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Preparation of Fe(III) and Ho(III) co-doped TiO_2 films loaded on activated carbon fibers and their photocatalytic activities

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ABSTRACT

Fe(III) and Ho(III) co-doped TiO_2 films and un-doped TiO_2 films loaded on activated carbon fibers (ACF) were prepared by sol–gel-adsorption method. The detailed surface characteristics of the loaded samples and their photocatalytic activities for the discoloration of methyl orange (MO) in water were carried out. The results showed that photocatalyst films were immobilized on the surface of ACF successfully, and the co-doping with Fe(III) and Ho(III) could restrain the forming of crack in TiO_2 films. Results also showed that MO could be removed rapidly from water by the loaded samples under UV irradiation because of the synergistic effects of two factors: absorption of ACF and photocatalytic degradation of photocatalyst films. The sample of Fe(III) and Ho(III) co-doped TiO_2 films calcined at 600 °C exhibited better and stabler photocatalytic activity than that sintered at 800 °C. The discolored ratio of MO was maintained at above 99% without any decline when the sample was used repeatedly, even at the fourth cycle.

1. Introduction

The photocatalytic oxidation of organic compounds by semiconductor photocatalyst TiO_2 has been extensively studied in the past decades [1–3]. It appears to be a promising material for environmental treatment. However, the photocatalytic activity of TiO_2 is partly limited by fast charge-carrier recombination and low interfacial charge-transfer rates of photogenerated carriers [4]. In order to improve the photocatalytic activity of TiO_2, many studies have been investigated, and results show that the doping with appropriate ions is one of the effective means [5–7]. Most of researches about the doping of TiO_2 are focused on single-doping. In recent years, co-doping with two kinds of ions has been studied by some scholars. They [8,9] found that the photocatalytic activity of TiO_2 can be further improved by co-doping with two kinds of ions because of the synergistic effects of them. In our previous experiment [10], we have also found that the photocatalytic activity of TiO_2 powders could be improved by co-doping with Fe(III) and Ho(III) in the suspension system because of the synergistic effects.

However, TiO_2 powders present some drawbacks in their separation and recovery from water in a slurry system after photocatalytic reaction, many researchers have been developing various ways to apply TiO_2 coating on various substrates in order to improve its repeating circles and broaden the applications of the semiconductor photocatalysts [11,12]. But the degradation efficiency of pollutant is usually decreased because of the mass transfer limitation [13] when some materials without adsorption capacity, such as stainless steel [14], glass [15], are used as substrates. To enhance mass transfer, much research has been devoted to immobilizing TiO_2 photocatalyst on porous substrates, such as silica [16], zeolite [17], alumina [18], activated carbon (AC) [19,20]. Among them, AC is most commonly employed as substrate for TiO_2 in gas and water treatment due to its porous structure and adsorption property. The loaded catalyst has made remarkable effects in the kinetics of disappearance of the pollutants, each pollutant being more rapidly photodegraded. The reason has been attributed to the fact that AC is able to adsorb the pollutants and then release them onto the surface of TiO_2, where the pollutants are immediately degraded [21,22]. However, most of the porous substrates are still in the form of granules, and the problem of separation and recovery of the photocatalyst from the reaction media still exists.

Activated carbon fibers (ACF) are one kind of highly microporous carbon materials, having a good adsorption and uniform pore structure. Generally, ACF are considered to have higher adsorption capacity and greater rates of adsorption and desorption process than granular activated carbons [23], so it have been widely used as catalyst substrate for different purposes [24,25]. Further more, ACF, in the form of felt, are preferable in handling than granular supports [26]. Therefore, some investigations have been devoted to immobilizing TiO_2 films on ACF [23,24,27].

The co-doping of TiO_2 [4,8,10] and the immobilization of TiO_2 on ACF [23,26] have been researched in earlier publications, respectively. However, to the best of my knowledge, the investigation

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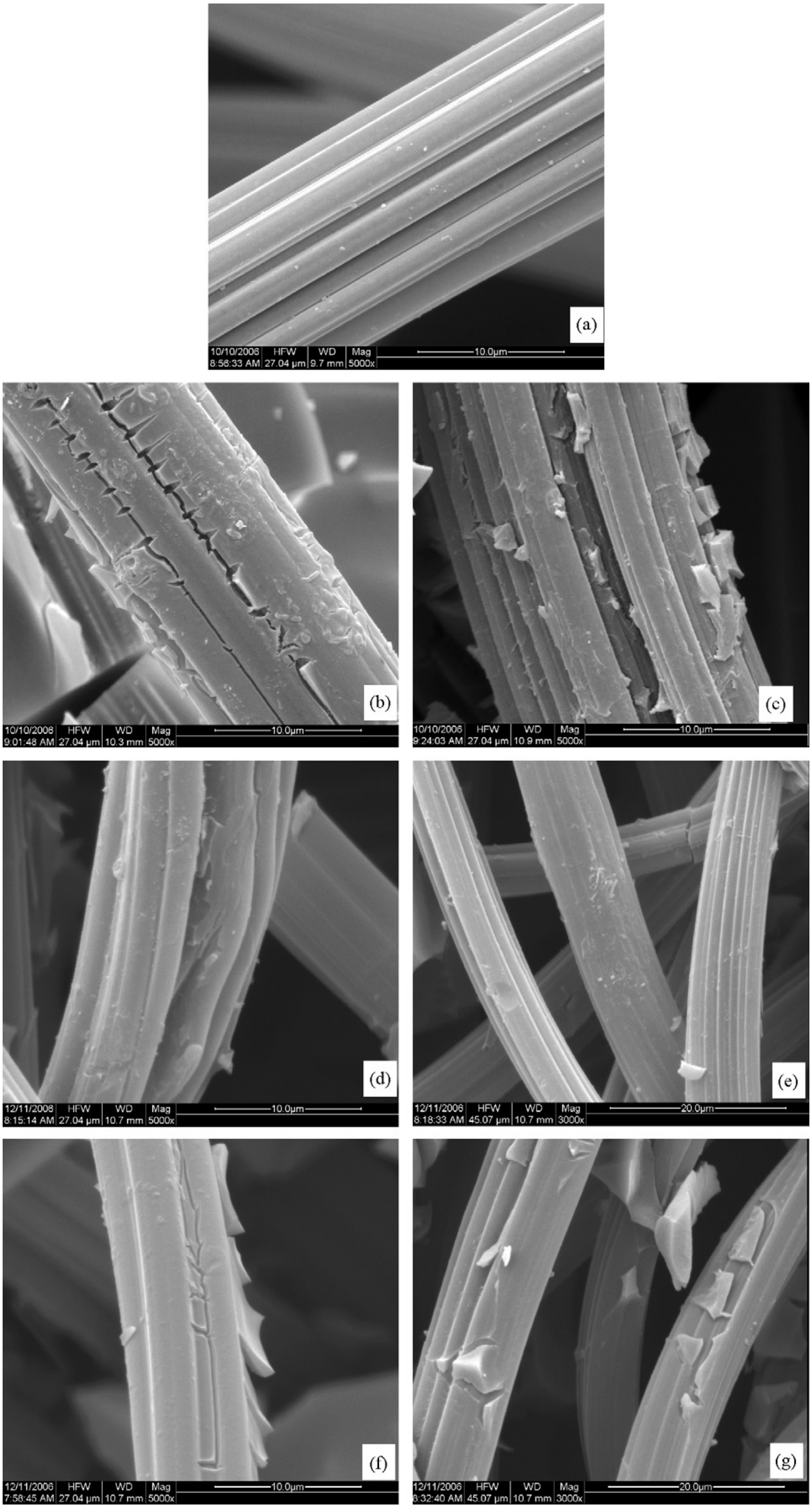

Fig. 1. SEM images of samples: (a) original ACF; (b) TiO_2/ACF-600; (c) TiO_2/ACF-800; (d) and (e) D-TiO_2/ACF-600; (f) and (g) D-TiO_2/ACF-800.

combining the co-doping and the immobilization, that is, immobilizing TiO_2 co-doped with two kinds of ions on ACF has never been reported. So in current work, the TiO_2 films co-doped with Fe(III) and Ho(III) were immobilized on ACF by a sol–gel-adsorption method. For comparison, un-doped TiO_2 films loaded on ACF were also prepared by the same way. Their photocatalytic activities were evaluated by the discoloration of methyl orange (MO) in water.

2. Experimental

2.1. Preparation of loaded sample

All the reagents used in this work were of analytical grade and were used without any further purification. TiO_2 sol doped with Fe(III) and Ho(III) was prepared by the same route introduced in the previous article [10]. The atomic concentrations of Fe(III) and Ho(III) were 0.05% and 0.5%, respectively. The obtained sol was added drop-by-drop onto a 6.4 g ACF felt to be adsorbed. Then it was dried at 80 °C in an oven, finally, calcined at different temperature (i.e. 600 and 800 °C) for 2 h in a nitrogen atmosphere. Un-doped TiO_2 loaded samples were prepared in the same way, except no Fe(III) and Ho(III) were added. The loaded approach was named as sol–gel-adsorption method in this work. For convenience, the sample of co-doped TiO_2 loaded on ACF was labeled as D-TiO_2/ACF-*T*, and the sample of un-doped TiO_2 loaded on ACF was signed as TiO_2/ACF-*T*, where *T* referred to the calcined temperature (°C).

2.2. Characterization

The surface morphology of TiO_2 films on ACF was observed by a scanning electron microscope (SEM, QUANTA200 model). The nitrogen adsorption was measured at 77 K using a micromeritics ASAP 2010M and the pore size distribution was calculated by the density functional theory (DFT) method [28].

2.3. Photoreactor and the activity evaluation of photocatalyst

The experiment of the photocatalytic degradation was carried out in a photoreactor shown in the previous publication [29]. The reactive bottle was a 250-mL cylindrical vessel with a water-cooled quartz jacket. Irradiation was provided by a 500-W high-pressure mercury lamp with major emission at 365 nm, located in the center of the quartz jacket. Air was bubbled through the reaction solution from the bottom to ensure a constant dissolved oxygen concentration. The temperature of the reactive solution was maintained at 30 ± 0.5 °C and the initial MO concentration was 120 mg/L. The loaded samples were used repeatedly, and each cycle lasted 30 min. Before the beginning of the next cycle, the remaining solution was replaced with 120 mg/L fresh MO solution. 4 mL solution was withdrawn at regular intervals, and the residual concentration of MO in solution was measured at 465 nm with a spectrophotometer (DR/2500, America HACH Company). The change of relative absorbance was used to record the change of concentration of MO in solution, that was $C_t/C_0 = A_t/A_0$ (C_t, A_t referred to the concentration and absorbance of MO in solution at *t* time, and C_0, A_0 referred to the concentration and absorbance of MO in solution at the initial time, respectively). All the experiments were triplicate, and the results presented were the mean values with a total error of less than 5%.

3. Results and discussion

3.1. Surface morphologies of samples

Fig. 1(a) shows the surface morphology of original ACF by SEM. Many long grooves have been observed on the surface of ACF. The surface morphologies of the loaded samples are shown in Fig. 1(b)–(g). It can be seen that the surfaces of TiO_2 films are not very homogenous because of the grooves on carbon fiber surface, and especially ribs and furrows are clearly observed on the film surface. The rough surfaces of TiO_2 films may contribute to increasing the surface area of loaded TiO_2 films, which can offer greater chance to adsorb organic compounds onto TiO_2 surface. Fig. 1(b) is the surface morphology of TiO_2/ACF-600. It can be seen that the TiO_2 films are split into numerous flakes due to shrinkage of the TiO_2 sol coating during calcined treatment [23]. The cracks in TiO_2 film are disadvantaged in extending the use-life of loaded photocatalyst because the flakes will break away from the surface of ACF in the progress of using. The film structures of TiO_2/ACF-800 shown in Fig. 1(c) have been disturbed completely and many TiO_2 fragments have broken away from the surface of ACF. Fig. 1(d) and (e) shows the images of the D-TiO_2/ACF-600. It can be observed that co-doped TiO_2 films are immobilized on the surface of ACF as a layer without any cracks. The morphology is different from the image of TiO_2/ACF-600 (Fig. 1(b)) and the result of earlier literature [23], in which the TiO_2 film is split into numerous flakes. When the calcined temperature ascends to 800 °C, only a few cracks appear in the co-doped TiO_2 films (shown in Fig. 1(f) and (g)). This phenomena indicates that the surface morphologies of films loaded on ACF are greatly influenced by the calcined temperature, and the splitting can be restrained by co-doping with Fe(III) and Ho(III).

3.2. Porous properties of samples

The nitrogen adsorption isotherms for original ACF and loaded samples are shown in Fig. 2. The pore volumes of all samples are filled below a relative pressure of about 0.02, and keep almost constant at higher relative pressure, indicating that they are highly microporous [30]. Comparing with original ACF, the saturated adsorbed volume of loaded samples is decreased greatly, which implies that some pores located ACF are covered by TiO_2 films loaded on ACF. Yuan et al. also mention the similar phenomenon in their article [26]. They found that some of the pores of ACF were blocked by the TiO_2 particles after TiO_2 particles were loaded on ACF. The film structure of TiO_2/ACF-800 is disturbed due to the high calcined temperature, and more surfaces of ACF are uncovered and play adsorption role, so the saturated adsorbed volume is the most among the four kinds of loaded samples. Co-doped TiO_2 films calcined at 600 °C are immobilized on the surface of ACF as a layer without any cracks in the films; more pores of ACF are blocked by TiO_2 films, which results in the least saturated adsorbed volume in the four kinds of loaded samples.

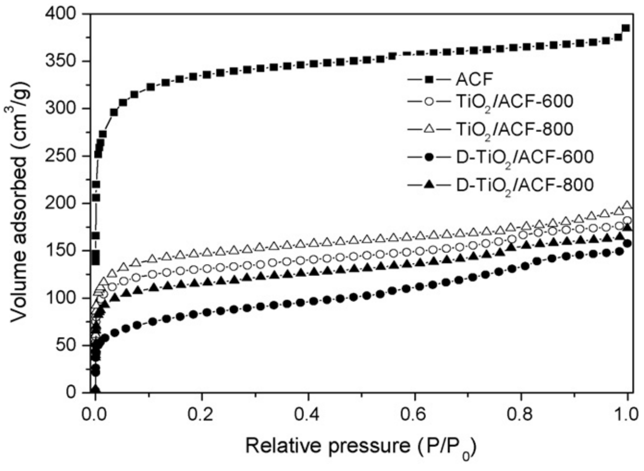

Fig. 2. Nitrogen adsorption isotherms of samples.

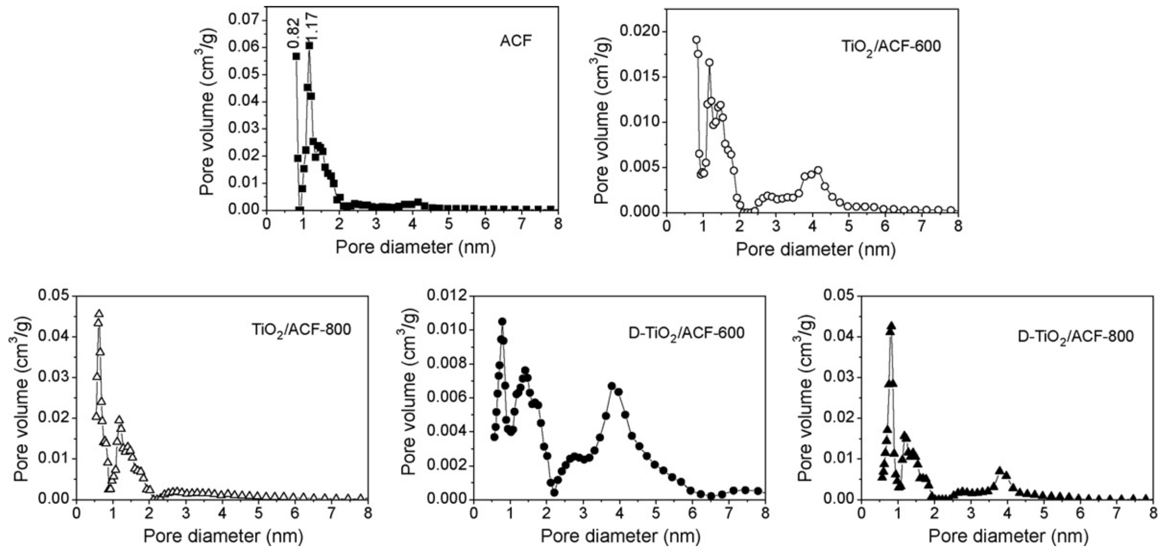

Fig. 3. Pore size distributions of samples.

The pore size distributions of all samples are calculated from DFT and shown in Fig. 3. Comparing with original ACF, the pore volumes of TiO_2/ACF samples decrease greatly, which also implies that some pores of ACF are covered by TiO_2 films. The pore size regions of original ACF and TiO_2/ACF samples are less than 2 nm and possess two sharp maximums at about 0.82 and 1.17 nm. This result seems to indicate that, although the pore volume decreased after loading with TiO_2, the pore structure of ACF remained well [26]. In addition, a small fraction of mesopores in the 3–5 nm range appears in loaded samples, which may be brought by the interspaces between the photocatalyst films.

3.3. Adsorption of TiO_2/ACF-600 for methyl orange in dark

The sorption of the dye is an important parameter in determining photocatalytic degradation rate [31]. In order to distinguish the functions of the adsorption of ACF and photocatalysis of TiO_2 film, the adsorption of MO on TiO_2/ACF-600 sample is tested in the dark under the same conditions as UV irradiation, and the results are shown in Fig. 4. It can be observed that most of MO molecules are removed within 15 min at the first cycle, and an obvious decrease in adsorption capacity can be found at the second cycle. When the sample is used once more, the residual concentration ratio C_t/C_0 of MO further increased, which indicates that the adsorption capacity of sample disappears gradually without UV irradiation [26].

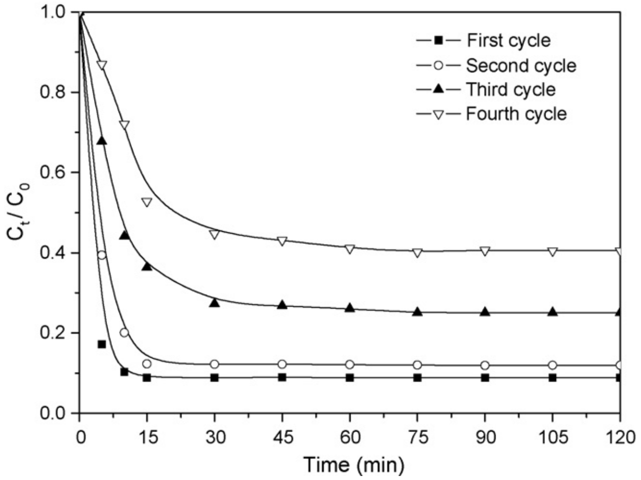

Fig. 4. Cyclic adsorption performance of TiO_2/ACF-600 in dark.

3.4. Photocatalytic activities of samples

Fig. 5 shows the photocatalytic degradation property of MO by using the loaded samples under UV irradiation. It is observed that the differences in discoloration effects of the four loaded samples are unobvious at the first cycle. The case slightly changes at the second cycle because the four samples exhibit some differences for MO removal. The discrepancies are more obvious at the third and fourth cycles. It can be seen from the fourth cycle that the discoloration efficiency of D-TiO_2/ACF-600 is the best, and TiO_2/ACF-800 is the worst. Further more, the sample of D-TiO_2/ACF-600 exhibits better and stabler photocatalytic degradation property from the first cycle to the fourth cycle. The stable performance of ACF supported TiO_2 reveals that the TiO_2 films are strongly adhered to the ACF surface [13].

In comparing with Fig. 4, it can be deduced that MO molecules are rapidly removed from water under UV irradiation, and this may be attributed to the synergistic effects of two factors: absorption of ACF and photocatalytic degradation of photocatalyst films. The photocatalytic degradation rate is controlled by the stimulated and migratory velocity of photogenerated carriers [32], so the reactive rate of photocatalysis is slower a lot than that of adsorption. At the first cycle, adsorption reaction plays a main role because of the great adsorption capacity and the strong adsorption strength of ACF. Most of MO molecules are removed by adsorption. So the differences of the four loaded samples for MO removal are unobvious. After the remaining solution was replaced with fresh MO solution and the next cycle began, adsorption ability of sample decreases and photocatalytic degradation of TiO_2 film plays a main role gradually. So the differences of the four samples for MO removal become obvious in the next cycles. D-TiO_2/ACF-600 sample presents the best photocatalytic activity for MO removal from the first cycle to the fourth cycle, and the discolored ratio of MO is always maintained at above 99% without any decline, which may due to the fact that the optimal synergistic effect has been arrived between absorption of ACF and photocatalytic degradation of photocatalyst films. In addition, the effects brought by co-doping with Fe(III) and Ho(III) (described in the earlier papers [10,33]) may be other reasons why D-TiO_2/ACF-600 sample exhibits the high photocatalytic activity.

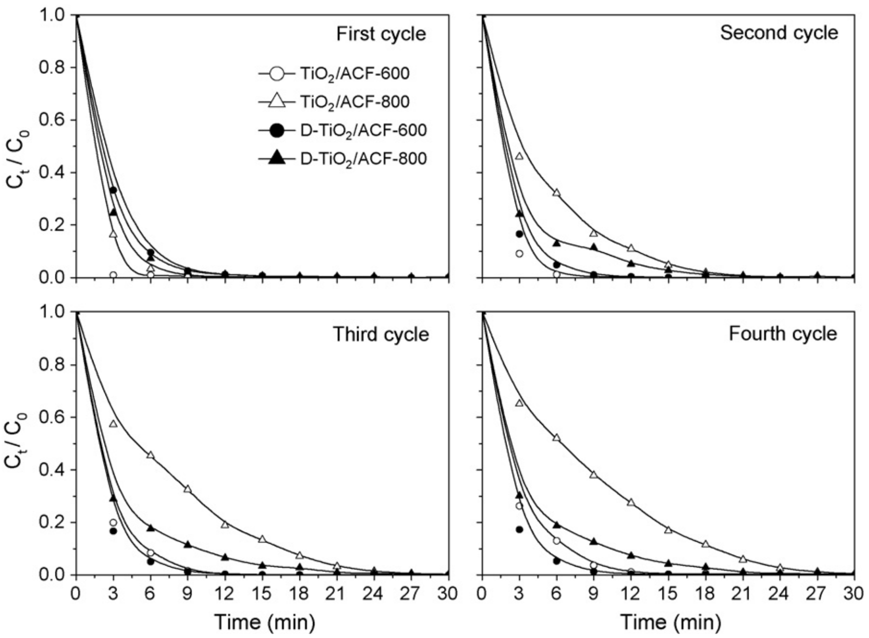

Fig. 5. Photocatalytic degradation of MO by loaded samples for four cycles.

4. Conclusions

Fe(III) and Ho(III) co-doped TiO_2 films and un-doped TiO_2 films loaded on ACF were prepared by sol–gel-adsorption method. The surface morphology of films loaded on ACF could be influenced greatly by the calcined temperature. MO in water could be removed rapidly by the loaded samples under UV irradiation because of the synergistic effects of two factors: absorption of ACF and photocatalytic degradation of photocatalyst films. The D-TiO_2/ACF-600 sample presented better and stabler photocatalytic degradation property from the first cycle to the fourth cycle. Thus, Fe(III) and Ho(III) co-doped TiO_2 film loaded on ACF may be an efficient material for decontaminating colored wastewater in textile industries. Further more, the co-doping with Fe(III) and Ho(III) could restrain the forming of crack in TiO_2 films, and the reason still requires further investigation in the future.

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