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Solar photocatalytic decolorization of azo dyes in water and textile wastewater on N-(Cr^{3+}, Fe^{3+}) doped-TiO_2 nanoparticle films: optimization of some operational parameters

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ABSTRACT

The photocatalystic decolorization of the mixture of three textile azo dyes, i.e. Reactive Red (RR) 193, RR 198 and RR 239, with N, or Cr^{3+} or Fe^{3+}doped TiO_2 film photocatalysts under solar light irradiation was studied. The effect of different factors, i.e. concentration of dopant, pH of the solution, additive of H_2O_2 and irradiation source on the photocatalytic decolorization efficiency of the TiO_2 film catalysts, was investigated. The optimal doping concentration is 0.2 at.% with N- or Cr^{3+}, with larger than 96% of the decolorizing efficiencies after 4 h irradiation time. The decolorization of the dyes was strongly enhanced by the addition of hydrogen peroxide in the pH of 3.0. Under solar light irradiation in the presence of H_2O_2, both N-doped and Cr^{3+}-doped TiO_2 thin film were also applied to photocatalytically decolorize a textile wastewater sample.

Keywords: Nanoparticle films; Photocatalytic decolorization; Azo-dyes; TiO_2; Solar energy

1. Introduction

Textile wastewaters or dye pollutants are one of the major sources of environmental contamination. Among chemically synthesized dyes, 350,000 ton azo dyes are produced each year, which are about 50% of the world dyes production [1]. It is estimated that over 15% of the synthetic textile dye are lost in waste streams during synthesis and processing [1].

These azo dyes are known to be largely non-biodegradable in aerobic conditions and be readily reduced under anaerobic conditions to hazardous, carcinogenic aromatic amines when incorporated into the body. Since the textile wastewater treatment has become one of the major concerning, many methods have been developed in the past decades. In the physical and chemical techniques such as adsorption, flocculation, separation, electrocogulation and chemical precipitation *etc.* one of the major problems is that the pollutants can be transferred from one place to another through azo dyes, which are not destructed. Therefore, it is necessary to solve the secondary pollution or waste disposal through further treatments [2]. Because the trace soluble dye (e.g. below 1 ppm) affects the

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water environment considerably and the decolorization of dye effluents is often more important than other colorless organic species [2], an effective effluent decolorization is usually required by most government regulations.

Among advanced oxidation processes, titanium dioxide (anatase) has been effectively used to photocatalytically degrade organic pollutants in recent years with ultraviolet (UV) light irradiation [3]. As a photocatalyst, since TiO_2 showed singular characteristics such as high photocatalytic activity, high photochemical reactivity, low cost, relatively good chemical stability and low environmental toxicity, it has been the most effective and promising photocatalyst in pollution treatment [4]. However, because of a wide band gap (e.g. ~3.2 eV) of TiO_2, UV irradiation with a wavelength shorter than 390 nm is required for photocatalytic activation. Therefore, only a small fraction (5%) of the solar spectrum can be absorbed if sunlight is used to photoexicite this catalyst for photocatalytic degradation of dye wastewater [5]. Solar energy is a free and abundant natural energy source. Improving the utilization efficiency of solar energy is one of the major goals of modern science and engineering and will have a great impact on technological application.

The photocatalytic activity of TiO_2 in UV and visible spectral regions is highly dependent on the preparing method and the content of the foreign element if any [6]. TiO_2 doped with transition metal (e.g. Cr [7,8] and V [9] *etc.*) ions or non-metallic atoms (e.g. N [10,11]) was demonstrated to show relatively high photocatalytic activity under visible light owing to band gap narrowing in literature. To our best knowledge, only few researches were reported that the natural sunlight can be used directly to photocatalytically degrade or decolorize azo dyes, though photocatalysts doped with TiO_2 have drawn a lot of attention. On the other hand, most TiO_2 photocatalysts are powder slurries in the application, the following matters are present: (a) the need for separation or filtration, (b) the difficulty of use in continuous flow systems and (c) the particle aggregation [12]. Therefore the photocatalytic system with TiO_2 photocatalysis film and sunlight possesses an attractable superiority, although the photocatalytic activity of TiO_2 thin film, at present, is lower than the slurry solution.

Sol–gel method is widely used because the method facilitates the synthesis of nanometer sized crystallized TiO_2 powder of high purity at relatively low temperature [13]. It was used in this work to prepare the nanostructured TiO_2 (anatase) doped with N, Cr^{3+} and Fe^{3+}, respectively. Three series of the doped TiO_2 thin films were further prepared as the photocatalysts. The photocatalytic activities of these film catalysts were evaluated by monitoring the decolorization of a mixture of three azo dyes (RR193, RR198 and RR239) in aqueous solution under sunlight irradiation. The effect of several decisive parameters, doping elements and concentrations of dopant, pH of the solution, H_2O_2 additive and light source used on photocatalytic decolorization of azo dyes were investigated and optimized. A textile wastewater was decolorized photocatalytically under the optimum condition and the result was compared with those with the artificial light sources.

2. Experimental

2.1. Materials

The analytical grade tetrabutyl titanate ($Ti(OC_4H_9)_4$, CAS no. 5593-70-4) was used as the precursor for the preparation of doped TiO_2 particles. The commercially available azo dyes, RR193, RR198 and RR239 (Fig. S1), were used to prepare a simulated dye wastewater with the mass ratio: 1:0.5:0.5. The concentrations of RR193, RR198 and RR239 were 10, 4.9 and 4.2 μM, respectively. All reagents were analytical reagent grade and distilled water was used in the experiment.

2.2. Preparation and characterization of doped titania powders

The titania powder samples were doped with N or Cr^{3+}, Fe^{3+} with different M/Ti molar ratio through a sol-gel process [14]. Typically, to prepare solution I, 0.0063 g of NH_4Cl (CAS no. 12125-02-9) was dissolved in 30 mL of absolute ethanol, followed by the addition of 1.2 mL of nitric acid (1.5 M) and 2 mL of water. Tetrabutyl titanate (20 mL) was diluted in 40 mL of absolute ethanol and stirred vigorously at room temperature for 10 h to prepare solution II. Solution I was then added drop-wise until a sol appeared. The sol was concentrated with rotary evaporation at 100℃ and aged for 10 h. The N-doped TiO_2 sample with 0.2 at.% doping was obtained through grounding and calcining at 550℃ for 2 h. Other N-doped TiO_2 catalysts with 0.1, 0.5, 0.8, 1.0 and 2.0 at.% doping and the catalysts doped with $CrCl_3$ (CAS no. 10025-73-7) or $FeCl_3$ (CAS no. 7705-08-0)were prepared similarly. Molar percentage is the unit of the doping concentrations for the doped TiO_2 photocatalysts in this work. Optically transparent glass plates with sizes of 5 × 5 cm are ultrasonically cleaned in ethanol prior to use. The doped TiO_2 films were prepared through the immobilization of TiO_2 powders on glass plates with a colorless homemade binder. The detail of the process is described elsewhere [14]. The glass plate was loaded uniformly with a mash consists of 0.5 g of nanostructured TiO_2 powders and the binder, yielding a round film with a diameter of 3.9 cm. The round film was then dried at 100℃ for 30 min. The total area of a TiO_2 film photocatalyst is approximately 11.9 cm^2. The surface morphology of the doped TiO_2 catalyst powders were characterized with a scan electron microscopy (SEM) (JSM16360LA, Japan). The crystalline structure of the powders was investigated through X-ray diffraction (XRD) analysis (D/MAX2500, Japan) with a Co $K\alpha$ radiation.

2.3. Photocatalytic reactor and light source

The experimental apparatus consist of photoreactors and solar light. A 250 mL of glass beaker was used as the photoreactor for photocatalytic decolorization of the simulated azo dye wastewater and textile wastewater. The glass plate loading the doped TiO_2 film was applied in the decorlorization of 200 mL dye solution with an initial concentration of 18.5 $mg\,L^{-1}$. The decolorizing efficiency was assessed through solar light or the artificial light sources, which included one 30 W low pressure mercury vapor lamp with the maximum intensity at 253.7 nm and a GZ-5000 model drug irradiation test instrument (light intensity of 3,500 ± 500 Lux). All solar photocatalytic experiments were carried out under similar conditions on sunny days of summer (May–June) between 10 am and 3 pm in Changzhou, China. The latitudes and longitudes are 31.47℃N and 119.58℃E, respectively.

2.4. Experimental procedure

For a typical photocatalytic decolorization experiment, 200 mL of the simulated dye wastewater at a given pH and 1.0 mL of 30% H_2O_2 was placed into the photoreactor. One piece of the glass plate loading the doped TiO_2 film was placed face-up on the bottom of the photoreactor. Then the simulated dye solution was irradiated by solar light. At given irradiation time interval, 11 mL of the solution irradiated was withdrawn into a 3-cm cell to determine the absorbance of the solution using a spectrophotometer (721 model, Shanghai Analytical Instrument Co., China) at a wavelength of 490 nm. After determination, the solution in the cell was returned to the photoreactor, to maintain the constant volume of the simulated dye wastewater during the experiment.

Since there was no change in the shape and peak positions as well as no new peaks were observed in the absorption spectrum of the dye solution during the course of the degradation, the absorbance is proportional to the concentration of the simulated dye solution. The decolorizing efficiency (*de*, or DE) was calculated with the following equation: $de(\%) = 100(A_0 - A_t)/A_0$, where A_0 is the initial absorbance and A_t is the absorbance at time t.

2.5. COD measurements

The chemical oxygen demand (COD) is determined through dichromate ($K_2Cr_2O_7$) titration method [15].

3. Results and discussion

3.1. Effect of doping elements and concentrations on the photocatalytic activity

The strongest peak at $2\theta = 25.3^\circ$ for all XRD patterns obtained with the doped TiO_2 particles show 101 anatase phase reflection (Fig. S2), indicating the anatase phase in the powders. No N-derived peaks from N-titanate were detected in all samples, suggesting that doping with N does not change the crystalline structure of anatase. The results are consistent with previous publications [16,17], which show similar results by doping with Cr^{3+}, Fe^{3+} at the lower doping concentration (<1.0%). The particle sizes of N-, Cr^{3+}- and Fe^{3+}-doped TiO_2 with 0.2% doping are calculated to be 31.7, 31.1 and 30.4 nm, respectively, through the Scherrer's equation. The SEM micrographs of N (Cr^{3+}, Fe^{3+})-doped TiO_2 powders show that the particle sizes are in the level of nanoparticle ranging from 30 to 200 nm.

Fig. 1 shows the effect of different doping concentrations for N-, Cr^{3+}-doped TiO_2 thin film catalysts on the photocatalytic decolorizing rate of the simulated wastewater. The doping concentration is obviously important to the decolorizing rate of the azo dye solution. Under solar light irradiation for 4 h, photocatalysts doped 0.2 at.% of N or Cr^{3+} showed the highest photocatalytic activities with 100% and 96.7% of *de* for Cr^{3+}- and N-doped TiO_2 film catalyst, respectively. However, the TiO_2 films show decreased decolorizing efficiency with further increase of doping concentration (>0.2 at.%). For example, the Cr^{3+}- and N- doped TiO_2 films show the decolorizing efficiencies of 86.9 and 90.8%, respectively, at doping concentration of 1.0 at.%. The similar photocatalytic activity for Fe^{3+}-doped TiO_2 film was also observed (the data not showed). For the optimal doping concentration (0.2% dopants), the results are also consistent with the best doping concentration (0.25% [8], and 0.1% for both Cr-TiO_2 and Fe-TiO_2 [18]) reported in the most recent literature. This could attribute to that photogenerated holes

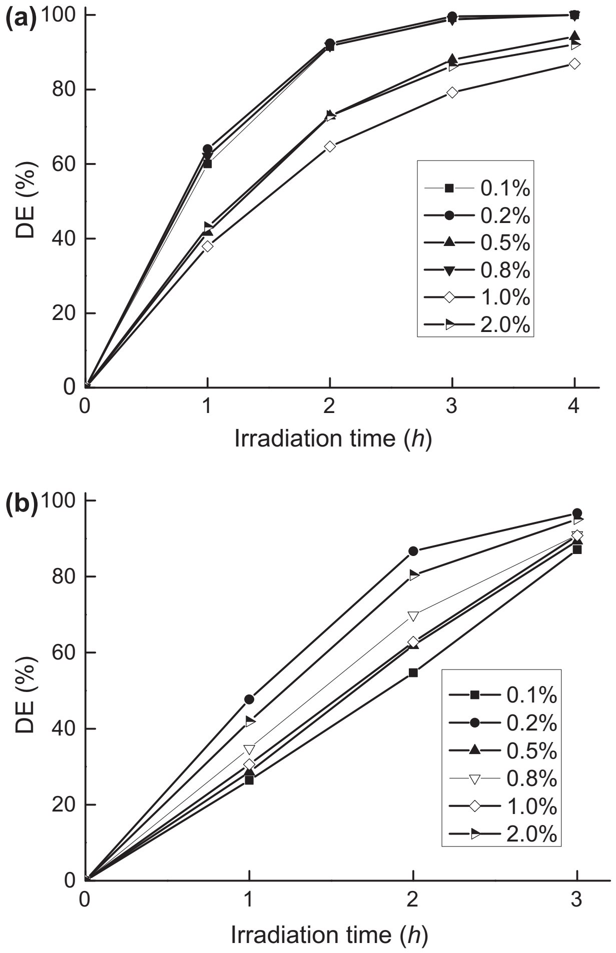

Fig. 1. Effect of the doping concentration: (a) for N-doped TiO_2 thin film catalyst on the rate of photocatolytic decolorization of the stimulated dye wastewater ($V = 200$ mL) at the given dosages (pH of 3.0 for the initial stimulated dye wastewater and 30% H_2O_2 additive of 1.0 mL) under solar light irradiation and (b) for Cr-doped TiO_2 thin film catalyst on the rate of photocatolytic decolorization of the stimulated dye wastewater ($V = 200$ mL) at the given dosages (pH of 3.0 for the initial stimulated wastewater and 30% H_2O_2 additive of 1.0 mL) under solar light irradiation. Symbols represent different doping concentration of the dopant.

and electrons in the presence of low doping levels of dopants are well separated thereby increasing the efficiency of the catalyst.

It is known that the band gap energy (E_g) of pure anatase TiO_2 is 3.2 eV, thus TiO_2 has no absorption in visible region (>400 nm). For the doping TiO_2 samples with N or Cr^{3+}, or Fe^{3+}, the distinct shifts of the absorption edges of TiO_2 into visible light region have been observed and different band-gap narrowing has been reported [7,10,18,19]. In the case of Cr^{3+} ion doping, band-gap narrowing is related to the preparation conditions of Cr^{3+} doped TiO_2 such as ion doping concentration and calcination temperature [8]. The band gap energy for the Cr-TiO_2 with 0.25% doping concentration is shifted to 2.6–2.9 eV when calcination temperature changed from 600 to 800℃. The different shift for the band gap energy of Cr-TiO_2 such as 2.00 eV [7] or 2.86 eV [18] was reported. Nitrogen doping was shown to extend the light absorption onset from 380 nm to visible light. Silveyra et al. [20] reported that the band gap energy for N-TiO_2 (N-TiO_2 600) was 2.93 eV.It is proposed that the substitution of the lattice oxygen with nitrogen might narrow the band gap by mixing N 1s and O 1s states [10,19]. The band gap energy of the TiO_2 doped Fe^{3+} ion was observed to shift to 2.50 eV [18] or <3.10 eV [21]. Thus, the high photocatalytic activities of N-or Cr^{3+}- or Fe^{3+}-doped TiO_2 thin film catalysts in the present study under solar light irradiation can likely be explained by narrowing band gap energy of these doped TiO_2 samples, which gives rise to that the adsorption of light is extended from the UV to the visible region, and enhances absorption in the visible region. On the other hand, the physical properties of TiO_2 such as crystal structure, crystal size distribution, surface property and so on, also influence the photocatalytic activity of TiO_2 photocatalyst [22–24]. The superior photocatalytic activity of N-(or Cr^{3+}- or Fe^{3+}-) doped anatase thin film, which here is 0.2% N-, Cr^{3+}- or Fe^{3+}- doped TiO_2 with particle sizes range from 30 to 200 nm, could relate more or less to the synergic effects of the physical properties of the photocatalysts.

3.2. *Effect of experimental parameters*

At the beginning the blank experiments under solar irradiation were carried out under following conditions: Without any photocatalyst and the neutral simulated dye wastewater (pH 7.0) in the absence of H_2O_2, and without photocatalyst and the simulated dye wastewater at pH 3.0 in the presence of H_2O_2 (additive of 1.0 mL of H_2O_2). After 4 h of irradiation, only 9.72 and 13.15% respectively, of the solutions undergo the decolorization. The effect of the operational parameter, such as pH of the solution, addition of H_2O_2 and photocatalytic reaction time, on the photocatalytic decolorization of the simulated dye wastewater in water has been investigated.

3.2.1. *Effect of pH*

Since pH is one of the important parameters, it is necessary to investigate the effect of initial solution pH on the photocatalytic decolorization efficiency of the doped TiO_2 film photocatalysts. Fig. 2 shows the effect of initial pH, in the range from 2.0 to 9.0, of the wastewater solution on the decolorization efficiency. The decolorization at initial $pH < 4.0$ shows larger rates than that at $pH > 4.0$, indicating the increase of the decolorizing rate with a decrease in pH. Photocatalytic decolorization shows the highest activity at pH 3.0 for two series of TiO_2 thin film catalysts. At pH 3.0, the efficiency (*de*) of the simulated wastewater obtained with 0.2% Cr^{3+}-doped TiO_2 film under solar light irradiation for 4 h is 88.6%, compared with 76.4% at pH 2.0, 47.5% at pH 5.0 and 49.2% at pH 9.0, respectively. The photocatalytic activities of Cr^{3+}-doped TiO_2 film catalyst was increased with the increase of initial pH of the solution when $pH > 6$. This behaviour seems to be characteristic for some photocatalytic systems using TiO_2 or modified TiO_2 photocatalysts and similar results have been obtained by the photodegradation of azo dyes such as direct blue 71 [25], reactive black 5 [26] and acid black 1 [27]. The reason for the higher degradation efficiency above pH 7 is that the significant abundance of OH^- anions in the medium and near the surface of the catalyst that leads to the generation of hydroxyl radicals [25].

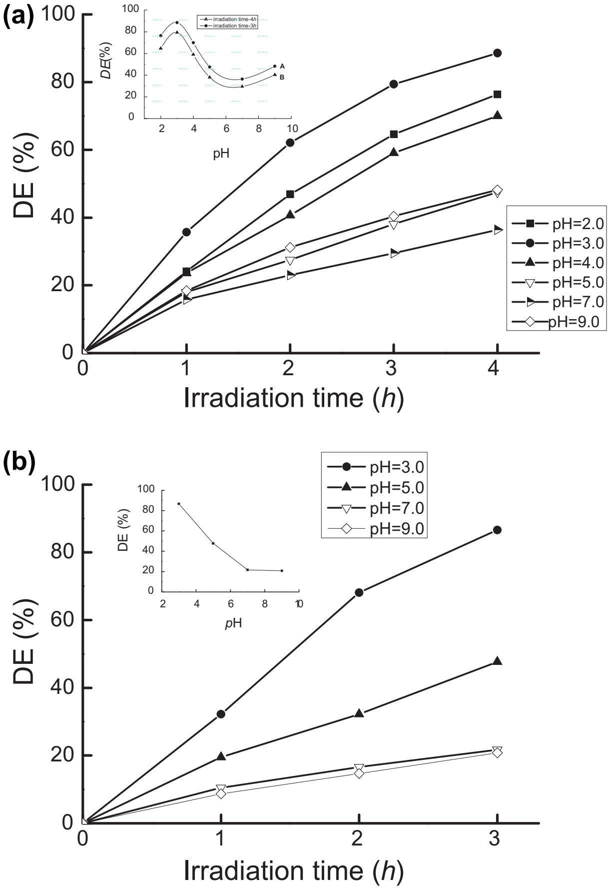

Fig. 2. Effect of the initial pH on the rate of photocatalytic decolorization of the stimulated wastewater ($V = 200$ mL) containing H_2O_2 (30% H_2O_2 additive of 1.0 mL) under solar light irradiation with: (a) 0.2% doping concentration of Cr(III) for Cr^{3+}-doped TiO_2 thin film catalyst and with (b) 0.2% doping concentration of N for N-doped TiO_2 thin film catalyst. The insets in (a) and (b) show the change of the decolorizing rate with the increase of pH of the initial stimulated dye wastewater.

However, the different behavior can be observed with the N-doped TiO_2 film catalysts (Fig. 2(b)). The 0.2% N-doped TiO_2 also shows that the largest decolorizing rate is at initial pH 3.0 and speedy decrease of the decolorizing rate with the increase of solution pH. Above pH 5 a decrease in the value of *de* was found with the increase of pH and *de* value was maintained to a minimum (~21%) at pH from 7 to 9 at the same irradiation duration of 3 h. In $TiO_2/UV/H_2O_2$ photocatalytic process, Soutsas et al. [28] reported the similar pH dependence for decolorization efficiency of four azo dyes (Remazol Red RR, Remazol Yellow RR, Procion Crimson H-exl and Procion Yellow H-exl). Compared to the insets in Fig. 2(a) and (b), it is also worthy to be noted that there are obvious differences in pH dependence of decolorization efficiency of mixed azo dyes in alkaline solution. To the best of our knowledge, this is the first example of different pH dependence of decolorization efficiencies of the N- and Cr^{3+}-doped TiO_2 film photocatalysts observed in the heterogeneous photocatalytic process (solar irradiation/doped TiO_2/H_2O_2).

The effect of solution pH on the photocatalytic activity may be the results from the surface charge of TiO_2 (point of zero charge, *pzc*, of TiO_2 at pH 6.25 [29] or 6.80 [30]) and its relation to the dissociation of sulfonic acid groups in the azo dyes during the photooxidation reaction. The adsorption of the azo dye molecules onto the TiO_2 surface is probably the first step and determines the efficiency of photooxidation [31]. Under acidic or alkaline condition the surface of titania (TiOH) can be protonated or deprotonated respectively, according to the following reactions ((1)–(2)) [32]:

$$TiOH + H^+ \rightarrow TiOH_2^+ \quad (1)$$

$$TiOH + OH^- \rightarrow TiO^- + H_2O \quad (2)$$

Thus, the titania surface will remain positively charged in acidic medium ($pH < 6.2$ or 6.8) and negatively charged in alkaline medium ($pH > 6.8$). According to *pzc* of TiO_2, the surface is presumably positively charge at $pH < 6.2$ (or 6.8) and negatively charge at $pH > 6.8$. The pH changes can influence the adsorption of the azo dye molecules on the surface of TiO_2. Since sulfonic acid group in these azo dye molecules is negatively charged, the acidic solution favors the adsorption of the dyes onto catalyst surface via electrostatic attraction, leading to the increase of the decolorization efficiency. From the view point of adsorption of film catalyst, the highest decolorization efficiencies at pH 3.0 for two series of TiO_2 thin film catalysts could relate with adsorption saturation of azo dye molecules on these catalyst surfaces. On the other hand, the positive holes of TiO_2 are also an important oxidation species at low pH. Both may cause an efficient electron-transfer process happening on vis/TiO_2/water interface and the faster decolorizing rates at acidic pH.

As mentioned above, a decrease in the value of *de* obtained with N-TiO_2 film photocatalyst was found with the increase of pH at pH from 7 to 9, even though there are the significant abundance of $OH^{\cdot -}$ anions in the alkaline medium, which should favor the photogeneration of hydroxyl radicals ($OH^{\cdot -}$). This indicates a decrease in the adsorption of OH^- anions on N-doped TiO_2 surface, compared with Cr-doped TiO_2 surface. We can presume that there is a difference on the solid surfaces between N-TiO_2 and Cr-TiO_2. The electronegativity of nitrogen substituted oxygen sites on the solid lattice surface is smaller than oxygen and further could impair the adsorption of Ti^{4+}, giving rise to decreasing of hydroxyl radicals at the TiO_2/water interface.

3.2.2. The effect of H_2O_2 additive

Generally, the addition of oxidants *e.g.* H_2O_2 or $S_2O_8^-$ to dye wastewaters facilitates the photo-oxidation of the dyes. The effect of H_2O_2 on sunlight decolorizing the simulated dye wastewaters through 0.2% N-doped TiO_2 film is in Fig. 3. It is clearly shown from Fig. 3 that the decolorization of the dyes was strongly enhanced by the addition of hydrogen peroxide in the pH of 3.0. Interestingly, for the 200 mL of simulative dye solution, H_2O_2 at lower concentration (1 ~ 2 mL, $c_{H_2O_2}$: 49 ~ 97 mM) shows higher photocatalytic decolorizing efficiency than that at higher concentration ($V_{H_2O_2} > 3$ mL). Among all, the addition of 1.0 mL of H_2O_2 shows the highest decolorizing efficiency because more hydroxyl radicals ($OH^{\cdot}$) are produced through the following reaction pathways (Reactions (3)–(5)):

$$H_2O_2 + hv(\text{UV or solar light}) \rightarrow 2OH^{\cdot} \tag{3}$$

$$H_2O_2 + TiO_2(e_{CB}^-) \rightarrow OH^{\cdot} + OH^- + TiO_2 \tag{4}$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow OH^{\cdot} + OH^- + O_2 \tag{5}$$

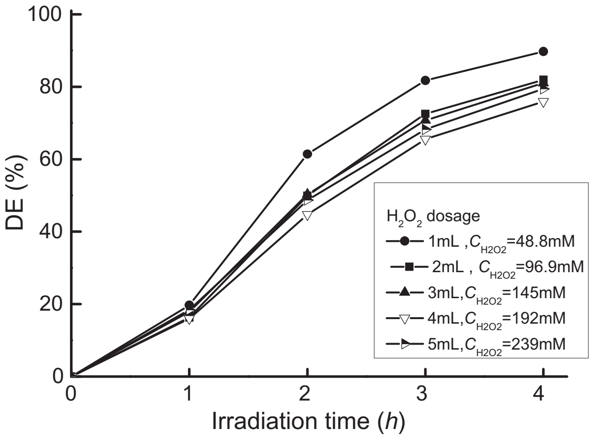

Fig. 3. Effect of the added amount of H_2O_2 on the photocatalytic decolorization of the stimulated dye wastewater ($V = 200$ mL) under solar light irradiation. Five added amounts of H_2O_2 (1.0, 2.0, 3.0, 4.0 and 5.0 mL of 30% H_2O_2 additive) were tested. Conditions: catalyst: 0.2% N-doped TiO_2 thin film, pH of the initial stimulated wastewater: 3.0.

Hydroxyl radicals can strongly oxidize azo dye molecules adsorbed on the surface of the catalyst, and then form small colorless molecules. Moreover, the electron-cavity recombination could be hindered at suitably low concentration of H_2O_2. On the other hand, H_2O_2 becomes the scavenger of both hydroxyl radicals and the cavity of TiO_2 valence band at high concentration [31], resulting in the lower photocatalytic decolorization efficiency.

Besides the amount of oxidants, the photocatalytic reaction time also affects the sunlight catalytic decolorizing rate (seen in Figs. 1–3). The absorbance at 490 nm (A) is used to denote the concentration of the dye and monitor the photo degradation because of the linear correlation between these two parameters. The photocatalytic decolorizing rate decreases dramatically after 3 h from the start of the reaction. The apparent rate constants (*k*) of three catalysts doped with 0.2% of Cr^{3+}, N or Fe^{3+}, are calculated through Langmuir–Hinshelabod kinetics model. The results are fitted with the equation $\ln (A_o/A_t) = kt$ and shown in Table 1. These photocatalytic reactions had nearly identical *k* values with the correlation coefficients $R > 0.985$ in Table 1, indicating the first-order kinetics.

For 200 mL of simulated dye wastes, the sunlight/Cr^{3+}- or N-doped TiO_2 gives the highest activity of the photocatalytic decolorization with the H_2O_2 addition of 1.0 mL at pH equals to 3.0. The decolorizing efficiency of the N-doped TiO_2 film is 100% and the COD removal percentage is 90.9% under the condition after sunlight exposure for 4 h. Therefore, our

Table 1
The decolorization rate constants of stimulated dye wastewater on different catalysts*

Film catalyst	k (h^{-1})	r
0.2%N-doped TiO_2	2.41	0.9885
0.2%Cr(III)-doped TiO_2	2.27	0.9875

*For a 200 mL of the stimulated wastewater sample, other experimental conditions were that 1 mL of H_2O_2 additive, initial pH 3.0, one piece of TiO_2 film catalyst and solar light as irradiation source.

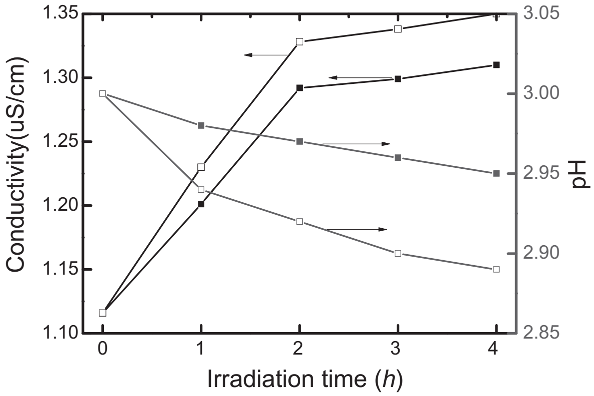

Fig. 4. Change of conductivity and pH of the stimulated solution during the photodegradation of the stimulated dye wastewater ($V = 200$ mL) under solar light irradiation with N-doped TiO_2 film catalyst (□) and with 0.2% Cr^{3+}-doped TiO_2 film catalyst (■). The pH and conductivity (uS/cm) of the initial stimulated wastewater were 3.0 and 1.12, respectively.

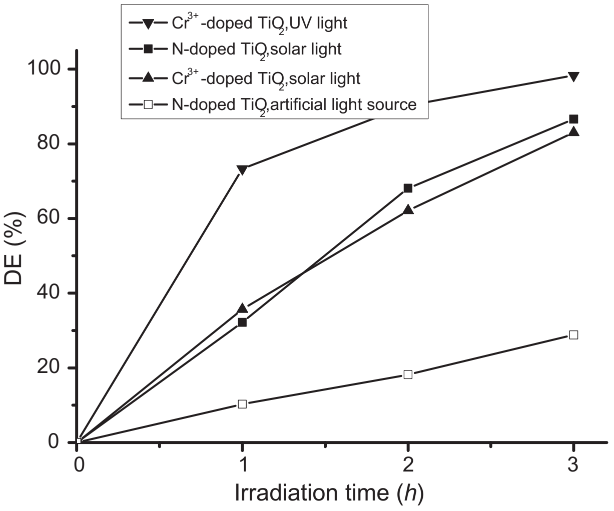

Fig. 5. Effect of light source on the photocatalytic decolorization rate of the simulated dye wastewater ($V = 200$ mL). Conditions: the initial pH and 30% H_2O_2 additive for simulated dye wastewater samples were 3.0 and 1 mL, respectively. The initial absorbance of the simulated dye wastewater samples was 0.97 for irradiation with solar light or UV light and 0.340 for irradiation with visible light (3500 lx light source). Catalysts: 0.2% N-doped TiO_2 (■ or □) and 0.2% Cr^{3+}-doped TiO_2 thin film (▼ or ▲).

sunlight/N-doped TiO_2 gives an excellent photocatalytic efficiency to degrade simulative azo dye wastewaters by breaking the chromophore azo bond of the dye molecule.

A vital-red mono-dye solution (vital red 193, 2.7 μM) is photocatalytically degraded through Cr^{3+}-doped (0.2%) TiO_2 or N-doped (0.2%) TiO_2 film. Fig. 4 shows that the dye solution gives increased conductivity with the decrease of pH during the photocatalytic degradation, which suggests that the large dye ions are photodegrated into small organic and inorganic ions *e.g.* NO_3^-, SO_4^{2-} [33]. Among the three photocatalysts, the largest increase of the conductivity and pH are resulted from N-doped TiO_2 film photocatalyst during the sunlight catalytic decolorization. In other words, N-doped TiO_2 film photocatalyst shows higher photocatalytic activity than Fe^{3+}-doped TiO_2 (not shown) and Cr^{3+}-doped TiO_2. This result is slightly different from that in Fig. 1, which shows that Cr^{3+}- and N-doped TiO_2 film gives the decolorizing efficiencies of 100 and 96.7%, respectively, under irradiation of sunlight for 4 h.

3.2.3. The effect of irradiation source

The intensity of sunlight at ground level varies with latitude, geographic location, season, cloud coverage, atmospheric pollution, altitude above sea level, and solar altitude. The magnitude of the direct solar irradiation intensity for a given earth latitude and season are estimated to be 952.58 and 952.40 W/m^2, through Liu-Jordan model [34] and Meinel's formula.

The effect of two different artificial light sources, a 30 W UV light (Jiangyin, China) and a GZ-500 model 3500 lx light source of the pharmaceutical irradiation instrument, is also investigated for comparison on the photocatalytic decolorizing rate with 0.2% N-doped or 0.2% Cr^{3+}-doped TiO_2 film catalysts. Fig. 5 shows the photocatalytic decolorizing efficiencies of 0.2%

N-doped and Cr^{3+}-doped TiO_2 film catalysts. N-doped TiO_2 film photocatalyst with solar irradiation gives about the efficiencies of three times than that with the visible light source. Moreover, N-doped TiO_2 film shows slightly higher efficiencies than Cr^{3+}-doped TiO_2 film. The interday fluctuation of decolorizing efficiencies is also investigated. Cr^{3+}-doped TiO_2 catalyst gives a larger fluctuation range (79.4 ~ 98.2, with the average of 88.6) of *de* than N-doped TiO_2 film catalyst (84.5 ~ 98.8, with the mean of 89.2), under the same solar light irradiation and irradiation time (3 h) in three clear days. Cr^{3+}-doped TiO_2 film catalyst in UV irradiation for 3 h shows the decolorizing efficiencies 1.2 times as that in the sunlight. Fig. 5 also shows the photocatalytic decolorizing efficiencies with the 3500 lux light source. Due to the limited photocatalytic decolorizing efficiency with the light source, a diluted simulated solution with initial absorbance of 0.340 was chosen. The 0.2% N-doped TiO_2 film shows much lower catalytic activity in the visible light exposure than in the sunlight exposure. The reason may be that there is only a small fraction of UV light ($470\,\text{nm} > \lambda > 400\,\text{nm}$) in this artificial light source. As be seen from Fig. 5, although the smaller value of *de* (37.4%) obtained by using 0.2% N-doped TiO_2 film catalyst under the visible light is as 1/3 as that with UV light after the light exposure for 4 h, the results do provide a strong evidence that there are the enhanced photocatalytic activities of decolorization of mixed azo dye using the doped TiO_2 catalyst under visible light, compared with no photocatalytic activity of pure anatase TiO_2 as mentioned above. The different enhanced photocatalytic activity of Cr^{3+}- or Fe^{3+}-doped TiO_2 catalyst was also observed (data not shown). These phenomena may be explained by both the photosensitized oxidation mechanism and charge carrier trapping mechanism [7,21]. In the former case, excitation of the adsorbed azo dye takes place by visible light to appropriate singlet or triplet states, subsequently followed by electron injection from the excited dye molecule onto the conduction band of the TiO_2 particles, whereas the dye is converted to the cationic dye radicals ($\text{Dye} \cdot +$) that undergoes degradation to yield products [32,35]. In the later case, generation of the photogenerated oxidizing agents (superoxide anion ($O_2^{\cdot -}$) and hydroxyl radicals ($OH^{\cdot}$)) takes place in another pathway via d–d transition of doped metal ions (M^{3+}) in doped catalysts (i.e. charge transfer transition between the interacting ions) and subsequent reaction with adsorbed O_2 or OH^- in the surface lattice of TiO_2. M^{3+} can act as photogenerated hole trapper, due to the energy level for Cr^{3+}/Cr^{4+} or Fe^{3+}/Fe^{4+} above the valence band edge of TiO_2. The trapped holes in M^{4+} can migrate to the surface absorbed hydroxyl ion to produce hydroxyl radicals by reaction (6) [7,21]:

$$M^{4+} + OH^-(\text{ads}) \rightarrow M^{3+} + OH^{\cdot}(\text{ads}) \tag{6}$$

M^{3+} easily traps photo generated electrons (e^-) and forms M^{2+} which reacts with the surface adsorbed oxygen molecules to produce superoxide anion ($O_2^{\cdot -}$). The related reactions is (Reactions (7)–(10)) [36,37] is summarized below:

$$M^{3+} + e^- \rightarrow M^{2+} \tag{7}$$

$$M^{2+} + O_2(\text{ads}) \rightarrow M^{3+} + O_2^{\cdot -} \tag{8}$$

$$M^{2+} + Ti^{4+} \rightarrow M^{3+} + Ti^{3+} \tag{9}$$

$$Ti^{3+} + O_2(\text{ads}) \rightarrow Ti^{4+} + O_2^{\cdot -} \tag{10}$$

The positive holes (h^+), hydroxyl radicals, superoxide anions ($O_2^{\cdot -}$) and superoxide radicals ($HO_2^{\cdot}$), which are generated from the N- or Cr^{3+}-doped TiO_2 catalysts in the irradiation of solar light under an acidic condition, show very strong oxidizing ability by breaking azo groups of dyes. In addition, in the presence of H_2O_2 under an acidic condition, the photocatalytic decolorization of azo dyes is considered to simultaneously undergo direct photocatalytic oxidation, indirect photocatalytic oxidation and photosensitized oxidation.

3.2.4. Recovery of photo-catalytic activity for TiO_2 film catalysts

The possibility of reutilization of 0.2% N-doped TiO_2 film catalyst was also studied. After photo-catalytic decolorization, the film catalyst was taken out from the reactor and dried at 110°C for 2 h before the next usage. It was found that the efficiencies of the recovered N-doped TiO_2 film catalyst were ≥70% under the solar light irradiation and the same optimum experimental conditions. The results indicated that the TiO_2 thin film catalyst can be recovered through a simple drying step.

3.3 The application of the doped TiO_2 film catalysts

Three systems, sunlight/N-doped (0.2%) TiO_2, sunlight/Cr^{3+}-doped (0.2%) TiO_2 and sunlight/Fe^{3+}-doped (0.2%) TiO_2 are used to photocatalytically decolorize industrial dye wastewaters of a local textile factory. In order to measure the absorbance conveniently, the dye wastewaters is filtered and diluted with tap water with the volume ratio V_{waste}:V_{water} = 1:2. The initial absorbance of the diluted solution is 0.972. The results of the photocatalytic with 1.0 mL of H_2O_2 at pH 3.0 are shown in Fig. 6. The decoloization with N- or Cr^{3+}-doped TiO_2 catalysts in UV exposure are also shown in Fig. 6. These systems under UV light show identical decolorizing efficiencies (60%), which are better than in sunlight exposure. The

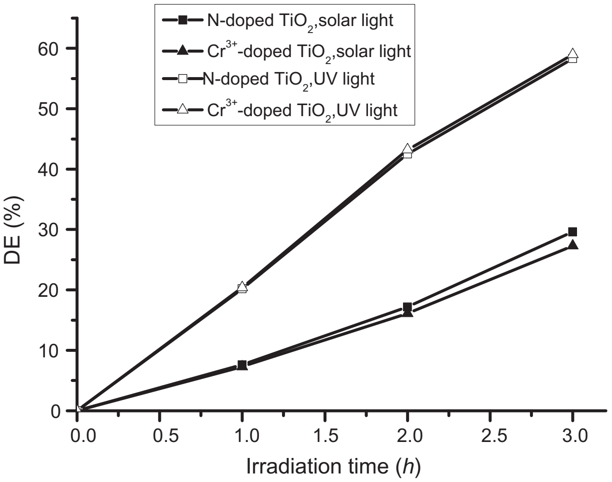

Fig. 6. Photocatalytic decolorization efficiencies of real textile wastewater samples on 0.2% N-doped TiO_2 and 0.2% Cr^{3+}-doped TiO_2 thin film catalysts using solar light and UV light at the given conditions (initial pH of 3.0 and 30% H_2O_2 additive of 1.0 mL for the textile wastewater ($V = 200$ mL). For the sake of convenient to evaluation, the real textile wastewater solution was diluted with water into its initial absorbance (*A*) 0.972.

sunlight/N-doped (0.2%) TiO_2 give the best decolorizing efficiency of 29.6%, although the dye industrial wastewater is a very complicated mixture. It should be mentioned that such results were achieved by only one piece of doped catalytic film (0.5 g) with 11.9 cm^2 of surface area. Since the photocatalytic decolorizing reaction takes place on the surface of the catalyst, more photocatalyst films and larger exposed area for photocatalytic activity will facilitate the decolorizing rate. Obviously, photocatalytic decolorization treatment of the textile wastewater by using the sunlight/N- or Cr^{3+}-doped TiO_2 film photocatalytic decolorizing systems studied in the present work does not require any energy sources such as artificial light sources and electric energy, and there is no waste disposal. Thus these systems are low-cost, environment-friendly, effective photocatalytic systems for azo dye and textile dye wastewaters, and appear their good potential in the application and to merit further exploration.

4. Conclusion

Sol-gel prepared N-, Cr^{3+}- or Fe^{3+}-doped TiO_2 nano-photocatalysts are used to photocatalytically decolorize the mixture of azo dye wastewaters. At low doping concentrations these doped TiO_2 catalysts give excellent decolorizing activities to azo dyes in sunlight exposure and N-doped (0.2 at.%) TiO_2 give the highest photocatalytic activity. The experimental parameters *e.g.* initial pH of the solution and the amount of H_2O_2 are also important to the photocatalytic decolorizing efficiency. In the presence of H_2O_2, the sunlight/N-doped TiO_2 and sunlight/Cr^{3+}-doped TiO_2 systems show 29.6% and 27.3% of the decolorizing efficiencies (*de*) of industrial dye wastewater of, respectively, after the exposure for 4 h. The heterogeneous photocatalytic processes, sunlight/N- and Cr^{3+}-doped TiO_2 film photocatalysts, are low-cost, environment-friendly and effective photocatalytic decolorizing systems for azo dyes in solution.

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