. It can be forecasted that the nano TiO₂ catalyst doped with upconversion luminescence agent is a promising photocatalyst utilizing sunlight which will widely be used to treat various wastewaters.

1 Experimental

1.1 Apparatus and materials

Three basic color lamp (FL40T8EXD/36, Toshiba, Japan); UV-Vis spectrometer (LAMBDA-17, Perkin-Elmer, USA); Fluorescent spectrometer (F-4500, 150W Xe lamp, Hitachi Japan). Methyl orange (Aldrich, USA); nano TiO₂ (Rutile, Aldrich, USA); Er₂O₃ (Aldrich, USA); CdF₂ (Aldrich, USA); BaF₂ (Aldrich, USA).

1.2 Preparation of upconversion luminescence agent

Five grams mixed powders as total amount of CdF₂, BaF₂ and Er₂O₃ with molar ratio of 40:60:0.8 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 TiO₂ photocatalyst. The upconversion luminescence property was detected by spectrofluorimeter under excitation of 488 nm wavelength visible light. The upconversion fluorescence spectrum was shown in Fig. 1.

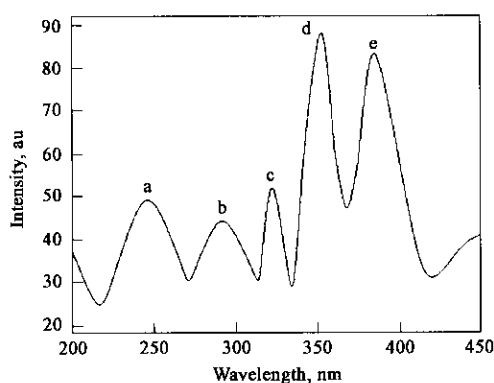


Fig. 1 Emission spectra of upconversion luminescence agent
a: ${}^2I_{11/2} \rightarrow {}^4I_{5/2}$ (243 nm); b: ${}^2I_{11/2} \rightarrow {}^4I_{3/2}$ (291 nm); c: ${}^2I_{11/2} \rightarrow {}^4I_{11/2}$ (324 nm); d: ${}^2I_{11/2} \rightarrow {}^4I_{9/2}$ (351 nm); e: ${}^2H_{9/2} \rightarrow {}^4I_{11/2}$ (378 nm)

1.3 Preparation of nano TiO₂ doped upconversion luminescence agent

The mixture of 0.16 g upconversion luminescence agent and 7.84 g nano rutile TiO₂ powder were added into 100 ml beaker containing 30 ml distilled water and adequately dispersed by ultrasound of 80 kHz frequency and 50 W output power for 15 min. The suspended liquid was 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 rate of 2.0 °C/min and then the temperature was maintained at 500°C for 3.0 h and the doped nano TiO₂ powder was attained. For comparison, the original nano TiO₂ powder was also treated by the same procedure. The X-ray diffraction (XRD) and transmission-electron microscope (TEM) of undoped and doped nano TiO₂ powders were determined as shown in Fig. 2 and Fig. 3, respectively.

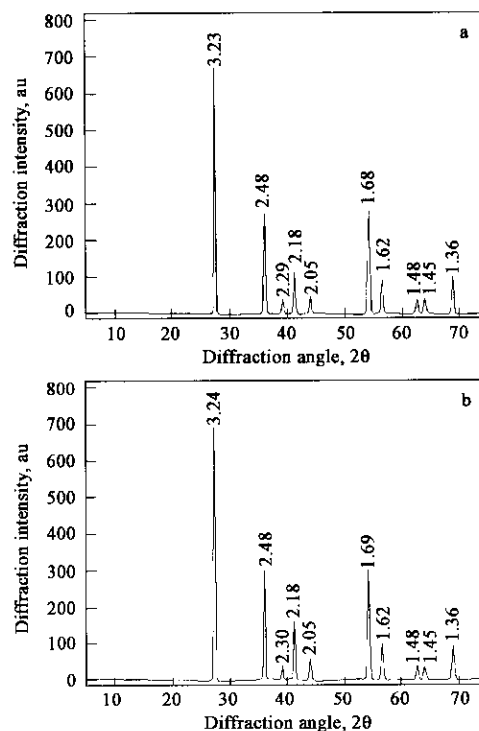


Fig. 2 XRD of nano TiO₂ powders
a. undoped nano rutile TiO₂; b. doped nano rutile TiO₂

1.4 Analysis method

The UV-Vis spectra of the original methyl orange solution and degradative methyl orange solution were determined by UV-Vis spectrophotometer in the wavelength range from 190 to 700 nm. The maximal absorbency of methyl orange solution below the concentration 100 mg/L abides by Lambert-Beers' law and the standard calibration curve of methyl orange solutions is used to estimate the degradation ratio of methyl orange.

1.5 Measurement of photocatalytic activity of doped nano TiO₂ catalyst

A hundred milliliters methyl orange solution (10 mg/L) prepared and 100 mg nano TiO₂ doped with upconversion luminescence agent powder were put into the conical flask, and the mixed solution was stirred for 20 h without any irradiation for the purpose to attain the balance between absorption and desorption. Then small amount of mixed solution was taken out and centrifuged. The separated upper methyl orange solution was used for determining UV-Vis spectra as shown in Fig. 4. After that, six 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 methyl orange solution till to 20 h. For comparison, the photocatalytic activity of

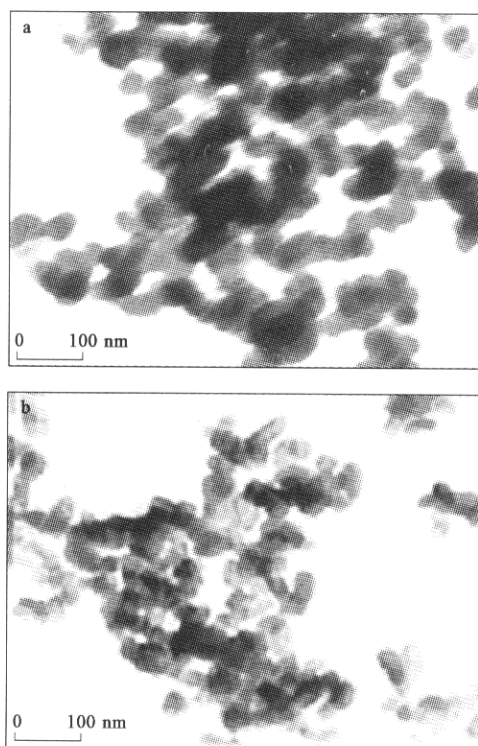


Fig. 3 TEM of nano TiO₂ powders
a. undoped nano rutile TiO₂; b. doped nano rutile TiO₂

undoped nano TiO₂ was also measured following the same procedure and all the results were shown in Fig. 5. The systemic temperatures were controlled within $25.0 \pm 0.2^\circ\text{C}$ throughout whole experiment.

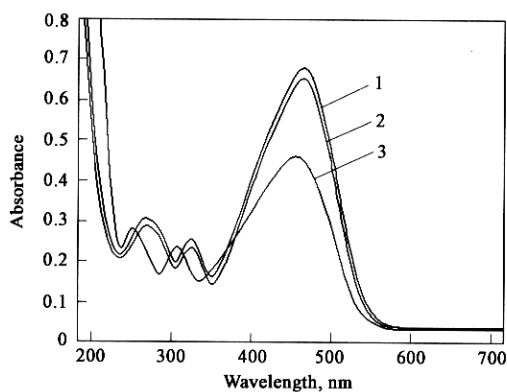


Fig. 4 UV-Vis spectra of methyl orange solution
1: 0.0 h (original solution); 2: 20.0 h (lightproofing after adding doped TiO₂); 3: 20.0 h (irradiating after adding doped TiO₂)

2 Results and discussion

2.1 Fluorescence spectra of upconversion luminescence agent

When the prepared upconversion luminescence agent, $40\text{CdF}_2 \cdot 60\text{BaF}_2 \cdot 0.8\text{Er}_2\text{O}_3$, was excited with visible light irradiation of 488 nm wavelength, five emission peaks in the region of 200–450 nm (Fig. 1) were detected. These signals were thought to correspond with $^2I_{11/2} \rightarrow ^4I_{15/2}$ (a: 243 nm), $^2I_{11/2} \rightarrow ^4I_{13/2}$ (b: 291 nm), $^2I_{11/2} \rightarrow ^4I_{11/2}$ (c: 324 nm), $^2I_{11/2} \rightarrow ^4I_{9/2}$ (d: 351 nm) and $^2H_{9/2} \rightarrow ^4I_{11/2}$ (e: 378 nm),

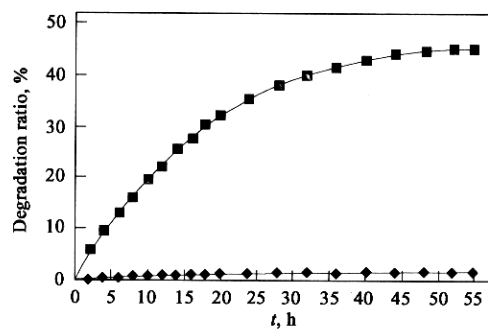


Fig. 5 Influence of irradiation time on degradation ratio of methyl orange
■: irradiation + doped nano TiO₂; ◆: irradiation + undoped nano TiO₂

respectively. All these signals exhibited quadratic dependence on pump power, suggesting that only two photons are involved in the upconversion process. The wavelengths of these emission peaks were all shorter than that effectively exciting TiO₂ catalyst, which shows that this upconversion luminescence agent can supply the ultraviolet light that the nano TiO₂ catalyst need.

2.2 XRD and TEM of doped nano TiO₂ catalyst

The XRD shows that the doped TiO₂ powder basically retains the rutile structure other than the positions and intensities of some diffraction peaks change slightly comparing the undoped TiO₂ powder. However, it is noteworthy that some diffraction peaks (Fig. 2b) of doped TiO₂ powder appreciably broaden comparing with ones (Fig. 2a) of undoped TiO₂ powder, which indicates that the granularities of doped TiO₂ particles become thin because of ultrasonic dispersion and boiling function. The TEM proves the guesswork mentioned above. Fig. 3 shows that the granularities of undoped TiO₂ particles spread at about range of 50–70 nm (Fig. 3a), while the doped TiO₂ particles become smaller than undoped TiO₂ particles and their granularities are only 20–30 nm (Fig. 3b).

2.3 UV-Vis spectra of methyl orange solution

Fig. 4 shows three UV-Vis spectra of original methyl orange solution (curve 1), mixed solutions of methyl orange and doped nanometer TiO₂ powder without visible light irradiation (curve 2) and under visible light irradiation (curve 3), respectively. The methyl orange solution gives three absorption peaks in the range of 200–600 nm corresponding to the benzene ring and azo bond in methyl orange molecule without adjusting any pH values. It is found that the methyl orange is obviously degraded in the presence of doped nano TiO₂ powder under the visible light irradiation at 20 h compared with the original methyl orange solution. Furthermore, it can be judged that the adsorptive amount of methyl orange on the surface of doped nano TiO₂ powder hardly influence the calculation of the degradation ratio in the presence of doped nano TiO₂ powder. In addition, all absorption peaks obviously decline along with the visible light irradiation, which indicate the benzene ring and azo bond in methyl orange molecule are simultaneously destroyed under the associated function of visible light irradiation and doped nano TiO₂ powder.

2.4 Influences of irradiation time on the degradation ratio of methyl orange

Fig. 5 shows the comparison of photocatalytic degradation ratio of methyl orange between the doped and undoped nano TiO₂ powders under the visible light irradiation at different moment. It can be seen that the photocatalytic activity of doped nano TiO₂ powder is obviously better than that of undoped nano TiO₂ powder. The degradation ratio in the presence of doped nano TiO₂ powder increase fleetly with the visible light irradiation and attain about 46.5% at 55 h, while the degradation ratio in the presence of undoped nanometer TiO₂ powder is only 1.66% at exceeding 55 h.

2.5 Photocatalytic principle of nano doped TiO₂ catalyst

Many researches have been bound up in extending the absorption range of TiO₂ catalysts for light adopting manifold methods, but we think it is unadvisable. Theoretically, in order to assume the role of the photocatalyst effectively, the TiO₂ powder must absorb the ultraviolet light ($\lambda < 387$ nm). The various wavelength lights can all excite the TiO₂ powder to produce the free electrons and cavities on the surface or in the interior of the TiO₂ particles. All free electrons should be identical in the energy and 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 the 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.6, firstly, the upconversion luminescence agent doped in the nano rutile TiO₂ powder absorbs the visible lights and then turn them into ultraviolet lights that can effectively excite the nano TiO₂ particles to generate the high active cavities. These cavities having high oxidative ability not only can directly decompose the organic pollutants in wastewaters around them but also can degrade the organic pollutants indirectly through oxidating H₂O molecular to get \cdot OH radicals that possess strong oxidative ability.

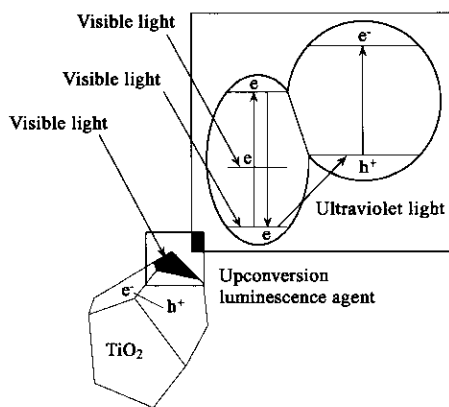


Fig. 6 Principle on excitation of nano TiO₂ doped upconversion luminescence agent by visible light

3 Conclusions

A new upconversion luminescence agent, 40CdF₂ · 60BaF₂ · 0.8Er₂O₃, was synthesized and its upconversion

luminescence character was also determined by fluorescent spectrometer. The fluorescent spectra show that the 40CdF₂ · 60BaF₂ · 0.8Er₂O₃ 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. This upconversion luminescence agent was mixed into nano rutile TiO₂ powder by ultrasonic and boiling dispersal and the novel doped TiO₂ photocatalyst having high photocatalytic activity under visible light irradiation was obtained. The degradation ratio of methyl orange in the presence of nano TiO₂ doped with upconversion luminescence agent can attain about 46.5% within 55 h under visible light irradiation in the mixed solution, while the corresponding degradation ratio in the presence of undoped nano TiO₂ powder is only 1.66% even above 55 h.

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