Research Article
Antibacterial Activity of Visible Light-Activated TiO₂ Thin Films with Low Level of Fe Doping

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Development of effective antibacterial visible light-activated photocatalytic materials in industries including wastewater treatment and food industry has attracted increasing attention. In this work, Fe-doped TiO₂ thin films with different doping levels on a glass substrate were prepared by the sol-gel dip-coating method. The as-prepared films were characterized by Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM). Raman spectroscopy and XRD results show the crystalline phase of titanium dioxide was anatase, and the range of the crystal size for the films was 19.24–22.24 nm. XPS results indicate that iron was in the form of Fe³⁺ in Fe-doped TiO₂ films. Regarding the antibacterial properties of TiO₂ films, the order of antibacterial activity of TiO₂ films was 0.1 at% Fe³⁺ > 0.5 at% Fe³⁺ > 1.0 at% TiO₂ > bare TiO₂ > 2.0 at% Fe³⁺ > 3.45 at% Fe. 0.1 at% of Fe is the optimum dopant ratio related to antibacterial activity. 0.1 at% Fe-doped TiO₂ film is highly efficient in inactivating E. coli under 3 h of visible light irradiation, and it remains efficient even in real dye waste water.

1. Introduction

Visible and solar light-active semiconductor photocatalysis has been greatly documented for antibacterial application in food industry, environmental, hospital, and wastewater treatment [1–8]. Among these semiconductor materials, TiO₂ is probably the most widely studied one owing to a great deal of advantages, i.e., low cost, ready availability, high chemical stability, nontoxicity, environmental friendliness, etc. [9–11].

As early as in 1999, Fujishima et al. [12] reported that TiO₂ can kill bacteria on its surface. Since then, there has been increasing attention in the antibacterial property of TiO₂. However, anatase TiO₂ has a relatively large band gap of 3.2 eV and can only be activated under the irradiation of UV light (λ ≤ 387 nm), which limits its utilization in visible and solar irradiation [13]. Therefore, in order to extend the spectral response to visible light region, efforts to combine TiO₂ with other elements such as metal deposition [11, 14–17], nonmetal doping [18–21], and metal and nonmetal codoping [22, 23] have been carried out. Doping TiO₂ with transition metals such as Fe [11, 24], Cr [25], Cu [26, 27], and Zn [28] is a simple and effective method. More recently, antibacterial properties of TiO₂ with various morphologies such as graphene nanosheet doped TiO₂ [29], titania nanotubes [6], and Fe-Ag/TiO₂ bimetallic nanowires [30] were reported.

Fe has attracted extensive attention because its octahedral trivalent radius (0.079 nm) is similar to that of titanium’s octahedral tetrahedron (0.075 nm) [10]. Introduction of iron in the titania crystal lattice can form a new energy level between the valence band and conduction band, resulting in an extension of light absorption of TiO₂ into the visible region [4, 31, 32]. The antibacterial property of Fe-doped TiO₂ under UV irradiation has been widely studied [10, 33–37], which shows the Fe-doped TiO₂ has excellent antibacterial properties against E. coli and S. aureus, some of which can be as high as 100% [10, 35]. Antibacterial activity of Fe³⁺-doped TiO₂ nanoparticles was studied by Boonyod S et al. [38], which reported that 0.5 mol % Fe³⁺/TiO₂ can destroy E. coli after 20 min with UV irradiation. More recently, AL-Jawad et al. [11] found that the antibacterial efficiency of 6% Fe-doped TiO₂ thin films against E. coli and S. aureus can both reach 100% under UV light. However,
these reports mostly tested antibacterial properties of Fe-doped TiO$_2$ under UV irradiation, rarely under visible light irradiation. Arellano et al. [34] reported the antimicrobial activity under visible light irradiation of TiO$_2$ thin films with 3 wt% and 5 wt% of Fe on the glass substrate by the spin-coating method. They found that doping TiO$_2$ film with 5 wt% of Fe treated at 800°C can eliminate the bacteria completely after 60 min.

In order to explore the effect of iron content on the antibacterial properties of TiO$_2$ thin film visible light irradiation, TiO$_2$ films with different iron contents by the sol-gel dip-coating method on the glass substrate were prepared in our work. These series of Fe-doped TiO$_2$ thin films were characterized by Raman spectroscopy, XRD, XPS, and AFM. The optimum dopant ratio is 0.1 at%, with the best antibacterial activity even in real dye waste water.

2. Experimental

2.1. Preparation of TiO$_2$ Thin Films. Fe-doped TiO$_2$ thin films were prepared by the sol-gel dip-coating method. For the preparation of sol, 10 ml of Ti(OBu)$_4$ as precursor solution was added to 26 ml of ethanol under stirring at room temperature, and continued stirring vigorously for 0.5 h. After stirring, a mixed solution containing 20 ml of ethanol, 1.05 ml of concentrated hydrochloric acid, some water and different amounts of FeCl$_2$·6H$_2$O was added dropwise to the above solution under stirring followed by a 2-hour hydrolysis period and 24-hour ageing period, resulting in the Fe-doped sol. The atomic ratios of Fe to Ti were 0, 0.1, 0.5, 1.0, 2.0, and 3.45 at%.

For the preparation of the films, ordinary glass slides were used as the supporting substrate (75.0 mm × 25.0 mm × 1.2 mm) after soaked in acid pail for 24 h and ultrasonic cleaning with ethanol for 3 times. The cleaned and dried glass slides were dipped in the above sol for 1.5 min and then withdrew at 1.94 mm·s$^{-1}$. After the gel films came to dryness at room temperature, they were calcined in muffle furnace at 450°C for 2 h in air. For the preparation of multilayered films, the gel films were left in the furnace at 450°C for 10 min after each coating cycle and finally calcined at 450°C for 2 h. In our experiments, the coating was repeated from one to five times, and the thickness of the TiO$_2$ films is 150 nm–370 nm, as shown in supporting information (Figure S1). Five-layered films were used for characterization and antibacterial test.

2.2. Characterization. Raman spectra were recorded with a confocal Raman spectroscopy with the Raman shift ranging from 0 to 1000 cm$^{-1}$ (Jobin Yvon, HR 800). The crystal phase and crystal size of the obtained TiO$_2$ films were investigated by X-ray diffraction (Philips, MPD-MPDXPERT) with the diffraction angles scanning from 2θ = 15°–90°, using the 0.154 nm of Cu Kα radiation source. X-ray photoelectron spectroscopy was taken on an XSAM800 XPS system with a Cu Kα source. Morphology of the thin films was observed using an atomic force microscope (AFM, SPI-300HV) with the scanning range of 1000 nm × 1000 nm under the scan pattern of noncontact.

2.3. Antibacterial Test. The antibacterial test was carried out in the aseptic room throughout the experiment. The antibacterial activity of the Fe-doped TiO$_2$ films and bare TiO$_2$ films was evaluated by the method of GB/T 5750.12–2006 [39]. The strain of *Escherichia coli* (*E. coli* ATCC 8739) was cultured in the solid medium and liquid medium, respectively. The lactose peptone suitable for *E. coli* growth was used to configure liquid medium and agar for medium configuration. Firstly, the bacteria were prepared using nutrient agar [39] and cultured in an incubator at 37 ± 1°C for 24 h, and then the prepared bacteria were transferred to a tube with a sloping solid medium and cultured again. After this, a small amount of bacteria were placed in a conical flask containing liquid medium followed by 24 h of culture. The initial concentration of bacterial solution was approximately 1 × 10$^7$ CFU/mL, and the concentration of experimental bacterial solution was achieved by dilution of 10 times with sterilized distilled water by a series of dilution methods.

A photocatalytic reactor used in the antibacterial test is shown in Figure 1, in which a 500 W xenon lamp (it mainly provides visible light in the range of 400–700 nm) used to simulate the solar light was positioned inside the reactor surrounded by a circulating water jacket to cool the reaction temperature. Four films were placed vertically on a shelf in a covered beaker which is inoculated with 500 ml of 10$^7$ CFU/ml of bacteria. At the other side of the reactor, the reference with 4 bare TiO$_2$ films was configured in the same way. The sample and reference were parallel to the light source. The magnetic stirrer was used to ensure that the solution is mixed evenly throughout the experiment. The antibacterial rate of bacteria of the TiO$_2$ films can be calculated by following formula:

$$\text{R} = \left( \frac{c - a}{c} \right) \times 100\%,$$

where R is the antibacterial rate, %; c is the colony count of reference samples, CFU/ml, and the method of colony count is shown in supporting information: experimental section; and a is the colony count of TiO$_2$ films, CFU/ml.

3. Results and Discussion

The peak patterns of Raman spectra show that all the Fe-doped films exhibit five anatase TiO$_2$ peaks around 144, 196, 397, 517, and 639 cm$^{-1}$ which can be attributed to Ti-O vibrations [6, 40] (Figure 2). There was no peak due to iron oxide even for the heavily doped sample with 2.0 at% of Fe. Moreover, the intensity of characteristic peaks of Fe-doped TiO$_2$ tends to decrease gradually as the amount of the Fe dopant increases because Fe doping leads to lattice distortion and change in the crystallite size (Table 1) [41].

The XRD patterns (Figure 3) exhibit expected diffraction peaks at 25°, 38°, 48°, 53°, 55°, 62°, and 75° indexed as the (101), (004), (200), (105), (211), (204), and (215) crystalline plane of anatase TiO$_2$, respectively (JCPDS file no. 21–1272 [11]). Raman and XRD spectra show that no peaks of iron oxide were observed. Hence, the iron in the Fe-doped TiO$_2$ films should be highly dispersed in the titanium dioxide lattice.
The XPS pattern of 1.0 at% of Fe-doped TiO₂ film shows that the peak of Fe 2p can be fitted into two peaks at binding energies of 723.8 and 711.1 eV, which are attributed to Fe 2p₁/₂ and Fe 2p₃/₂, respectively, and the two peaks correspond to those of Fe³⁺ (Figure 4).

AFM imaging was used to observe the surface morphology of the samples. It was observed that the films are composed of nanocrystalline islands of different sizes. For bare TiO₂ films, it forms scattered ellipsoidal nanoparticles of various sizes on the glass substrate, with an average particle size around 42 nm (Figure S3). After Fe-doping, the thin and dense needle-like nanoparticles appeared on the surface of the films with more deep valley formation by voids and peaks formation by protrusions between the nanoparticles (Figure 5). In our experiments, the nanocrystalline particles on the surface of the film are connected into flakes in the atomic ratio of Fe:Ti 2:0 at%, resulting in massive deep valleys and obvious peaks (Figure S4). This confirms that the crystal size of TiO₂ is changed and indicates changes in the roughness of the samples. The roughness data are in good agreement with this prediction, with increasing roughness for Fe-doped TiO₂ films (Table 1).

The effect of obtained Fe-doped TiO₂ films on the antibacterial activity of *E. coli* was determined by evaluation of the growth of the cultures under irradiation from a xenon lamp source, compared with the growth of the bacterial cultured in TiO₂ film only. Figure 6(a) showed the agar plate was covered with bacterial colonies before illumination. After 3 h of photocatalytic reaction, 0.1, 0.5, and 1.0 at% of Fe-doped TiO₂ film was much better to prevent the growth of colonies of *E. coli* as can be seen in Figure 6(c), compared with the bare TiO₂ film (Figure 6(d)) which showed limited antibacterial property.

To determine the appropriate amount of Fe doping, samples containing 0, 0.1, 0.5, 1.0, 2.0, and 3.45 at% of Fe-doped TiO₂ films were used in antibacterial testing. Figure 7 shows the antibacterial rate at each time point for both reference and test samples. After one hour of the experiment, 0.1, 0.5, and 1.0 at% of Fe-doped TiO₂ films showed much higher antibacterial rate than that of the bare TiO₂ film, and it has reached more than 60% in 0.1% of Fe-doped TiO₂ film.
At the end of the experiment, the antibacterial rate of TiO₂ films with doping ratio of less than 2.0 at% was much higher than that of bare TiO₂ film and it decreased with the increase of Fe dopant ratio above 2.0 at%. The order of antibacterial activity of TiO₂ films was as follows: 0.1 at% Fe > 0.5 at% Fe > 1.0 at% TiO₂ > bare TiO₂ > 2.0 at% Fe > 3.45 at% Fe-doping TiO₂. 0.1 at% of Fe is the optimum dopant ratio.

The antibacterial effect of obtained films was further investigated on the total bacteria in the real dye waste water. Dye waste water has the characteristics of large quantity, large alkalinity, deep chroma, and high content of organic pollutants, so it is still very difficult to deal with. Also, it contains a large number of microorganisms, including bacteria and fungi. 0.1 at% of Fe-doped TiO₂
film was selected to carry out this experiment by the same method as that of *E. coli* above. The dye waste water collected from a printing and dyeing factory was left for 24 h. The total bacteria in the supernatant were cultured and counted. It was then diluted to $1 \times 10^5$ CFU/mL for subsequent experimental measurements. The antibacterial properties of the film were tested under the illumination of a xenon lamp in the sterile room. The antibacterial rate of 0.1 at% of Fe-doped TiO$_2$ films was up to 97.57%, which is much higher than that of the bare TiO$_2$ film (Figure 8). This test showed that the Fe-doped TiO$_2$ films still have good antibacterial activity in a complex and real waste water, such as the coexistence of many bacteria and the presence of a large amount of organic compounds.

The modified TiO$_2$ nanomaterials such as Fe, Co, and V are reported that can extend the spectral response of TiO$_2$ to the visible region [2, 10, 17, 42–46]. When the absorption range of TiO$_2$ is induced to the visible light region, the photocatalytic reaction occurs under the irradiation of solar light. The reaction involves the production of photogenerated holes and photoexcited electrons. These photogenerated holes can react with water to produce *OH on the surface of the photocatalyst, and the photoexcited electrons can reduce oxygen to produce O$_2^-$ which can be further oxidized by photogenerated holes to form O$_2$. Then, the photogenerated holes can continue to react to produce other

![Figure 6](image1.png)  
**Figure 6:** Agar plates before photocatalytic reaction (a) 0.1 at% of Fe-doped TiO$_2$ and (b) bare TiO$_2$, and after 3 h of photocatalytic reaction (c) 0.1 at% of Fe-doped TiO$_2$ and (d) bare TiO$_2$.

![Figure 7](image2.png)  
**Figure 7:** Antibacterial rate of (a) bare TiO$_2$, (b) 0.1 at%, (c) 0.5 at%, (d) 1.0 at%, (e) 2.0 at%, and (f) 3.45 at% of Fe-doped TiO$_2$ against *E. coli*.
highly oxidizing species such as H2O2 or \( \cdot \)OOH. These reactive oxygen species are toxic to the bacteria. They are in contact with bacteria on the surface of the obtained films and can degrade the cell of the bacteria by oxidizing the cell membrane, leading to loss of bacterial cell components and cell death. However, photocatalytic activity depends on the amount of doping agent. Excessive doping of metal will remain on the surface of the films and block reaction sites, resulting in a decrease in the activity of photocatalytic reaction [47]. Just as in our experiment, more than 2.0 at% of the Fe-doping TiO2 film shows a decrease in antibacterial activity.

4. Conclusion

Antibacterial properties of the TiO2 films under visible light with different molar ratios of Fe to Ti prepared by a sol-gel dip-coating method were studied and compared with the bare TiO2 film. The Fe-doped TiO2 films are mainly in the form of Fe\(^{3+}\). When the doping concentration is more than 2.0 at%, the antibacterial properties of the Fe-doped TiO2 films was lower than that of the bare TiO2 films. Low level of Fe doping less than 2.0 at% showed excellent antibacterial activity even in real dye waste water.

Data Availability

The data used to support the findings of this study are included within the article and supplementary information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

C. X. designed the study. D. M. performed most of the reactions. X. L. performed some bacterial activity tests. Y. X., Y. Y., and Y. D. performed some characterization and analysis. D. M. and C. X. wrote the paper.

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Supplementary Materials

Figure S1: thickness of TiO2 films with films with different coating layers. Figure S2: X-ray diffraction patterns of 2 at% of Fe-doped TiO2 at different calcined temperatures. Figure S3: statistical results of particle size in a bare TiO2 film (a) and 0.1 at% Fe-doped TiO2 films (b). Figure S4: 3D AFM images of TiO2 films with different Fe-doping amounts. Experimental section: colony counting method. (Supplementary Materials)

References


