

EFFECT OF Fe DOPED ON THE SUPERHYDROPHILIC PROPERTIES AND ANTIBACTERIAL ACTIVITY OF TiO₂ THIN FILM PREPARED BY SOL-GEL DIP COATING

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Abstract

In this paper, we present some studies Fe undoped and doped on TiO₂ thin films is prepared by sol-gel dip coating technique. Effects of doped iron on the characteristics of the films were studied using RAMAN spectra. Morphology surface of thin film are investigated by FESEM. Superhydrophilic properties and antibacterial activity of modified TiO₂ films were evaluated by studying under visible light and UV irradiation. The superhydrophilic efficiency of modified TiO₂ films by this method is affected by the concentration of doped iron.

Keywords: Sol-gel dip coating, Superhydrophilic, Antibacterial, Visible light, UV irradiation.

1. INTRODUCTION

Among various oxide semiconductors, titania appears promising and important for the use in environmental purification due to its strong oxidizing power, nontoxicity and long-term photo stability [1-4]. Besides the usual photocatalytic activity, photoinduced super-hydrophilic properties of TiO₂ thin films have attracted much attention in recent years [1, 5, 10-12]. By utilizing this super-hydrophilic surface of TiO₂ thin films, we can develop anti-fogging or self-cleaning glass, mirrors and other ecological building materials [1]. However, in photocatalytic applications, the activity of pure TiO₂ is limited due to the high recombination rate of e⁻ – h⁺ pairs. In order to improve photoreactivity of TiO₂-based photocatalysis, the e⁻ – h⁺ recombination rate needs to be reduced [1]. In many of these TiO₂ device applications, suitable electronic properties (namely well positioned bandgap) are improved by controlled doping. It is generally recognized that the substitution doping of TiO₂ with iron Fe(III) has a profound effect on the charge carrier recombination [5]. In intrinsic TiO₂ the mean lifetime of an electron-hole pair is about 30 ns. Doping with 0.5 % Fe(III) drastically increases the charge-carrier lifetime, which is extended to minutes or hours [5-7]. The second role of iron doping is to decrease the

activation energy of the anatase-to-rutile phase transition. Previous studies on the determination of lattice parameters of nanocrystalline materials have shown their grain size dependence. The lattice parameters were found to differ from the ones for the coarse-grained materials [8]. The coordination environment of the dopants is affected not only by the nature of the dopant such as ionic radii and concentration but also by the synthesis method [9]. Iron-doped TiO₂ powder has been obtained by wet chemical synthesis [1], sol-gel method [11], thermal hydrolysis [10],

In this work, we report the effects of without and with Fe³⁺ doping to the superhydrophilic and properties of TiO₂ thin films were fabricated by the sol-gel dip coating technique. The characteristics of the prepared Fe.TiO₂ were determined.

2. EXPERIMENTAL

2.1. Preparation of Fe doped in TiO₂ thin films

All chemicals were of analytical grade and used without further purification. Distilled water was used in all experiments.

In a typical experiment, a mixture of ethanol (13.456 ml) and Acetylacetone (1.05 ml) solution was stirred evenly. Then small amounts of TPOT (2.96 ml) were added slowly into the mixture while

stirring (A solution). A solution consisting of ethanol (2 ml) and distilled water (0.18 ml) was added slowly to the A solution under vigorous magnetic stirring to form a yellow homogeneous solution.

A solution consists of ethanol (2 ml), H₂O (0.18 ml), Fe(NO₃)₃·9H₂O and HNO₃ (1 ml) was mixed under magnetic stirring to form a homogeneous solution (C solution). The Fe doping concentrations were designed to be 0, 1.5, 3.5, 5.5 and 7.5 atm%, the resulting films are labeled as F0, F15, F35, F55 and F75.

The A solution and the C solution mixed and stirred until it reached the required viscosity.

Fe doped in TiO₂ sol was used to deposition Fe .TiO₂ thin films on glass substrates by the sol-gel dip coating technique. The TiO₂ thin films to dry naturally for 24 hours then dried at 100 °C for 1 hour and at last it heated at 500 °C for 1 hour. This process is repeated some times to achieve the thickness of the thin film as desired.

The microstructures and morphologies of the F0, F15, F35, F55 and F75 thin films were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany), Field Emission Scanning Electron Microscopy image (FESEM, Hitachi S-4800).

2.2. Superhydrophilic

Super-hydrophilic ability of the films study following to: We put the samples into the sealed chamber and illuminated with ultraviolet light UV 30W power for about 90 mins take the form sample placed on the horizontal plane, small green ink droplets are coated on the sample. Observed phenomenon occurs and Photographic observations by high-quality digital camera.

3. RESULTS AND DISCUSSION

2.3. Material characteristics

The XRD patterns of the F0, F15, F35, F55 and F75 thin films in the range of 2θ between 30° and 70° are given in Fig. 1. It is identified that the diffraction peak centered around 25.24° is ascribed to the anatase TiO₂ for undoped Fe³⁺ thin films as illustrated in F0 (JCPDS No. 73-1764). The XRD patterns of the TiO₂ thin films with an Fe³⁺ doping amount increasing from 1.5 % to 7.5 % are demonstrated in F15 and F75, respectively. It has been registered that the diffraction peak (2θ = 25.24°) also belong to the anatase TiO₂.

In addition, no characters peaks of iron oxides phases appeared for all samples. The possible reason for this might be iron-containing compound existed as amorphous phase or this may be due to the fact that Fe³⁺ ions may substitute Ti⁴⁺

ions and insert into the crystal lattice of TiO₂, since the radii of Ti⁴⁺ and Fe³⁺ ions are similar. For a coordination number of 6, Fe³⁺ and Ti⁴⁺ have similar ionic radius (0.79 Å versus 0.75 Å), so it can be inferred that iron ions might insert into the structure of TiO₂ and located at interstices or occupied some of the lattice sites of TiO₂, forming an iron–titanium solid solution [6]. These results support that the current doping procedure allows uniform distribution of the dopants to form solid solution.

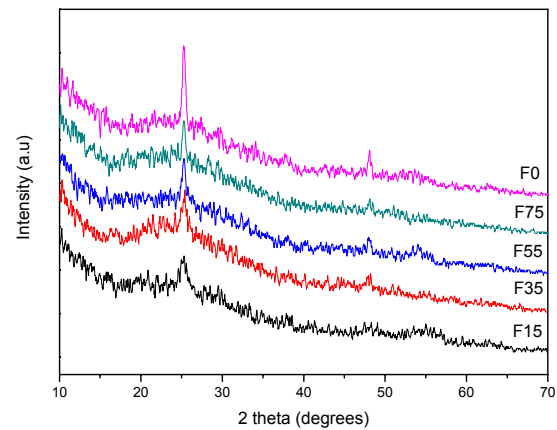


Figure 1: XRD patterns of the F0, F15, F35, F55 and F75 samples

The grain size was evaluated using the full width at half maximum (FWHM) of the intense (1 0 1) diffraction peak of anatase TiO₂ according to the Scherer equation:

$$D = \frac{0,89\lambda}{\beta_{hkl} \cos \theta}$$

Where D is the crystalline size in nm, λ is the wavelength of the incident radiation in nm, k = 0.90 which is a constant, θ is the Bragg angle taken in radians, and β_{hkl} is the FWHM in radians.

The estimated crystalline size of the F0, F15, F35, F55 and F75 thin films was about 26 nm; 26 nm; 23,4; 21.1 nm; and 18.9 nm. The error in this estimation was ±0.3 nm. The addition of Fe³⁺ could occupy regular lattice site of TiO₂ and distorted crystal structure, because the decrease in crystalline grain sizes of TiO₂ (from 26 to 18.9 nm) when the Fe content increased (from 0 % to 7.5 % atm%) it can be caused by a number of defects in the anatase crystallites produced by the substitution of part of the Ti⁴⁺ site by Fe³⁺ ions. The results are consistent with the R. Meshach et al. [7].

FE-SEM experiments were carried out to investigate the microstructure of the samples. Figure 2 presents the FE-SEM images of F15, F35, F55 and F75 samples. As seen in figure 2, The samples was a

uniform film with nanosize and non-cracks, consisting of nearly spherical nanoparticles of 10÷30 nm.

Table 1: Crystallite sizes, band-gap energies E_g and absorption wavelengths λ of the undoped and Fe^{3+} doped samples

Samples	Particle size, nm	Wave length, nm	Band gap, eV
F0	26	360	3.44
F15	26	405	2.8
F35	23.4	415	3
F55	21.1	425	2.9
F75	18.9	440	3.06

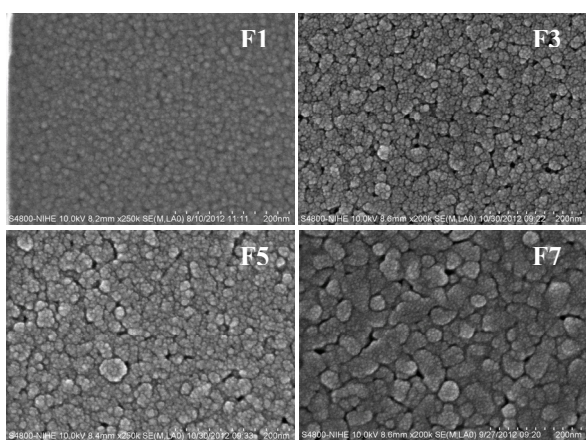


Figure 2: FESEM images of the Fe doped TiO_2 thin films: (a) F15; (b) F35; (c) F55 and (d) F75

The particle form and size of these samples were similar to those of the F15 sample. In the case of F35, F55 and F75, the morphology was different from that observed on F15.

The UV-VIS spectra of the films are shown in Fig. 3. It can be seen that, in both the UV (400 nm) and visible (400÷800 nm) regions, the transmission generally decreased with increasing Fe dopant levels. Further, the absorption edge shifted to longer wavelengths with increasing Fe dopant levels, thereby increasing the radiation absorption. The presence of interference fringes in the transmission spectra indicates that the films are smooth and microstructurally homogenous.

The band gap of the samples was determined by the equation:

$$E_g = \frac{1239.8}{\lambda}$$

Where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption edge in the absorbance spectrum shown in Fig. 4. The calculated

band-gap energies and the corresponding wavelengths are presented in table 1. The values indicate that the absorbance in the visible region of the doped samples increases with the concentration of the Fe^{3+} dopant which is consistent with the changes in the color of the samples from white to brownish beige.

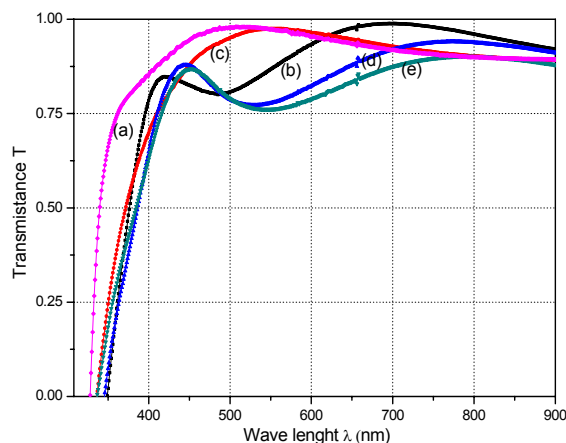


Figure 3: Transmittance spectra data of Fe doped TiO_2 thin films: (a) F0; (b) F15; (c) F35; (d) F55 and (e) F75

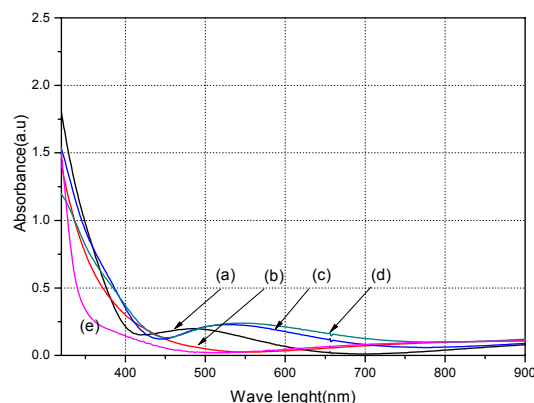


Figure 4: Absorbance spectra data of Fe doped TiO_2 thin films: (a) F15; (b) F35; (c) F55; (d) F75 and (e) F0

The relationship between the band-gap energy E_g and the Fe^{3+} content is shown in Fig. 5. It reveals that the band-gap energy decreases steeply at low Fe^{3+} concentrations. At high Fe^{3+} concentrations E_g continues decreasing but it changes much more slowly. In contrast to the results of earlier studies, an intensive study of all possible combinations of E_g and Fe^{3+} concentration (c) resulted with an exponential equation of the form [8]:

$$E_g = 2.77e^{-0.16c}$$

with the correlation coefficient $r^2 = 0.97$. The relative error on E_g found is only 3 % on the average.

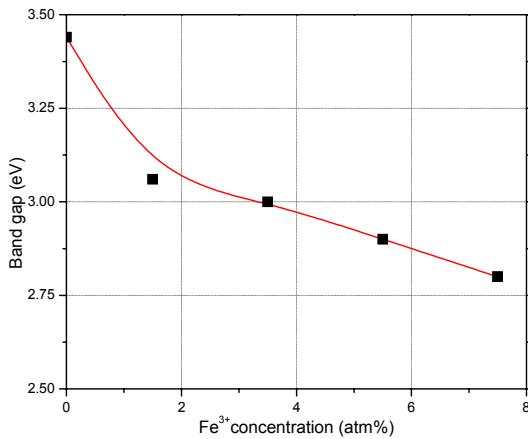


Figure 5: Plot of the band-gap vs. Fe³⁺ concentration of the doped samples

2.4. Superhydrolysis properties

Superhydrolysis properties of samples were observed under UV and visible light irradiation.

Images observed superhydrophilic ability of samples: F15, F35, F55 and F75 shown in figure 6. As we can see, in part glass substrate had not coated TiO₂, the blue ink droplet was still shrink and almost no spread. In part of coated doped Fe, the blue ink droplet was spreader and formed thin film. In all four cases Fe doping, the survey results are almost same.

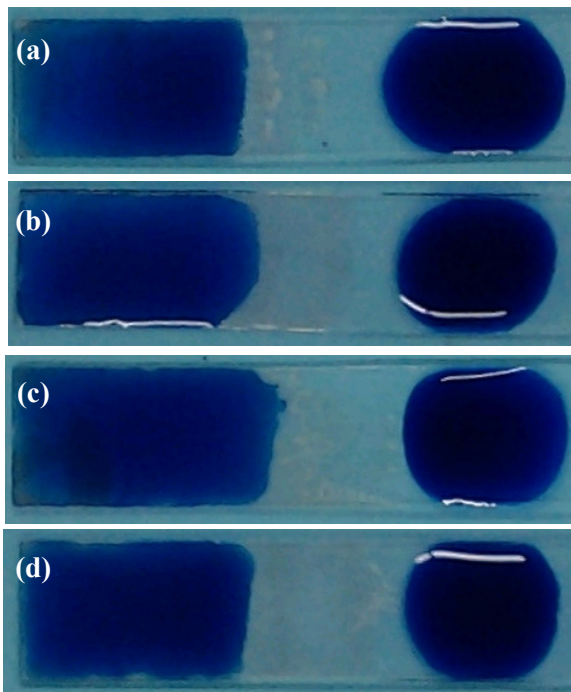


Figure 6: Images observed superhydrophilic ability of samples: (a) F15; (b) F35; (c) F55 and (d) F75

Combining with the above result on UV-Vis

spectra, the better hydrophilicity for Fe doped TiO₂ thin film can be attributed to the doped TiO₂ thin film with a narrower band gap. Hence, the narrower the band gap of the film is, the more the film accepts photon energy, and the greater the film creates superhydrophilicity.

Figure 7 shown that superhydrophilic ability observed under compact irradiation at 3 hours. In all four cases Fe doping, the survey results are almost same. Super-hydrophilic effect is very good.

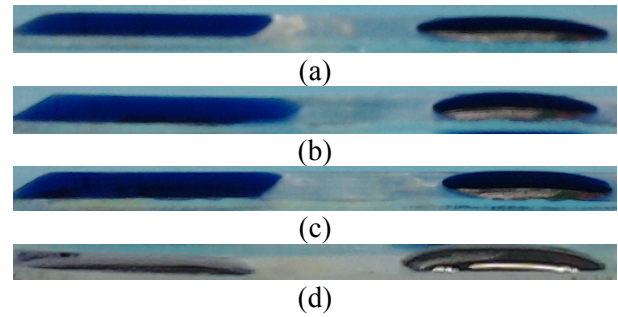


Figure 7: Images observed superhydrophilic ability of samples under visible light irradiation: (a) F15; (b) F35; (c) F55 and (d) F75

4. CONCLUSION

The TiO₂ thin films doped with different Fe³⁺ concentration could be prepared by sol-gel dip coating technique. After compact lamp irradiation, the films have a good superhydrophilic chrematistic, and Fe doping can enhance water spreading on the thin film surface. The role of Fe doping is attributed to the decreases in the band gap of the TiO₂ thin films after Fe doping, and the increase in the ability of the films to absorb long wavelength photon energy.

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REFERENCES

1. Akira Fujishima, Kazuhito Hashimoto, Toshiya Watanabe. *TiO₂ photocatalysis Fundamentals and Applications* (1999).
2. Jiaguo Yu, Xiujian Zhao, Jincheng Du and Wenmei Chen. *Preparation, Microstructure and Photocatalytic activity of the porous TiO₂ anatase coating by sol-gel processing*, J. Sol-Gel Sci. Technol.,**17**, 163-171 (2000).
3. C. Garzella, E. Comini, E. Tempesti, C. Frigeri, G Sberveglieri. *TiO₂ thin films by a novel sol-gel*

processing for gas sensor applications, Sensors and Actuators, **B 68**, 189-196 (2000).

4. Chao Liu, Xihu Tang, Cehui Mo, Zhimin Qiang. *Characterization and activity of visible-light-driven TiO₂ photocatalyst codoped with nitrogen and cerium*, Journal of Solid State Chemistry, **181**, 913-919 (2008).
5. N. Mahdjoub, N. Allen, P. Kelly, V. Vishnyakov. *SEM and Raman study of thermally treated TiO₂ anatase nanopowders: Influence of calcination on photocatalytic activity*, Journal of Photochemistry and Photobiology A: Chemistry, **211**, 59-64 (2010).
6. Diana V. Welliaa, Qing Chi Xua, Mahasin Alam Ska, Kok Hwa Lima, Tuti Mariana Limb, Timothy Thatt Yang Tana. *Experimental and theoretical studies of Fe-doped TiO₂ films prepared by peroxo sol-gel method*, Applied Catalysis A: General, **401**, 98-105 (2011).
7. J. Ben Naceur, R. Mechiakh, F. Bousbih, R. Chtourou. *Influences of the iron ion (Fe³⁺)-doping on structural and optical properties of nanocrystalline TiO₂ thin films prepared by sol-gel spin coating*, Applied Surface Science, **257**, 10699-10703 (2011).
8. Kais Elghniji, Atef Atyaoui, Stefano Livraghi, Latifa

Bousselmi, Elio Giamello, Mohamed Ksibi, *Synthesis and characterization of Fe³⁺ doped TiO₂ nanoparticles and films and their performance for photocurrent response under UV illumination*, Journal of Alloys and Compounds, **541**, 421-427 (2012).

9. C. Y. W. Lin, D. Channei, P. Koshy, A. Nakaruk, C. C. Sorrell. *Effect of Fe doping on TiO₂ films prepared by spin coating*, Ceramics International, **38**, 3943-3946 (2012).
10. Wenjian Weng, Ming Ma, Piyi Du, Gaoling Zhao, Ge Shen, Jianxun Wang, Gaorong Han. *Superhydrophilic Fe doped titanium dioxide thin films prepared by a spray pyrolysis deposition*, Surface & Coatings Technology, **198**, 340-344 (2005).
11. Hongbo Jiang, Lian Gao. *Enhancing the UV inducing hydrophilicity of TiO₂ thin film by doping Fe ions*, Materials Chemistry and Physics, **77**, 878-881 (2002).
12. Jiaguo Yu, Minghua Zhou, Huogen Yu, Qingjie Zhang, Ying Yu. *Enhanced photoinduced superhydrophilicity of the sol-gel-derived TiO₂ thin films by Fe-doping*, Materials Chemistry and Physics, **95**, 193-19 (2006).

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