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Microstructure and visible light photocatalytic activity of Fe–TiO₂ films on steel by PEO

M. Wang^{1,2}, Y. C. Lei⁴, Y. L. Wang^{*1,4}, M. Zhou^{1,3}, Q. Zhu⁴, B. Wu¹, G. Amoako¹ and H. Ding¹

Fe doped TiO₂ ceramic films were fabricated on carbon steel by plasma electrolytic oxidation. The microstructure of the film was characterised, and the photocatalytic activities of the films were evaluated. The results showed that the phases of the films were anatase TiO₂ and Al₂TiO₅. The film surface was rough and porous. With increasing the treatment time, the pores on film surfaces gradually became deep and large, which made the film surfaces rougher. Fe–TiO₂ films showed red shift in photoresponse towards the visible region. The photocatalytic activities of the films were evaluated by photocatalytic oxidation of Rhodamine B aqueous under visible light irradiation. The results revealed that the film showed visible light photocatalytic activity. With increasing treatment time, the degradation rate of rhodamine B gradually increased and the highest degradation rate was ~80% in visible light irradiation for 6 h.

Keywords: Titanium dioxide film, Fe doped, Photocatalytic activities, Visible light, Rhodamine B, Plasma electrolytic oxidation

Introduction

Recently, photocatalytic oxides and the photocatalysis field have been extensively studied by researchers due to their increasing importance. Among various oxide photocatalysts, titanium dioxide has been reported to be one of the most effective photocatalysts and has been widely studied.^{1–3} However, the practical applications of TiO₂ are limited because TiO₂ shows its photocatalytic activity only when it is exposed to UV light.^{4,5} Therefore, increasing the photocatalytic activity of TiO₂ in visible light is the pursuit of researchers. TiO₂ doped with some metal or non-metal elements has been reported to be a feasible way to obtain composite TiO₂, which can be activated by visible light.^{6,7} Among the various forms of TiO₂ such as film, powder and bulk, the films, which are usually fixed on some substrates, are the most widely used due to their high efficiency and stability.

Many methods such as sol–gel^{8,9} and chemical vapour deposition techniques¹⁰ have been developed to synthesise doped TiO₂ films. In this article, Fe doped TiO₂ films were synthesised on carbon steel by a relatively new and simple method called plasma electrolytic oxidation (PEO). PEO is a newly developed electrochemical technique performed at room temperature and mild surroundings and is used to prepare metal oxide films on

metal substrates.¹¹ Preparation of functional films on steels by PEO was rarely reported. Here, the microstructure of PEO film on steel was characterised, and the photocatalytic activity of the films was evaluated by photodegrade action of Rhodamine B irradiated with visible light. The mechanism of photoactivity enhancement of the doped films was discussed.

Experimental

Film preparation

Q235 carbon steels were first processed into a round size with a diameter of 15 mm and a thickness of 2 mm. The samples were then polished and cleaned before PEO treatment. The PEO experimental system contains a homemade single polar pulsed electrical power source and stainless steel electrobath. During PEO treatment, the carbon steel substrates were used as anode and the stainless steel electrobath served as cathode. The running water around the stainless steel electrobath was used as the cooling system to keep the electrolyte at room temperature. The schematic view of the PEO system is shown in Fig. 1a.

The aqueous aluminate solution containing some NaAlO₂ and NaH₂PO₄ was used as electrolyte. TiO₂ powder was added to the electrolyte, and a polytetrafluoroethylene stirrer was used to keep the powder suspended. The PEO process was carried out for 30 min under a stable current density of 8 A dm⁻² with a fixed frequency of 3000 Hz. In order to study the structure and photocatalytic activity of the film, samples were treated for 10, 20 and 30 min respectively.

Film characterisation

The surface and cross-sectional morphology of the ceramic coating was investigated by scanning electron

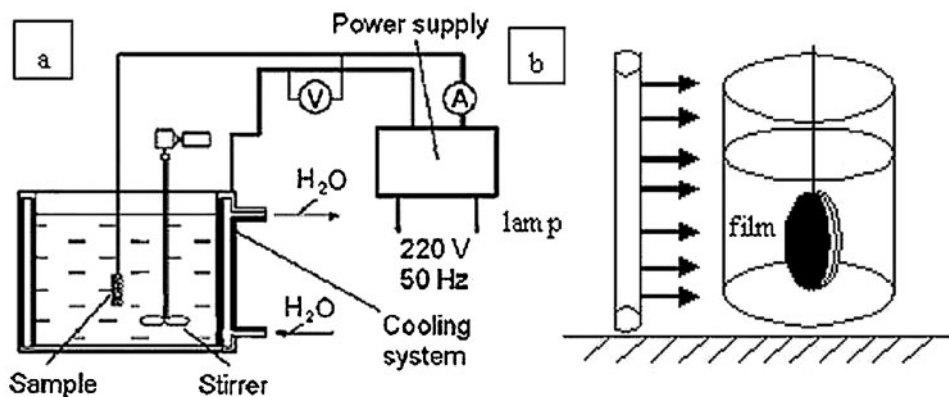
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1 Schematic view of PEO system and photocatalytic measurement system: *a* PEO system; *b* photocatalytic measurement system

microscope (Hitachi S-570); the phase and element composition were measured by an X-ray diffractometer (XRD, D/max-rB, Japan, Cu target, K_{α} radial) and energy dispersive X-ray spectroscopy (EDS, Oxford Model 7537, England) respectively. The samples thicknesses were measured using an eddy current based thickness gauge (TT260, Time Company, China). The surface roughness of PEO coatings was tested by a roughness tester (JB-4C, Shanghai, China). The absorption spectra of the samples were collected by an ultraviolet-visible spectrophotometer.

Photocatalytic activity measurement

The photocatalytic activities of the films were tested by photodegradation of Rhodamine B (10 mg L^{-1}) in 10 mL aqueous solution. A coated sample with a surface area of 2 cm^2 was immersed into Rhodamine B solution. A halogen lamp (40 W) was placed perpendicular to the coated sample. The whole test lasted for 6 h, during which the samples were collected at different time intervals for testing to obtain the concentration change of photodegradation. The concentration change of Rhodamine B with respect to the irradiation time was tested with a UV spectrophotometer by measuring the

absorbance of Rhodamine B. The photodegradation of Rhodamine B is measured by removal ratio

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%$$

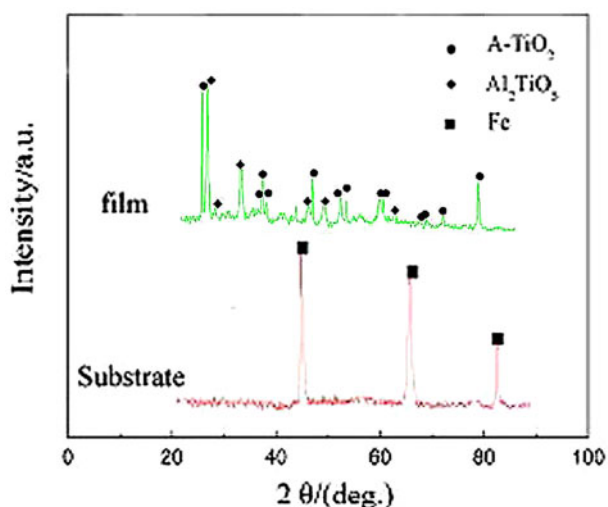
where η is the degradation rate, and C_0 and C_t are the initial absorbency and the reaction absorbency of Rhodamine B solution, respectively.

Results and discussion

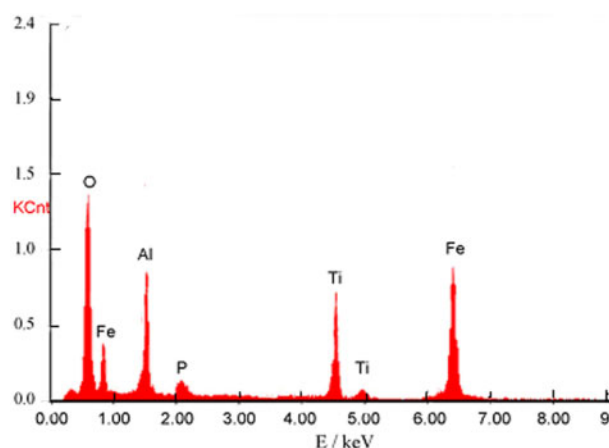
Phase and element composition of film

The XRD patterns of the obtained film (30 min treated) and the carbon steel substrate are shown in Fig. 2. It is seen that many feature peaks of anatase-TiO₂ (A-TiO₂) are presented in the figure, which shows that the film mainly consisted of A-TiO₂. In addition, some feature peaks of Al₂TiO₅ are seen in Fig. 1, implying existence of Al₂TiO₅ in the film. Therefore, the film is composed of crystal A-TiO₂ and Al₂TiO₅. No characteristic peaks of the doping specie Fe and its chemical compounds are detected by XRD. This suggests that no crystal phase of chemicals containing Fe elements was present in the film.

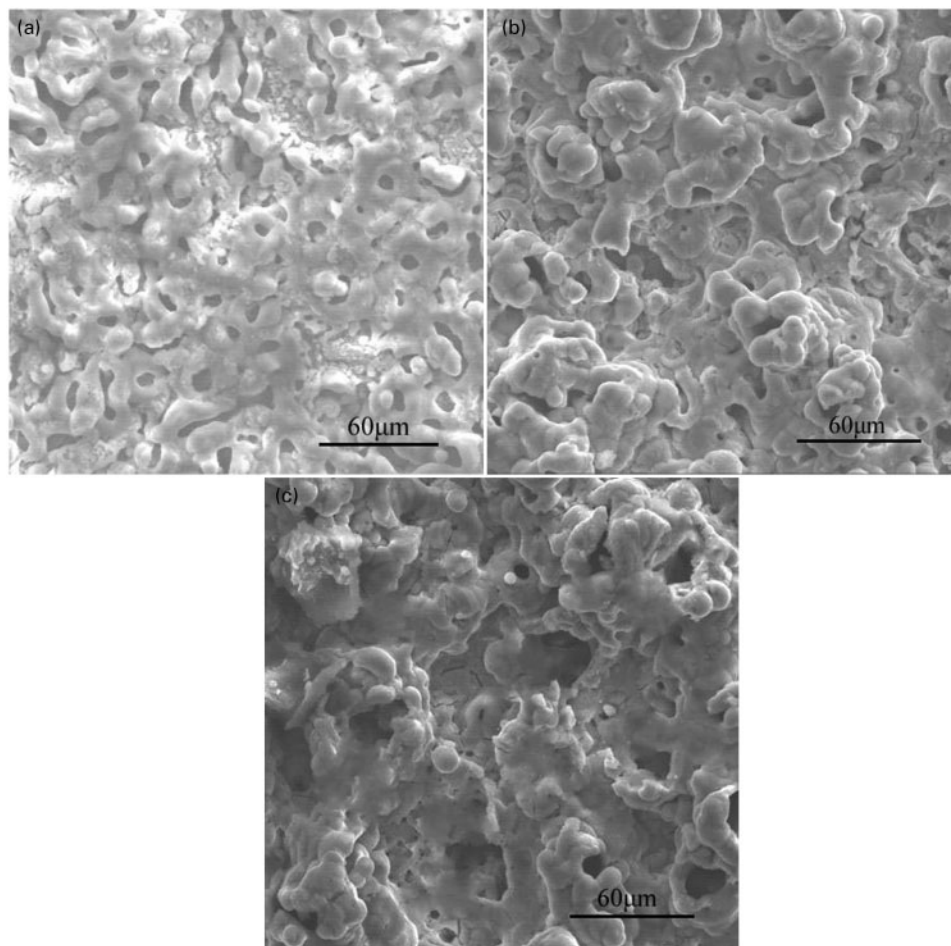
In order to further study the elemental composition of the film, EDS test of the sample surface was used and the



2 X-ray diffractometry pattern of obtained film on carbon steel substrate



3 Energy dispersive X-ray spectroscopy patterns of film surface



4 Surface morphologies of film obtained with different treatment time: a 10 min; b 20 min; c 30 min

pattern is shown in Fig. 3. From Fig. 3, it is seen that apart from the elements O, Al and Ti detected by XRD, other elements such as Fe and a little P were also detected in the film. Comparing the EDS and the XRD analyses, it can be concluded that the obtained film is Fe doped into composite TiO₂ film.

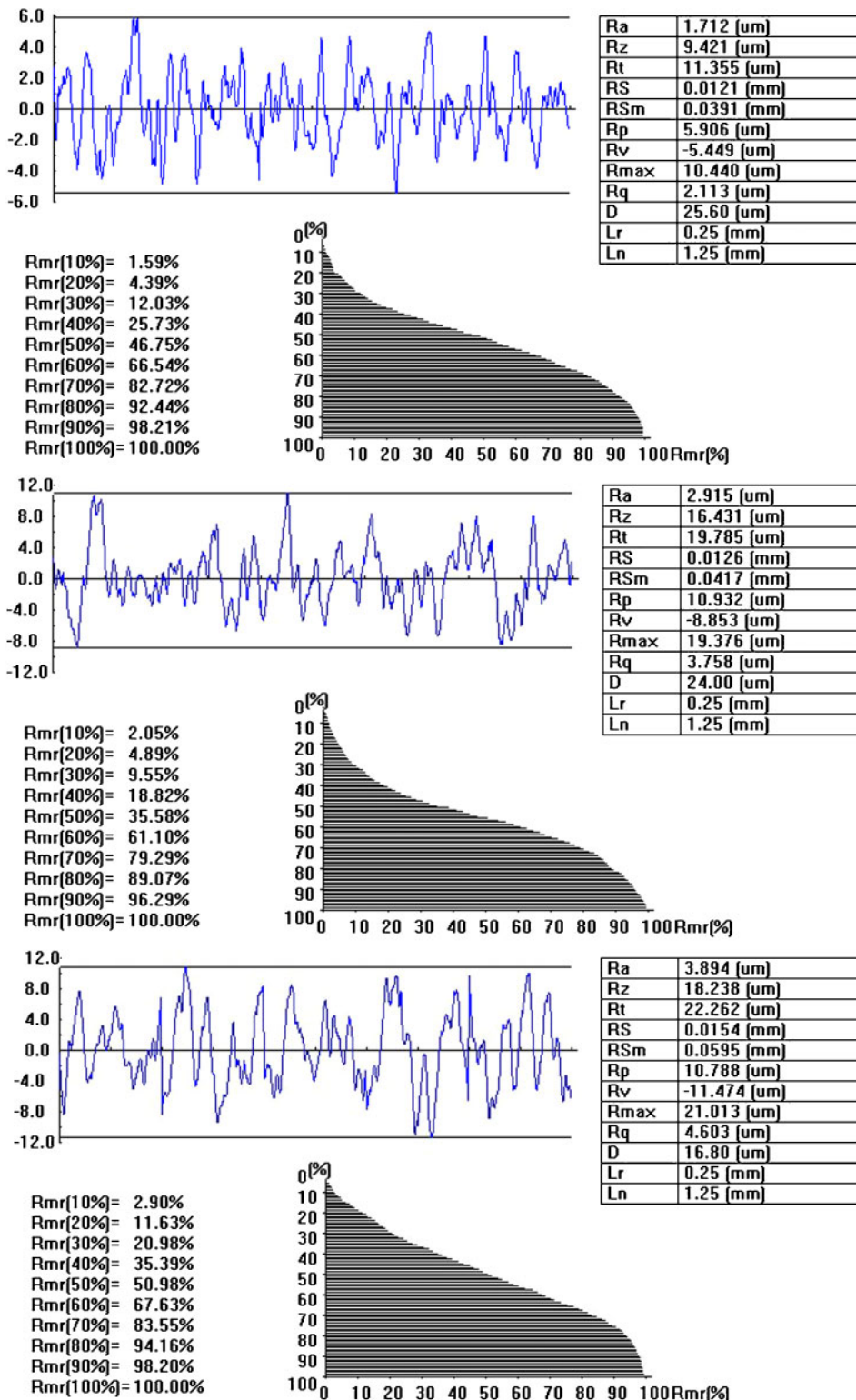
Surface morphology and surface roughness

Figure 4 illustrates the surface morphologies of films with various treatment times. In an overview, the films show porous and rough surfaces. There are many pores and particles on the surface. For films giving short time treatment, the pores are irregular. From Fig. 4a and b, it is seen that with increasing treatment time, the pores gradually become round and the depth and diameter also increase. Further increasing the treatment time (see Fig. 4c), the pores again become irregular. From the film surface, it is also seen that the surface gradually becomes coarser with increasing treatment time, which resulted from the deeper and larger pores. Usually, a porous surface is a typical characteristic of PEO prepared films.^{12,13} However, here, the pores are deeper and larger. This was attributed to the high peak current densities used. The PEO process on steels usually needs higher current densities than those on valve metals. The pores are actually the discharge channels during PEO, and high peak current densities will result in intense discharges. Therefore, large and deep pores will form, especially during extended treatment of samples.

The surface roughness of the films treated with different time is shown in Fig. 5. It shows that with increasing treatment time, the surface roughness of the films gradually increases. The variation of surface roughness of the films agrees with variation of surface morphology. With increasing treatment time, deeper and larger pores develop on the film surface, which results in higher surface roughness. Therefore, considering the surface morphology and surface roughness, it can be inferred that the surface porosity of the film increases when increasing treatment time.

Thickness and surface hardness

The variation of thickness and surface hardness of the films with treatment time are shown in Figs. 6 and 7 respectively. It is seen that the thickness of the film increases when increasing the treatment time. It can also be seen that during much of the treatment period, the film shows high growth rate, and a relatively low growth rate can be found near the end of the treatment process. Figure 7 shows that when the treatment time increases, the surface hardness of the films first increases and then shows little changes, and finally decreases gradually. Usually, during the PEO process, the film initially grows faster and then slows down since the discharges become less near the end. The film grows through the discharge reaction during PEO.¹¹ The surface hardness is closely related to the surface structure of the film. A coarser and much porous surface of the film surface results in a loose



5 Surface roughnesses of films treated with different times: a 10 min; b 20 min; c 30 min

surface structure of the film, which decreases the surface hardness.

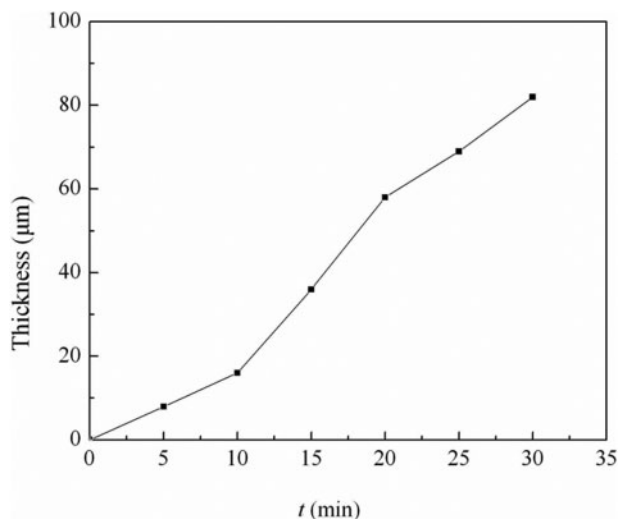
Ultraviolet-visible spectroscopy

The ultraviolet-visible absorbance spectra of the films treated with different times are shown in Fig. 8. It is seen that all the Fe-TiO₂ samples show a significant absorption in the visible between 400 and 500 nm.

Pure TiO₂ film without Fe doping shows no obvious absorption in the visible region.¹⁴ Therefore, Fe doped TiO₂ films result in the shift of the absorbance region towards longer wavelengths.

Photocatalytic activities of films

The photocatalytic degradation of Rhodamine B of different time treated Fe-TiO₂ samples under visible



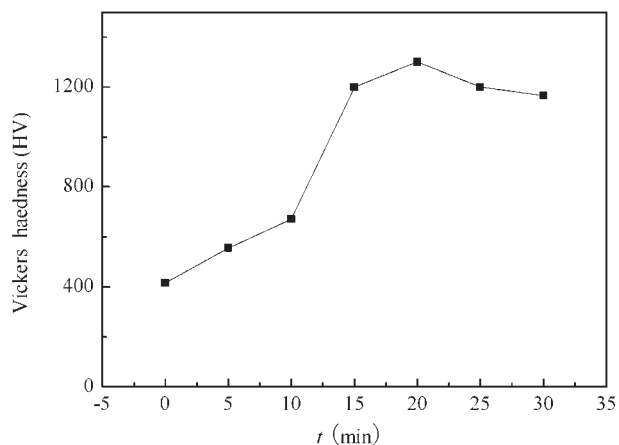
6 Variation of thickness of films with treatment time

light irradiation was evaluated, and the results are shown in Fig. 9. It is obvious that the Fe-TiO₂ films show good photocatalytic activities. With increasing treatment time, the removal ratio of Rhodamine B gradually increases, which reflects that the photocatalytic activity also gradually increases. For 6 h irradiation under visible light, the removal ratio of Rhodamine B of the sample treated in 30 min reaches ~80%.

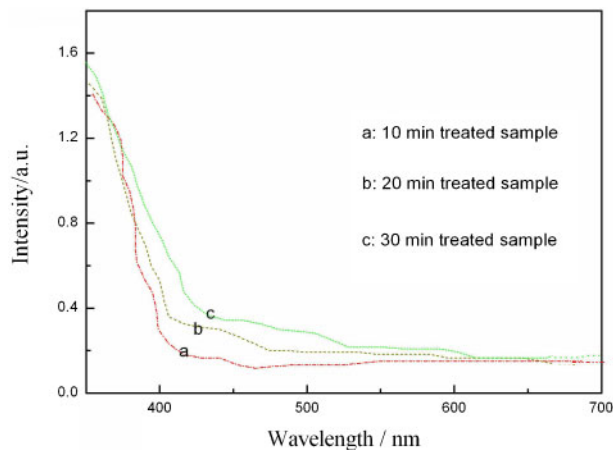
The visible light photocatalytic activity of the Fe-TiO₂ films is attributed to the Fe in the film, which results in an additional stronger absorbance in the visible light range. This has been reported by many researchers.¹⁵ In addition, the porous surface of the film is very useful for catalysis. The increase in the photocatalytic activity with increasing treatment time can be ascribed to the surface structure of the film. Longer time treated samples result in a coarser surface, which offers more surface area for the photocatalytic reaction. The method reported here offers a feasible way to obtain visible light responded TiO₂ photocatalyst.

Conclusion

Fe-TiO₂ films were prepared on carbon steel by PEO. The films were composed of A-TiO₂ and Al₂TiO₅. Elemental Fe was doped into the films. The film surfaces



7 Variation of surface hardness of films with treatment time

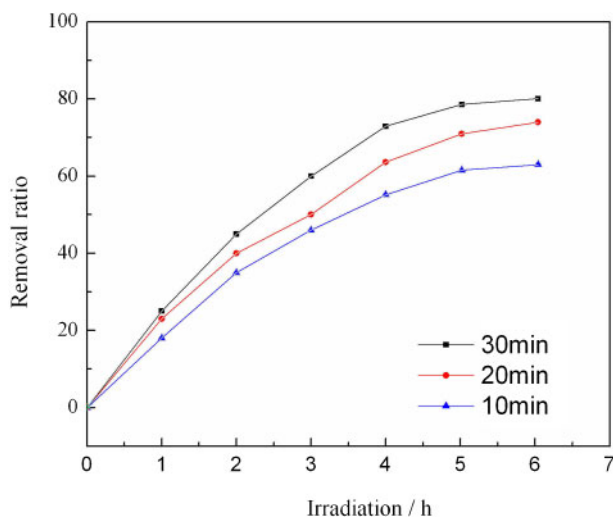


8 Ultraviolet-visible absorption spectra of TiO₂ films obtained with different treatment

were porous and rough. With increasing treatment time, the pores on the film surfaces gradually became deep and large, and the film surface became rougher. Fe doped TiO₂ films showed red shift in photoresponse towards the visible region. The photocatalytic activity of the films was evaluated by the photocatalytic oxidation of aqueous Rhodamine B under visible light irradiation. The results revealed that the Fe doped film samples showed photocatalytic activities under visible light irradiation. With increasing treatment time, the degradation rate of Rhodamine B of the samples gradually increased and the highest degradation rate was ~80% in visible light irradiation for 6 h.

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9 Photocatalytic degradation of Rhodamine B of different times treated films under visible light irradiation

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