

The analysis of TiO₂ doping by different ferric salts

Zhibo Zhang^{1, a}, Yuhan Chen¹, Jingzheng Weng^{1, 2}, Hengfeng Hong¹

¹College of Materials Science and Engineering, Fujian Normal University, Fuzhou, Fujian Province 350100, China

²College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian Province 350002, China

^a670666053@qq.com

Keywords: TiO₂, Fe, photocatalysts, sol-gel

Abstract. The Fe doped TiO₂ (FET) gels were synthesized by different ferric salts and analyzed by thermal gravimetric analyzer and X-ray diffraction. The TG curves show that the valence states of Fe had a great influence on the preparation of FET gels, Fe³⁺ was easy to replace titanium atoms to form lattice and the anatase phase was effectively established when the calcination temperature over 400 °C. The XRD spectra indicates that the anatase phase constantly changed into the rutile phase when the calcination temperature over 600 °C and the nitrate is beneficial to the formation of mixed crystal.

Introduction

Titanium dioxide (TiO₂) is gaining more importance due to its chemical stability, inexpensive, non-toxic and abundantly available. However, the large bandgap (3.0-3.2 eV) severely results poor absorption of light in the visible region. In order to improve the visible photocatalytic activity of TiO₂, most studies have been devoted to enhance the visible photocatalytic activity of TiO₂ by doping metal ions [1-2], nonmetal ions [3-4] and semiconductor coupling [5-6]. After TiO₂ doping different valence states of metal ions, especially for metal ions with larger ionic radius would cause lattice distortion. The resulting would improve the separation of electron-hole pair and photo-quantum efficiency [7-10]. Choi et al. conducted a systematic study on 21 metal ions doped in TiO₂ colloids, and Fe³⁺ was found to be the most effective dopant for enhancement of photo-activity [11]. Li et al. found that the Fe³⁺ in the bulk phase can easily capture the photoinduced electrons to form active species and the Fe³⁺ on surface can promote the separation and migration of photo generated hole [12]. Moreover, compared with other catalyst dopants, like Au and Ag, Fe is an attractive choice for its non-toxicity and low-cost. Therefore, this study choose the ferric salts as iron sources to discuss the influence of different ferric salts and anionic on morphology of FET photocatalysts.

Experiment

Catalyst preparation

FET samples had been prepared by sol-gel process. The precursors were the different valence states of ferric salts, tetrabutyl titanate, ethanol, acetic acid and distilled water. In the synthesis process we had taken 60 ml of tetrabutyl titanate with 40ml of ethanol dissolved it in a magnetic stirrer for 1 h at room temperature. The solution was called as solution A and the other solution B was prepared by dissolving proper FeSO₄, FeCl₂, Fe₂(SO₄)₃, FeCl₃, and Fe(NO₃)₃ in 60ml ethanol, 45ml acetic acid and 21ml distilled water. The solution B was added drop wise to the solution A, under vigorous stirring under 50°C water bath. The resulted gels were kept in an oven at 120°C for 12 h, and the dry mixture was obtained. FET powders were prepared after the samples were ground and calcinated for 2 h. The Samples calcinated at different temperatures with the number of temperature, for instance, FET400 indicated that it was the sample calcinated at 400°C. The samples with different amounts of doping added the doping concentration in front of the abbreviation, for instance, 0.5%FET600 indicated that the doping concentration of the sample was 0.5% Fe and calcinated at 400°C.

Characterization of catalyst

At room temperature, the crystallization properties of undoped TiO₂ photocatalyst and FET photocatalysts obtained under different condition were investigated by X-ray diffraction (D/Max-2400, Philips, Holland). The TG curves of samples were measured by thermogravimetric analysis (TGA) with a TGA/SDTA 851e (Mettler-Toledo, Switzerland) with a flow of 20 mL/min N₂ flow under a heating rate of 10 °C/min. The different factors affected the FET photocatalysts of TG curves were investigated, such as calcination temperature, different valence of iron sources, different Fe doping concentrations and different types of anions.

Results and discussion

TG curves analysis

The phase change process of TiO₂ gels occurred during the heating process, and crystal region transformed constantly in this stage. The process also goes with the loss of crystal water and the decomposition of organic compounds.

Fig.1 (a) indicates that the total proportion of weight loss had a little difference between the TG curves of undoped TiO₂ gels and the TG curves of TiO₂ gels doped by divalent iron. The weight residual rate of samples doped by FeCl₂ and Fe(NO₃)₂ is respectively 75.43% and 75.28%, while the weight residual rate of undoped samples is 85.20%. The different gel's weight residual rate is mainly due to the different samples materials with different crystal water. Results indicate that the trend of undoped TiO₂ gels' thermal weight loss was as same as that of FET gels doped by divalent iron.

The decomposition process can be divided into three stages, the first stage is considered while the calcination temperature was less than 160°C. During the stage, the slope of TG curves are almost invariant with the increasing of temperature, that means the rate of thermal weight loss remains essentially constant. While temperature reach 160°C, the weight residual rate of samples doped by FeCl₂ and Fe(NO₃)₂ is respectively 94.72% and 94.98%, while the weight residual rate of samples undoped is 96.12%, the weight loss rate is largest: 4-6%. It mainly belongs to the loss of the volatile components in the samples, such as water and ethanol. The loss of the components inside the crystal region is considered seldom. The second stage is considered while the calcination temperature was raising from 160°C to 400°C. In the previous period of the second stage, the slope of TG curves are grow slowly. After the temperature up to 190°C, the slope of TG curves are quite steep. The thermal weight loss of this stage can be considered belongs to the crystal water what cannot be fixed in the gel structure and the loss of all kinds of additives in materials. After the temperature up to 350°C, the slope of TG curves become smooth and transit to horizontal smoothly. The calcination temperature above 420°C is considered belongs to the third stage of the thermal decomposition process. During this stage, the TG curves keep nearly horizontal. It shows that most of the organic compounds had almost lost in the first stage and the second stage. The residual materials may be some inorganic substance which couldn't be decomposed during the thermal decomposition process.

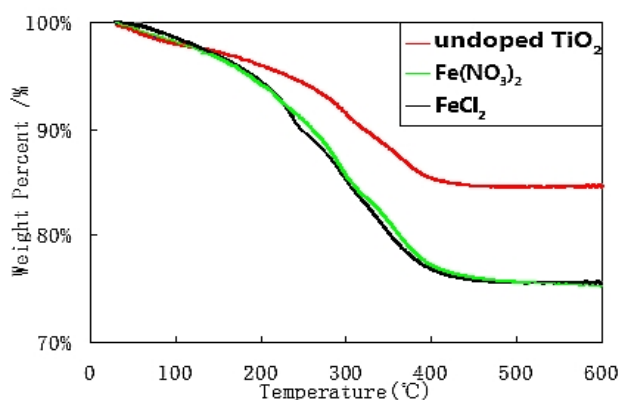
The TG curves of FET gels prepared by the trivalent iron salts (Fe(NO₃)₃, Fe₂(SO₄)₃ and FeCl₃) were shown in Fig.1 (b). The weight residual rate of samples prepared by the Fe(NO₃)₃, Fe₂(SO₄)₃ and FeCl₃ is respectively 96.7%, 95.9% and 96.5% and the different weight residual rate is also mainly due to the different samples materials combining with different crystal water. There is a significant difference while the temperature at 150°C-420°C. The slope of TG curves at 150°C-280°C and 320°C-420°C are basically identical, but there is a transition region at 280°C-320°C, the weight loss rate of the three kinds of FET gel change sustained. Because the molecular weight of Fe and Ti is respectively 55.85 and 47.9, when different atoms entered the crystal lattice, the different samples materials would cause the difference of weight loss. Therefore, it indicates that TiO₂ crystals was formed by TiO₂ gel and there is possible that iron atoms replaced titanium atoms to form lattice determined by the different weight loss rate. In addition, in the related research, Wantala confirmed that the form of Fe loaded on crystal surface was mainly Fe³⁺, which was determined by the XPS spectra. It was thought that Fe³⁺ entered the crystal lattice in the way of replacing Ti(IV) [13].

Comparing the TG curves of FET gels doped by divalent iron, there is no obvious transition region at 280°C-370°C, that consider as the period of the Fe replaced Ti in crystal lattice. Therefore, the Fe^{2+} was not easily to replaced Ti(IV) when FET gels doped by divalent iron. This is due to different ions had different size, the ionic radius of Ti^{4+} is 0.605Å while the ionic radius of Fe^{3+} is 0.645Å in high spin state. The ionic radius of Ti^{4+} and Fe^{3+} are similar, thus Fe^{3+} could replace Ti^{4+} in crystal lattice. The ionic radius of Fe^{2+} is 0.67Å, significantly greater than Fe^{3+} and the valence of Ti^{4+} , Fe^{3+} and Fe^{2+} is respectively +4, +3 and +2, in contrast, Fe^{3+} was more easily than Fe^{2+} to enter the crystal lattice.

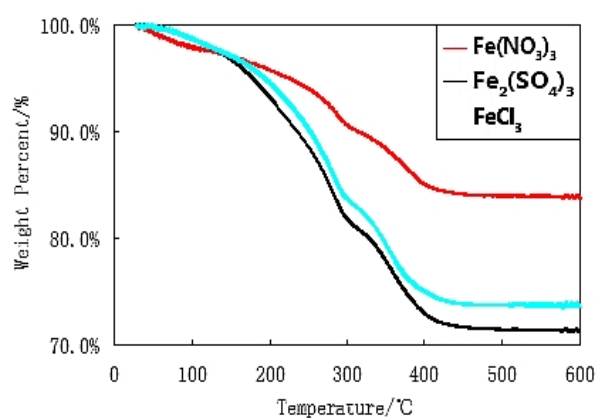
In a word, making TiO_2 gels doped by divalent iron was more difficult than making TiO_2 gels doped by trivalent iron.

The TG curves of FET gels prepared by different $\text{Fe}(\text{NO}_3)_3$ doping concentrations were shown in Fig.1 (c). Fig.1 (c) indicates that the degree of iron atoms replaced titanium atoms to form lattice significantly enhanced with the increase of doping amount. Therefore it can be concluded that the more doping amount was used, the more amount of Fe^{3+} entered the crystal lattice in the way of replacing Ti(IV).

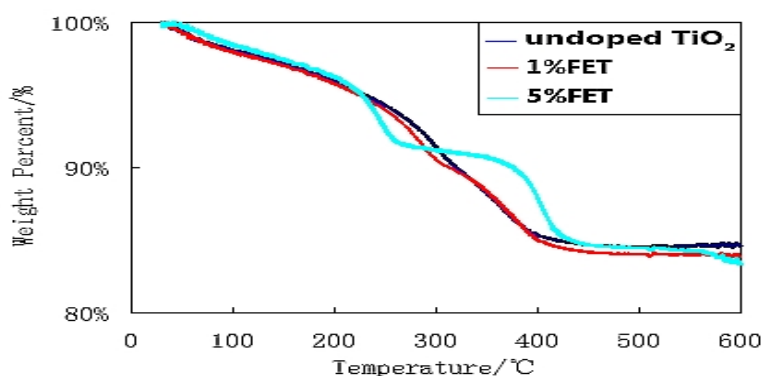
From the analysis above, in the thermal decomposition process from 30°C to 450°C, the gels lost weight continuously with the increase of temperature. There is a stage that the accelerating of weightlessness from 180°C to 420°C and no significant weightlessness from 420°C to 600°C. The different of gel's weight residual rate was mainly due to the different sample materials with different crystal water and the FET photocatalysts had same the trend during the TG process. Observing the TG curves, it can be found that the trend of the undoped TiO_2 gels' TG curves and the doped by divalent iron TiO_2 gels' TG curves are basically in coincidence, the three kinds of TiO_2 gels doped by divalent iron are global uniformly. This shows that the reagent containing Fe^{3+} dose not strong effect for the TiO_2 gels' phase formation temperature. But the TG curves of the three kinds of TiO_2 gels doped by divalent iron at 280°C-370°C had a difference with undoped TiO_2 gels in signs of change.



(a) The TG curves of FET gels that prepared by bivalent iron salts.



(b) The TG curves of FET gels that prepared by the trivalent iron salts.



(c) The TG curves of FET gels prepared by $\text{Fe}(\text{NO}_3)_3$ with difference of doping concentrations
Fig.1 TG curves of different FET photocatalysts

X-ray diffraction analysis

Fig.2 shows the XRD patterns of FET powders calcined at 450°C, 600°C and 800°C. The FET powders were prepared with TiCl_4 as titanium source and FeCl_3 as iron source. The doping level of FET powders were 0.5%.

After calcining at 450°C for 4 h, reflection peaks were found at 25.251°(101), 37.94°(004), 38.72°(112), 48.02°(200), 55.08°(221). Contrasting the standard XRD spectrum of TiO_2 (PDF NO 841286), these peaks of the FET'S XRD curves are belong to the characteristic diffraction peaks of anatase. The diffraction peaks had an offset by indexing the diffraction peaks with most intense peak at $2\theta = 24.5^\circ$ corresponding to the plane (101). The offset of diffraction peaks were caused by the dopant changed the variation of lattice constants. What's more, the ionic radius of Ti^{4+} is 0.605Å while the ionic radius of Fe^{3+} is 0.645Å in high spin state, therefore, Fe^{3+} entered the lattice would cause the interlayer spacing became bigger. The diffraction peaks moved to small angle because the Fe^{3+} entered the lattice. It is noticed, however, the diffraction intensity of $2\theta = 25.430^\circ$ (101) was 1200.

Fig.2 (b) shows that the diffraction intensity of $2\theta = 25.251^\circ$ (101) increased. This is probably due to the rising of temperature and crystal area. In the Fig.2 (b), there is the characteristic diffraction peaks of the anatase (PDF NO 841286) and part of the characteristic diffraction peaks of rutile($2\theta = 27.503^\circ$ (110), 41.232° (111)). It indicates that part of the anatase phase transformed to rutile phase while the temperature above 600°C. From Fig.2 (c), there is no the characteristic diffraction peaks of the anatase and left only the characteristic diffraction peaks of rutile($2\theta = 27.503^\circ$ (110), 41.232° (111)). It is noticed, however, the diffraction intensity of $2\theta = 27.6^\circ$ (110) increased to 6400. It shows that the anatase phase completely changed into rutile phase.

In a word, the diffraction intensity of FET powders was increasing with the rising of calcination temperature and the anatase phase constantly changed into rutile phase when the calcination temperature over 600 °C

Fig.3 shows the influence of different anions on the XRD spectra of FET powders prepared by the trivalent iron salts ($\text{Fe}(\text{NO}_3)_3$, $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3) at 600°C. The doping level of FET powders were 0.5%. At the diffraction peaks is $2\theta = 25.251^\circ$ (101), there is a great difference of diffraction intensity of FET powders prepared by the trivalent iron salts. The diffraction intensity of FET powders prepared by $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ were approximately 3800. The diffraction intensity of FET powders prepared by FeCl_3 was approximately 2400.

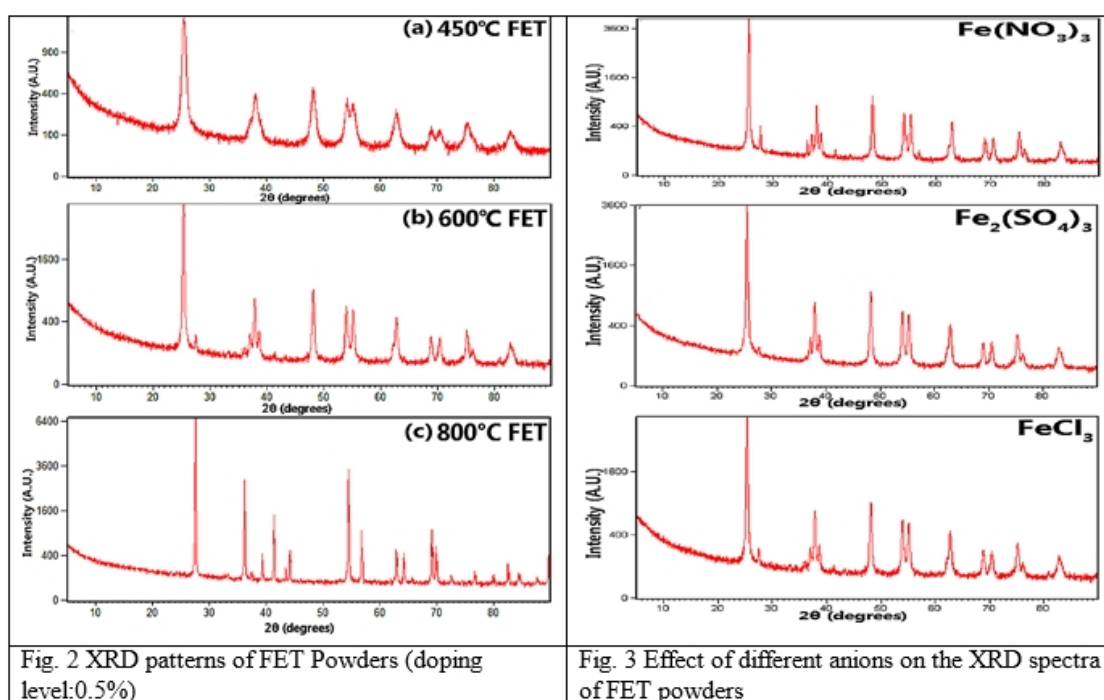


Fig. 2 XRD patterns of FET Powders (doping level:0.5%)

Fig. 3 Effect of different anions on the XRD spectra of FET powders

Conclusion

The samples of Fe doped TiO₂ (FET) gels were synthesized by different ferric salts. The FET gels was characterized by TG and XRD. The TG curves and XRD spectra indicate that the anatase phase was effectively established when the calcination temperature over 400 °C and the anatase phase constantly changed into the rutile phase when the calcination temperature over 600 °C. Moreover, the nitrate is beneficial to the formation of mixed crystal.

References

- [1] X.F. Lei, X.X. Xue, H. Yang, *Appl. Surf. Sci.* 321 (2014) 396-403.
- [2] S.C. Xu, S.S Pan, Y. Xu, Y.Y Luo, Y.X Zhang, G.H. Li, *J. Hazard. Mater.* 283 (2015) 7-13.
- [3] M.J. Powell, R.G. Palgrave, C.W. Dunnill, I.P. Parkin, *Thin Solid Films* 562 (2014) 223-228.
- [4] M.J. Mattle, K.R Thampi, *Appl. Catal. B: Environ.* 140-141 (2013) 348-355.
- [5] D.N Liu, G.H He, L. Zhu, W.Y. Zhou, Y.H. Xu, *Appl. Surf. Sci.* 258 (2012) 8055-8060.
- [6] S.B. Rawal, D.P. Ojha, S.D. Sung, W.I. Lee, *Catal. Commun.* 56 (2014) 55-59.
- [7] N.A. Roslan, H.O. Lintang, L. Yuliati. *Materials Research Innovations*, 2014, 18:465-469.
- [8] H.S. Borji, S. Nasser, A.H. Mahvi, et al. *Journal of environmental health science & engineering*, 2014, 12:101-101.
- [9] M.V. Martin, P.I. Villabrille, J.A. Rosso. *Environmental Science And Pollution Research*, 2015, 22(18):14291-14298.
- [10] J.C. Sin, S.M. Lam, I. Satoshi, et al. *Applied Catalysis B-Environmental*, 2014, 148-149:258-268.
- [11] W. Choi, A. Termin, M.R. Hoffmann. *J. Phys. Chem.* 98 (1994) 13669-13679.
- [12] X.Z. Li, F.B. Li, C.L. Yang. *J.Photochem.Photobiol.A: Chem*, 2001, 141 (2-3):209-217.
- [13] K. Wantala, L. Laokiat, P. Khemthong, N. Grisdanurak, K. Fukaya. *Taiwan Inst. Chem. Eng.* 41 (2010) 612-619.