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Preparation of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film and application in visible light photocatalytic degradation of organic dyes

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ABSTRACT

In this work, to solve the problem of low sensitivity of titanium dioxide (TiO_2) to visible light, the Er^{3+}:$Y_3Al_5O_{12}$ as up-conversion luminescence agent was mixed with TiO_2 and then Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film, a novel visible light photocatalyst, was obtained through sol–gel dip-coating method. The Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film was characterized by X-ray diffraction and scanning electron microscope. Its photocatalytic activity was examined through the degradation of some organic dyes under visible light irradiation. The degradation process of organic dyes was monitored by UV–vis spectrophotometer. Furthermore, some main influence factors on the photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film such as Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 mass ratio, layer number, heat-treated temperature, and heat-treated time were studied. The results indicate that three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film with 0.3:1 mass ratio heat treated at 500℃ for 60 min displays a high photocatalytic activity during visible light photocatalytic degradation of Azo Fuchsine. The recycling used times were also included in consideration. Finally, it can be predicted that the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film displays a good and broad-spectrum photocatalytic activity for degradation of most organic dyes.

Keywords: Up-conversion luminescence; Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film; Photocatalytic degradation; Organic dyes

1. Introduction

Wide band gap ($E_g = 3.2$ eV) semiconductor oxide, titanium dioxide (TiO_2), which attracts much attention in recent years, has been studied in a wide range of fields due to its unique physical and chemical properties, such as high refractive index, high dielectric constant, and photocatalytic activity [1–3]. These properties can be used in many applications, for example, the dissolution of hazardous volatile organic compounds (VOC), the removal of endocrine disrupters, the recovery of heavy metal, anti-fogging, decontamination, self-cleaning, etc. [4,5]. In particular, TiO_2 as a photocatalyst has been found to be extremely effective for the complete mineralization of virtually all organic compounds and for the inactivation of pathogenic micro-organisms present in contaminated water [6,7].

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However, highly dispersed TiO_2 particles in suspension are too difficult to be removed from aqueous phase after their application when they were used in the photocatalysis reaction. The filtration procedure requirements posed a considerable challenge to scale up bench-scale reactors in the experiment and practical application. Furthermore, the catalyst particles may become a cause of turbidity in the effluent as a secondary pollutant. The most regretful thing is that the TiO_2 particles could not be reused many times since they are difficult to be collected. Recently, many researches have been carried out to immobilize TiO_2 catalyst onto various substrates as thin films or membranes though their catalytic surface area becomes relatively lower than that of decentralized TiO_2 particles in suspension [6–8]. For instance, Ganesh Balasubramanian prepared TiO_2 films, respectively, on flat stainless steel substrates and on glass beads [9]. Kimoto proposed a pair of Polyvinylidene Fluoride (PVDF) films coated on transparent conductive electrodes (ITO electrodes) successfully [10]. Considering the full use of light and the preparation for manufacturing the corresponding equipment in future, we think that loading catalyst on the surface of glass is more reasonable.

In addition, it is worth noting that the absorption spectrum of TiO_2 is so narrow that it can only use ultraviolet light ($\lambda < 387\,\text{nm}$) to be activated [2,9,11]. However, the ultraviolet light in solar spectrum is less than 5%. As a result, such finite ultraviolet light is not enough to stimulate TiO_2 and the use efficiency of solar energy is severely limited. In this field, several methods have been put forward to solve the problem of low degradation efficiency of organic pollutants when using TiO_2 as a photocatalyst [12–14]. Generally speaking, great majority of them are through the doping methods to modify the TiO_2. Many researchers doped some metal ions (Fe, Co, and Ni) or nonmetallic elements (N, B, and S) into TiO_2 to improve its photocatalytic activity [15–18]. Through the above methods, the absorption spectrum of TiO_2 has been expanded to a certain degree, but it is still not satisfactory to utilize solar energy extensively. As a brand new design, using up-conversion luminescence agent may be a very promising way to improve utilization rate of the solar light. These up-conversion luminescence agents, such as $NaYF_4$:Yb/Er, $CaSc_2O_4$:Yb/Er, and SrS:Eu/Sm, can absorb two or more low-energy photons and then emit a higher energy photon to the extent that can transform red, green, and blue light in visible light region to ultraviolet light [19–21]. It could be conveniently available by doping with Eu^{3+}, Tm^{3+}, Er^{3+}, Ce^{3+}, and Pr^{3+} ions which have been used widely in many fields [22,23]. In recent years, we have done a lot of researches about the application of solar energy using up-conversion luminescence materials [24–27]. Some up-conversion luminescence agents have been used in the previous works, such as Er^{3+}:$Y_3Al_5O_{12}$, Er^{3+}:$YAlO_3$, and Er^{3+}:$YFeO_3$. Among them, Er^{3+}:$Y_3Al_5O_{12}$ has been widely used in photocatalytic degradation and hydrogen production due to its high-conversion luminescence efficiency and chemical stability [28,29]. Therefore, we have been trying to use the Er^{3+}:$Y_3Al_5O_{12}$ to prepare the TiO_2 composite film and then perform the visible light photocatalytic degradation. In this work, we devise an experiment which adds up-conversion luminescence agents owning to high up-conversion luminescence efficiency into TiO_2 sols to obtain the TiO_2 composite film. Based on this design, we get a kind of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite thin film by simple sol–gel dip-coating method which was deposited on soda lime glass at room temperature.

The purpose of this paper was to investigate the change of photocatalytic performance of TiO_2 film during degradation of organic pollutants after adding Er^{3+}:$Y_3Al_5O_{12}$ as up-conversion luminescence agent. In addition, the effects of heat-treated temperature and heat-treated time on the visible light photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film was considered. In succession, as an important factor influencing the photocatalytic performance of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film, the mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 were also studied. Besides, some key conditions such as layer number of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film, initial concentration of organic dye, photocatalyst amount, and kind of organic dyes were examined. Because the Azo Fuchsine was usually contained in the industrial dye wastewater, it was selected as a model contaminant in this work.

2. Experimental section

2.1. Materials

In the present study, the raw materials used were tetrabutyl titanate ($Ti(OBu)_4$), ethanol (C_2H_5OH), acetic acid (CH_3COOH), distilled water (H_2O), and nitric acid (HNO_3). $Ti(OBu)_4$ as TiO_2 precursor and CH_3COOH as inhibitor were all analytically pure made by Sinopharm Chemical Reagent Co., Ltd in China. C_2H_5OH (99.5%) was obtained from Shenyang XinHua Chemical Reagent Factory in china and HNO_3 (65%) was obtained from Veking Company in China. The erbium oxide (Er_2O_3, 99.999%), yttrium oxide (Y_2O_3, 99.999%), aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, analytical pure), and citric acid ($C_6H_8O_7{\cdot}H_2O$, analytical pure) were all purchased from Veking Company in China. The substrates were Fragata glass slide made in China whose specification is 25 × 75 mm and the thickness is about 1.2 mm. Furthermore, several organic dyes (methylene blue (MB), acid red B (AR-B), Congo red (CR), methyl orange (MO), and Rhodamine B (RM-B)) (99.99% purity, Tianjin Kaiyuan Reagent Corporation, China) were used to undergo the photocatalytic degradation under visible light irradiation.

2.2. Synthesis of Er^{3+}:$Y_3Al_5O_{12}$ as up-conversion luminescence agent

At first, $Y(NO_3)_3$ and $Er(NO_3)_3$ solutions were prepared by dissolving stoichiometric Y_2O_3 (2.2715 g) and Er_2O_3 (0.0128 g) into appropriate hot HNO_3 (30 ml) solution (about 60℃). Calculated amount of $Al(NO_3)_3{\cdot}9H_2O$ (12.6208 g) was dissolved in 30 mL H_2O [30]. Then $C_6H_8O_7{\cdot}H_2O$ was added as chelating agent and assistant solvent (mol ratio of citric acid: metal ion is 3:1). The created solution was stirred and heated at 50–60℃ until the transparent sol was successfully prepared. Afterward, the sol was heated at 80℃ for 30 min and became the semitransparent gel which was ground into fine homogeneous powders. The collected powders were heated at 500℃ for 50 min, and then kept at 1,100℃ for 2.0 h. The Er^{3+}:$Y_3Al_5O_{12}$ powder was obtained which needs to be grinded adequately.

2.3. Preparation of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films as photocatalyst

The $Ti(OBu)_4$ (TBT) was used as a precursor and the TiO_2 sol was prepared at room temperature as follows [31]. Firstly, the TBT (10 mL) was dissolved in C_2H_5OH (40 mL) and stirred for half an hour to get a precursor solution. Then a mixture solution, whose molar ratio of C_2H_5OH:H_2O:CH_3COOH was controlled at 1:10:2:1, was dropped into the precursor solution at a speed of one drop per second under a strong stirring. After that, the solution was continuously stirred until reaching a yellow transparent solution. The solution was then aged for a period of time to be used.

The pure TiO_2 and Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films were prepared via sol–gel process using sheet glass as substrate. For the preparation of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films, firstly, fully ground Er^{3+}:$Y_3Al_5O_{12}$ powders were added into TiO_2 sol kept under stirring for 1.0 h. And then a dip-coating method was used for the deposition of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films. Prior to the coating process, the sheet glass was washed with water, ultrasonically cleaned in C_2H_5OH for 20 min, and in acetone for 20 min, respectively. Then the sheet glass was dipped in the TiO_2 precursor sol with a withdrawing rate of 0.6 cm/s. After each coating, the films were first dried at 100℃ for 60 min. The films were then heat treated at different temperatures and different treatment times, respectively.

2.4. Procedure

Degradation experiments were carried out in a petri dish of 120 mm diameter under simulated visible light irradiation for 240 min. In this experiment, three prepared Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 films were used to treat the Azo Fuchsine solution with 10 mg/L concentration in 50 mL total volume. The films obtained in different conditions were abreast placed well into Azo Fuchsine solutions in petri dish. Before visible light irradiation, the above device was put in the dark for 30 min, which makes Azo Fuchsine molecules in aqueous solution reach the equilibrium of adsorption and desorption. In this period, it is found that the adsorption capacity is so small that the concentration change can be neglected in the calculation of degradation ratio. After an appreciable time of irradiation, the degradation of organic dyes was measured by UV–vis spectrometer. Three-basic-color lamp with irradiation intensity of 224 W/m^2 was used as a simulated visible light irradiation source.

2.5. Characterization

The prepared Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film were characterized by X-ray powder diffractometer (D-8, Bruker-axs, Germany, Ni filtered Cu $K\alpha$ radiation in the range of 2θ from 10° to 70°) and scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan). The UV–vis spectrometer (Cary 50, Varian Company, USA) was used to measure the photocatalytic activity through the degradation of some organic dyes in aqueous solution.

3. Results and discussion

3.1. X-ray diffraction patterns of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films

The XRD of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film with different mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 (three layers heat treated at 500℃ for 60 min) and with different layer numbers (0.3:1 proportion heat treated at 500℃ for 60 min) are shown in Fig. 1(a) and (b), respectively. In addition, the XRD of Er^{3+}:

$Y_3Al_5O_{12}/TiO_2$ film heat treated at different temperatures for 60 min and different heat-treated times at 500°C, respectively, is given in Fig. 1(c) and (d), respectively. As shown in the above figures, for relatively high heat-treated temperature, the crystal phases of nanosized TiO_2 are single anatase phase according to the characteristic diffraction peak at $2\theta = 25.50°$. However, for low heat-treated temperature (300°C), the amorphous phase of TiO_2 is mainly generated. Fig. 1(a) exhibits the typical XRD pattern of $Er^{3+}:Y_3Al_5O_{12}$ at $2\theta = 33.50°$. Obviously, when the $Er^{3+}:Y_3Al_5O_{12}:TiO_2$ is 0.4:1 the peaks of $Er^{3+}:Y_3Al_5O_{12}$ were more prominent than those of the other two, especially than that of $Er^{3+}:Y_3Al_5O_{12}:TiO_2 = 0.2:1$. For Figs. 1(b)–(d), because of relatively low content of $Er^{3+}:Y_3Al_5O_{12}$ in $Er^{3+}:Y_3Al_5O_{12}:TiO_2$ (0.3:1 proportion), the peaks of $Er^{3+}:Y_3Al_5O_{12}$ were inconspicuous. In addition, according to Fig. 1(b), it can be found that the peak intensity of four-layer $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ film was slightly stronger than that of three and two layers. It indicates that the $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ amount of four-layer film is much large, by contrast.

In general, the heat-treated temperature and heat-treated time during the preparation decide the crystal form of TiO_2 and combination of $Er^{3+}:Y_3Al_5O_{12}$ and TiO_2. Thus, they both affect the photocatalytic activity of $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite films. From Fig. 1(c), it can be seen that the $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite film heat treated at 700°C exhibits the highest diffraction peak at $2\theta = 25.50°$, and that at 300°C it hardly gives any diffraction peak. It indicates that the calcinations at lower temperature (300°C) lead to a low degree of crystallinity of TiO_2, and the $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite film is not well formed. At high temperature (700°C), on the one hand, the perfect crystal form of TiO_2 can be formed. However, it can be seen that the diffraction peaks at $2\theta = 38.24$°C (200) and 54.37°C (211), which belong to the characteristic diffraction peaks of rutile phase, appeared but very weak. On the other hand, the tightly combined $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite films can be obtained. Considering the high photocatalytic activity of anatase TiO_2, 500°C is generally used as heat-treated temperature, which can obtain the largest proportion of anatase TiO_2.

Fig. 1(d) showed that the diffraction peak intensity of $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite films increases along with the increase in heat-treated time. By careful

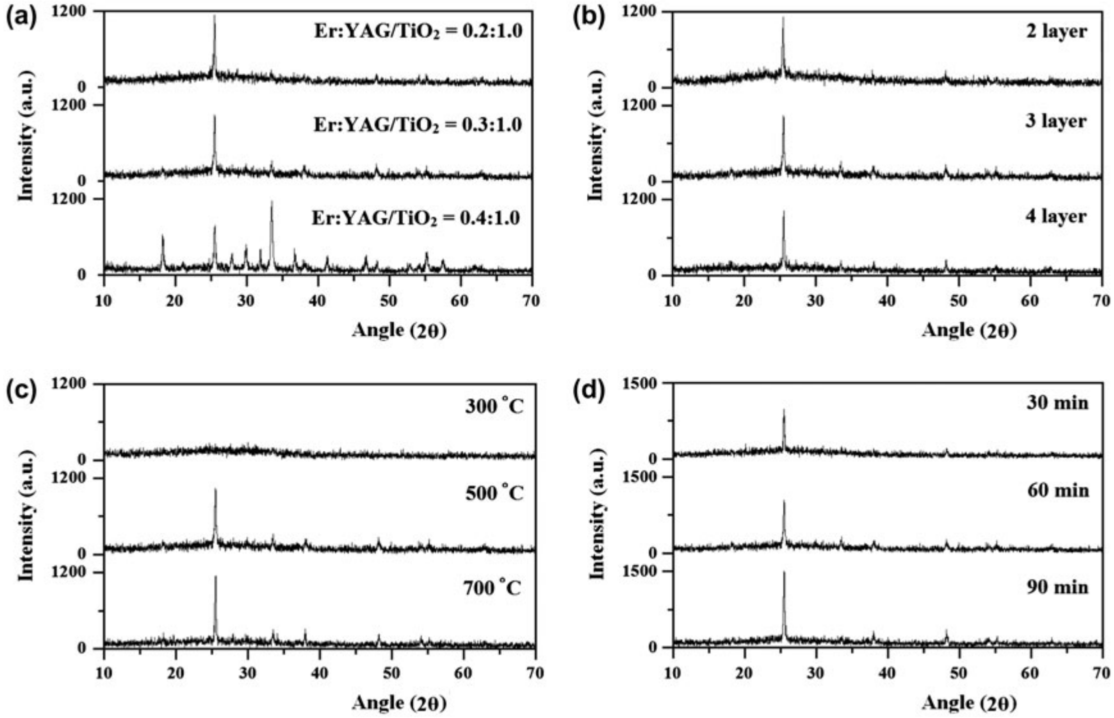

Fig. 1. XRD patterns of $Er^{3+}:Y_3Al_5O_{12}/TiO_2$ composite films with (a) different mass ratios of $Er^{3+}:Y_3Al_5O_{12}$ and TiO_2 (with three layers heat treated at 500°C for 60 min), (b) different layer numbers (with 0.3:1 mass ratios of $Er^{3+}:Y_3Al_5O_{12}$ and TiO_2 heat treated at 500°C for 60 min), (c) different heat-treated temperatures (with 0.3:1 mass ratios of $Er^{3+}:Y_3Al_5O_{12}$ and TiO_2 heat treated for 60 min), and (d) different heat-treated times (with 0.3:1 mass ratios of $Er^{3+}:Y_3Al_5O_{12}$ and TiO_2 heat treated at 500°C) (YAG: $Er^{3+}:Y_3Al_5O_{12}$).

observation, it could be found that the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film heat treated for 90 min exhibits the highest diffraction peak, which implies that long heat-treated time is in favor of the increase in TiO_2 crystallinity and formation of well-integrated Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films. Of course, considering the high photocatalytic activity of anatase TiO_2, 60 min is used as heat-treated temperature.

3.2. SEM images of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films

The external photos and SEM images of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films with different layer numbers are provided in Fig. 2. As shown in Fig. 2(a), it can be seen that, with the increase in the layer number of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film, the film thickness gradually increases. Simultaneously, the whiteness also increases, which indicates that the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film has become dense along with the increase in the layer number. In Fig. 2(b) (b-1, b-2, and b-3), the SEM images revealed that micro-sized gray particles, whose particle size is probably in the 80–100 nm range, were loaded on the surface of the glass, forming continuous and compact films. Also, on the basis of XRD measurement according to the Scherrer formula ($D = K\lambda/\beta\cos\theta$), the particle size could be calculated. The calculation results show that the average particle size is about 90 nm, which is consistent with the results obtained by SEM. Once again, thank you very much for your excellent work. In addition, it can be seen that there are a large number of particle with an average size of approximately 90 nm, which should be attributed to Er^{3+}:$YAlO_3$/TiO_2 particles. The nanosized Er^{3+}:$Y_3Al_5O_{12}$ particles have been basically coated by TiO_2 membrane through sol–gel method. The formed Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite particles in the form of films distribute on the surface of the glass.

3.3. Influences of molar proportion, layer number, heat-treated temperature, and heat-treated time on visible light photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film

As can be seen from Fig. 3(a), the degradation ratios of Azo Fuchsine in the presence of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film with different mass

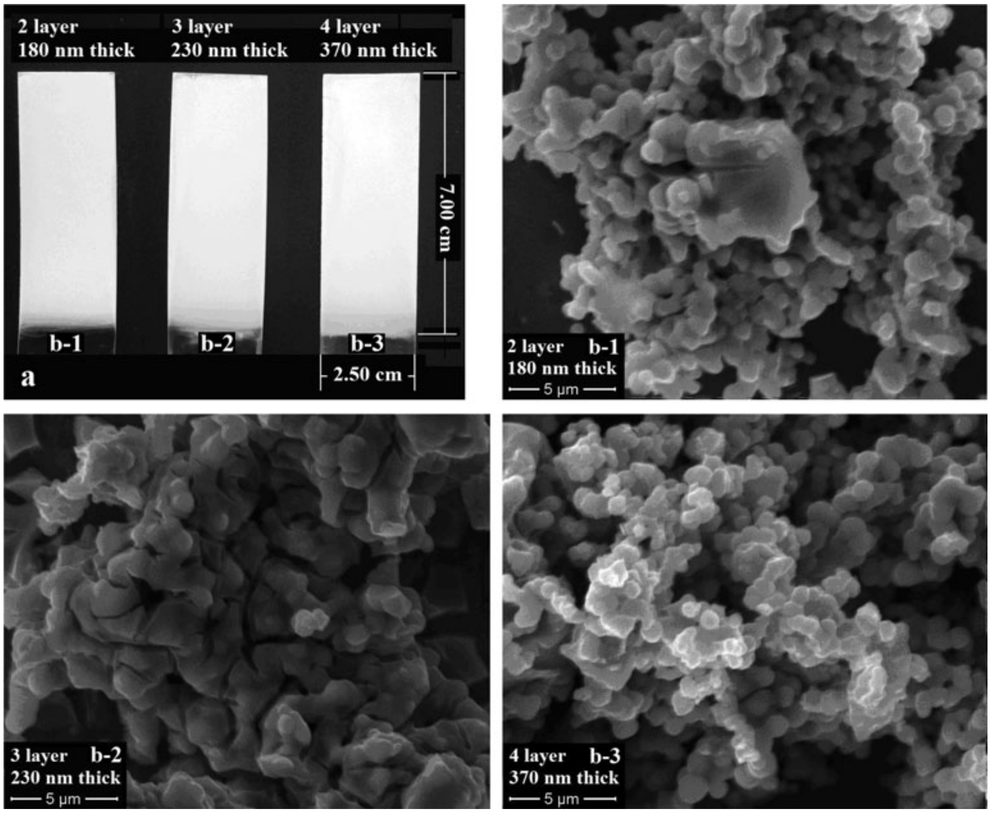

Fig. 2. SEM images of of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite films with different layer numbers (with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500°C for 60 min).

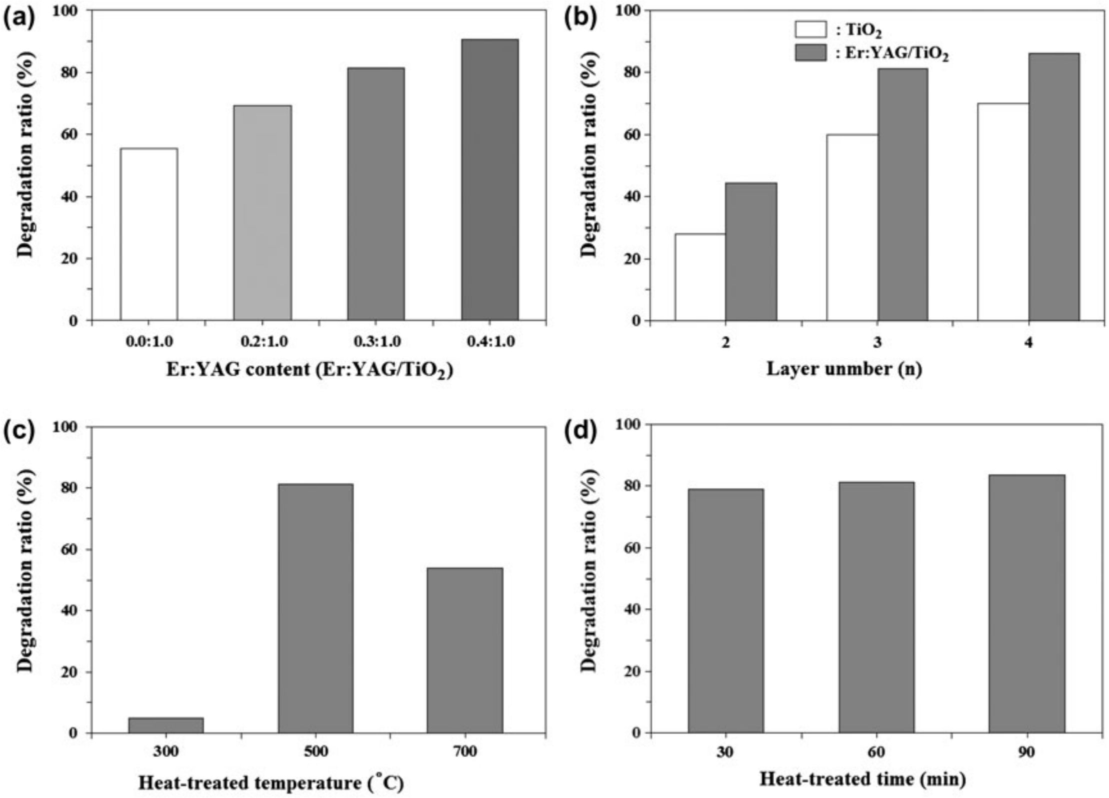

Fig. 3. The photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films with (a) different mass ratio of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 (with three layers heat treated at 500℃ for 60 min), (b) different layer numbers (with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃ for 60 min), (c) different heat-treated temperatures (with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated for 60 min), and (d) different heat-treated times (with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃) (YAG: Er^{3+}:$Y_3Al_5O_{12}$).

ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 are all higher than that (56.03%) in the presence of pure TiO_2 film. And when the mass ratio is 0.4:1.0, the photocatalytic degradation ration reaches the highest (90.58%). It indicates that the addition of Er^{3+}:$Y_3Al_5O_{12}$ obviously enhances the visible light photocatalytic activity of anatase TiO_2. However, the dose of Er^{3+}:$YAlO_3$ is increased to a certain extent, relative content of the catalyst is reduced, and thereby the photocatalytic reaction surface of pholocatalyst is reduced. So, the 0.3:1.0 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 were chosen as standard conditions in this experiment for comparison.

In the following, the effect of layer number on the visible light photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film was investigated and the corresponding experimental results are shown in Fig. 3(b). It can be found that for pure TiO_2 and Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films on sheet glasses, the degradation ratios of Azo Fuchsine both increase with the increase in layer number. However, the degradation ratios in the presence of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films are obviously higher than the corresponding ones in the presence of pure TiO_2 films at any layer number. It proves again that the photocatalytic activity of anatase TiO_2 can be enhanced using Er^{3+}:$Y_3Al_5O_{12}$. In addition, the photocatalytic activity of four-layer Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films is only slightly higher than that of three-layer Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films. It demonstrates that too many layer numbers of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films hardly enhance the photocatalytic activity compared with three-layer films. We think when the layer number of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films are three layers, the fixed area on the amount of catalyst has already saturated. Too many layer numbers of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite films not only showed significant improvement of photocatalytic activity, but also wasted the resources and increased the workload.

In general, heat-treated temperature and heat-treated time play an important role on the catalytic activity of semiconductor photocatalyst. In Fig. 3(c), it could be found that the Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film heat treated at 500°C exhibits the highest degradation ratio of 81.38%. Obviously, it is far above than that heat treated at 300 and 700°C. Maybe, when TiO_2 was calcined at 300°C, it didn't form anatase crystal phase which has high catalytic activity and only comes into being as carbonized material. Because of the above reason, its degradation efficiency is the lowest one with only 5.02%. When calcined at 700°C, some amount of TiO_2 has turn into rutile phase, which also leads to a low degradation rate (53.83%). In Fig. 1(c), it can also be seen that the diffraction peaks at $2\theta = 38.24$°C (200) and 54.37°C (211), which belong to the characteristic diffraction peaks of rutile phase, appeared even very weak. Therefore, the heat-treated temperature of 500°C is favorable to form the high-catalytic activity films as an employed condition in further experiments. In Fig. 3(d), as can be seen, after light irradiation for 240 min, the highest degradation ratio is attained in the presence of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film calcined at 500°C for 90 min and the corresponding degradation ratio is 83.64%. Whereas, the degradation ratio of Azo Fuchsine caused by Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film calcined at 500°C for 30 and 60 min are only slightly lower than that using 90 min heat-treated sample. Apparently, there are very small differences in final photocatalytical activity for sample calcinated at different times. Maybe, as Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film, it forms the highly active anantase phase easily. Once the highly active anantase phase forms, the Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film displays a high photocatalytic activity. Even though, considering the stability of composite film, we also chose the 60-min heat-treated time as experimental standard condition for the next step of the experiment.

3.4. UV–vis spectra of Azo Fuchsine solutions during degradation

UV–vis spectra of Azo Fuchsine solution under simulated visible light irradiation for 240 min in the presence of different prepared photocatalysts are shown in Fig. 4. In Fig. 4, the UV–vis spectra of Azo Fuchsine solution during degradation under pure and modified TiO_2 film were recorded with a UV–vis spectrophotometer in the wavelength range from 250 to 700 nm. As shown in Fig. 4, the maximum absorption peak of Azo Fuchsine original solution (a) appears at 525 nm in the visible region, which corresponds to the azo bond (–N=N–) as the most active site for oxidative attack in Azo Fuchsine molecule. Compared with the maximum absorption peak of Azo Fuchsine original solution, the absorption peak of Azo Fuchsine solution in the dark in the presence of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film hardly decreases, which indicates that the adsorption ability of Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film for Azo Fuchsine is very weak and it can even be neglected. One of the reasons may be that the surface area of the film form is smaller than that of particle form.

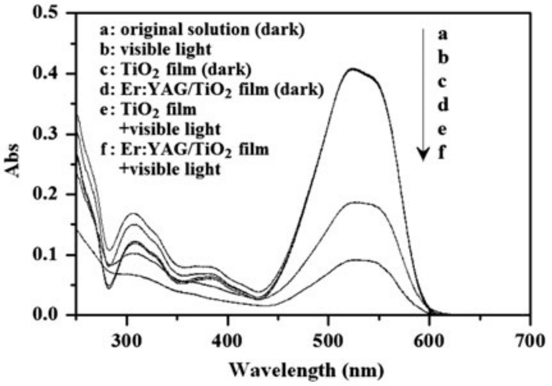

Fig. 4. UV–vis spectra of Azo Fuchsine solutions under different conditions (10 mg/L Azo Fuchsine concentration, 24–28°C temperature, 240 min visible light irradiation and three-layer Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ films with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500°C for 60 min). ((a) original solution in dark; (b) original solution under visible light irradiation; (c) pure TiO_2 film in dark; (d) Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ film in dark; (e) pure TiO_2 film under visible light irradiation; and (f) Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ film under visible light irradiation) (YAG: Er^{3+}:$Y_3Al_5O_{12}$).

3.5. Influences of visible light irradiation time, initial concentration, used times, and organic dye kind on photocatalytic degradation

In Fig. 5(a), it is also clearly seen that, under identical conditions including up-conversion luminescence agents content, layer number, heat-treated temperature, and heat-treated time, the Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film shows much higher activity. The degradation ratio of Azo Fuchsine based on the maximum absorption peak reaches 81.38% under visible light irradiation in the presence of the Er^{3+}:$Y_3Al_5O_{12}/TiO_2$ composite film, which is obviously higher than the corresponding degradation ratio (60.04%) in the presence of the pure TiO_2 film.

The effect of wide concentration range of Azo Fuchsine dye from 10 to 50 mg/L on the photocatalytic degradation was studied under visible light irradiation for 240 min for the purpose of simulating actual wastewater environment. As seen in Fig. 5(b), the reduction ratio of Azo Fuchsine decreased with increasing initial concentration. That is because the color of the solution is getting deep along with the

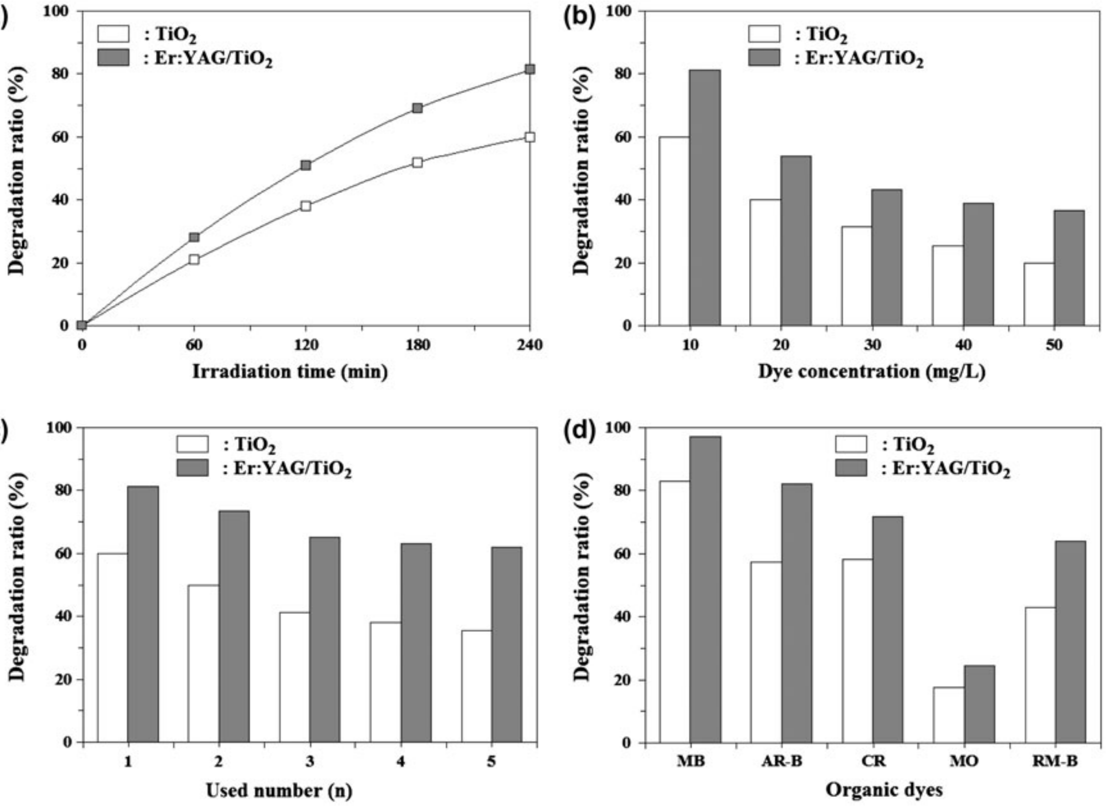

Fig. 5. Effect of (a) visible light irradiation (10 mg/L Azo Fuchsine concentration, 24–28℃ temperature, 0–240 min visible light irradiation and three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 films with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃ for 60 min), (b) initial Azo Fuchsine concentration (24–28℃ temperature, 240 min visible light irradiation and three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 films with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃ for 60 min), (c) used number (24–28℃ temperature, 240 min visible light irradiation and three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 films with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃ for 60 min), and (d) organic dye kind (10 mg/L organic dye concentration, 24–28℃ temperature, 240 min visible light irradiation and three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 films with 0.3:1 mass ratios of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2 heat treated at 500℃ for 60 min) on the photocatalytic degradation of organic dyes (MB: methylene blue; AR-B: acid red B; CR: Congo red; MO: methyl orange; RM-B: Rhodamine B; YAG: Er^{3+}:$Y_3Al_5O_{12}$).

initial concentration increasing, which restrains the absorption and transmission of visible light. In those cases, the photons get intercepted before they can reach the surface of the composite film, and the degradation efficiency is reduced accordingly. Furthermore, when the initial concentration increases, more organic substances are adsorbed on the surface of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film, therefore, there are only a fewer active sites for the adsorption of hydroxyl ions (OH^-), and the generation of hydroxyl radicals (·OH) will be reduced.

The reason why we are committed to make Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite load on glasses is that supported films can be reused and easily recycled. Fig. 5(c) just illustrates the five times recycling photodegradation rate of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film. Photocatalytic activity of the film is very stable after five times recycling, and the average rate of the five times is about 69.03% which is better than the 44.95% of pure TiO_2 film. However, photocatalytic activity of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film is decreased along with the increase in the used number. Because the interface of three layers is not stable when immersed in Azo Fuchsine for long time and some of the catalyst particles have been fallen off.

In order to imitate the real conditions of industrial pollution, several representative organic dyes, such as MB, AR-B, Congo red (CG-R), MO, and Rhodamine B (Rh-B), have been used to carry out the photocatalytic degradation experiment. All the experiments were run in the same conditions as well as previously used. As shown in Fig. 5(d), all of these organic dyes could be degraded to some extent in the presence of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film under visible light irradiation for 240 min. For these dye molecules, because of different molecular structures and chemical compositions, they have different charges after ionization. Therefore, the electrostatic attraction or repulsion will occur between organic dye molecules and photocatalyst particles, which result in the different degradation ratios. Even so, it is experimentally proved that the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film has promising applied perspective in using the degradation of various organic dyes.

Recently, some research groups have reported the luminescent characteristics of visible ultraviolet up-conversion in Er^{3+}:$Y_3Al_5O_{12}$ crystals and the corresponding up-conversion mechanisms are also discussed in detail [24]. When the Er^{3+}:$Y_3Al_5O_{12}$ as up-conversion luminescence agent is pumped by a 488 nm Ar^+ laser, the up-conversion signals at 271, 317, and 381 nm can be observed. Otherwise, the up-conversion signals at 320 nm can also be found by a 647-nm laser excitation [32]. Under multiple-pulsed excitation, the photon avalanche may take place too. The visible light section in solar light contains continuous pump wavelengths (between 400 and 700 nm) used as excitation source, and thus the up-conversion process may easily take place in Er^{3+}:$Y_3Al_5O_{12}$ crystals.

3.6. Photocatalystic degradation principle of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film

As illustrated in Fig. 6, the Er^{3+}:$Y_3Al_5O_{12}$ as up-conversion luminescence agent added into the TiO_2 film, under excitation of continuous visible light, can emit the ultraviolet light, which can effectively be absorbed by TiO_2 parts to generate the electron–hole pairs. The highly oxidative holes on valence band of TiO_2 not only directly decompose the organic dye molecules adsorbed on the surface of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film, but also oxidize H_2O or OH^- to produce $^{\cdot}OH$ with high reaction activity and indirectly degrade the organic dye molecules in aqueous solution. As we all know, the generation rate of $^{\cdot}OH$ by rutile phase TiO_2 photocatalyst was significantly lower than that of anatase photocatalysts. In addition, the electrons on the conduction band of TiO_2 may then react with oxygen (O_2) adsorbed on the surface, yielding various reactive oxygen species (ROS) including superoxide anion radical (O_2^-) which also becomes $^{\cdot}OH$ through a series of chemical reactions. These radicals can also degrade the surrounding organic dye molecules, leading to volatile degradation by-products or entire mineralization into CO_2, H_2O and mineral acids.

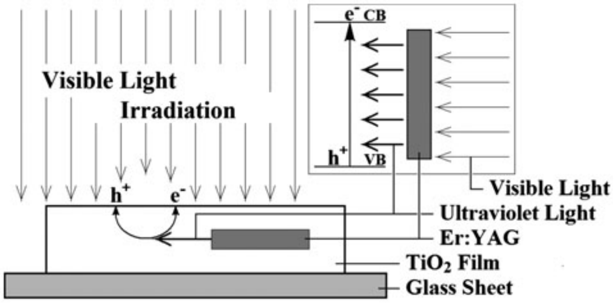

Fig. 6. Photocatalystic degradation principle of Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film under visible light irradiation (YAG = Er^{3+}:$Y_3Al_5O_{12}$).

4. Conclusions

In this study, the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film was prepared by sol–gel and dip-coating method on the surface of glass sheet. And then, its photocatalytic activity was evaluated through the degradation of some organic dyes in aqueous solution under visible light irradiation. The experimental results show that the visible light photocatalytic activity of prepared Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film depends on the mass ratio of Er^{3+}:$Y_3Al_5O_{12}$ and TiO_2, layer number, heat-treated temperature, and heat-treated time. Definitely, three-layer Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film with 0.3:1 mass ratio heat treated at 500℃ for 60 min displays the best visible light photocatalytic activity during degradation of organic dyes. At last, through the photocatalytic degradation of some representative organic dyes under visible light irradiation, it proves that the Er^{3+}:$Y_3Al_5O_{12}$/TiO_2 composite film is a feasible broad-spectrum photocatalyst utilizing solar light to treat dye wastewater.

Acknowledgments

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