

Local structure and optical absorption characteristic investigation on Fe doped TiO₂ nanoparticles^{*}

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Abstract: The local structures and optical absorption characteristics of Fe doped TiO₂ nanoparticles synthesized by the sol-gel method were characterized by X-ray diffraction (XRD), X-ray absorption fine structure spectroscopy (XAFS) and ultraviolet-visible absorption spectroscopy (UV-Vis). XRD patterns show that all Fe-doped TiO₂ samples have the characteristic anatase structure. Accurate Fe and Ti K-edge EXAFS analysis further reveal that all Fe atoms replace Ti atoms in the anatase lattice. The analysis of UV-Vis data shows a red shift to the visible range. According to the above results, we claim that substitutional Fe atoms lead to the formation of structural defects and new intermediate energy levels appear, narrowing the band gap and extending the optical absorption edge towards the visible region.

Key words: titanium dioxide, local structure, photocatalysis

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1 Introduction

In recent years, due to its low cost, non-toxicity, easy-synthesis, long-term stability and high efficiency [1], a lot of attention has been devoted to TiO₂ photocatalysts to find solutions useful to treat environmental pollution problems and the continuous increasing demand of energy [2]. However, its narrow range of response in the ultraviolet actually limits large-scale industrial applications [3].

Recently, much research has been carried out to investigate metal ion-doping TiO₂ systems to improve the photocatalytic activity [4]. Different studies have reported doping with suitable transitional metals [5–10]. Among them, iron was considered to be one of the most appropriate candidates because the radius of Fe³⁺ (0.645 Å) is similar to the Ti⁴⁺ (0.605 Å) and Fe³⁺ can be easily incorporated into the crystal lattice of TiO₂ [11].

The local structure around iron strongly affects the photocatalytic activity properties of Fe-doped TiO₂. As an example, if Fe ions in doped samples are aggregated to α -Fe₂O₃ precipitates, doping may affect the catalytic effect of TiO₂ [12]. Therefore, an accurate determina-

tion of local structural information around iron is mandatory. X-ray absorption fine structure (XAFS) is a powerful method to investigate the local structure around a specific component and can be used to obtain the local structural information around a selected atom [13].

In this work, the local structure around Fe atoms in doped TiO₂ nanoparticles prepared by the sol-gel method with different Fe concentrations were investigated by using X-ray diffraction (XRD) and XAFS techniques to identify where Fe ions go inside the TiO₂ matrix and to improve optical absorption.

2 Experimental section

2.1 Sample preparation

Pure and Fe-doped TiO₂ nanoparticles (Fe_xTi_{1-x}O₂) were prepared by the sol-gel method and the molar ratios of the Fe dopants (x) were 0.6% and 6.0% [14]. Pure amounts of Fe₂(SO₄)₃ and Fe(NO₃)₃ with a certain mass ratio were dissolved in distilled water under continuous stirring for 2 h and then 0.05 mol/L Na₂CO₃ solution was dropped, wisely added to the above solution under continuous stirring for 2 h, and the resulting solution was

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evaporated by heating and stirring at 353 K for 4 h. The mixture was put into the oven at 393 K for 10 h and then calcined in the muffle at 873 K for 10 h.

2.2 Measurement

The ultraviolet-visible (UV-Vis) absorption spectra were performed with an Analyst 800 in the spectral range from 200 nm to 800 nm. XRD patterns were collected using Cu K α ($\lambda=0.154$ nm) radiation in the 2θ range from 20° to 80° . Fe and Ti K-edge spectra of the prepared samples were collected at the U7C beamline of the National Synchrotron Radiation Laboratory (NSRL, China). XAFS data were analyzed by the UWXAFS3.0 software package according to standard data analysis procedures [15].

3 Results and discussion

To detect the crystalline order and/or to identify different ordered phases, we performed XRD measurements in these TiO₂ nanoparticles doped with different Fe concentrations. From Fig. 1, we can see that all samples are characterized by a mixture of an anatase and a rutile phase without diffraction peaks eventually associated with other iron oxide or impurity phases, but for all the synthesized Fe_xTi_{1-x}O₂ samples, the anatase phase accounts for the vast majority. It is worth mentioning that, compared with the pure sample, the intensity of some peaks of the rutile phase decreases in the doped samples, such as peaks at $2\theta=36.48^\circ$, 41.73° , 44.30° , 56.89° , and 69.48° . The data points out that Fe doping could affect the crystallization of the TiO₂, especially that of the rutile phase. Regarding the (101) crystalline reflection ($2\theta=25.3^\circ$) of the anatase phase, increasing the content of Fe ions from 0.6% to 6% its intensity increases and shifts to lower angles. This result clearly points out that Fe ions may increase the disorder and expand the lattice size of the structure of Fe_xTi_{1-x}O₂ nanoparticles.

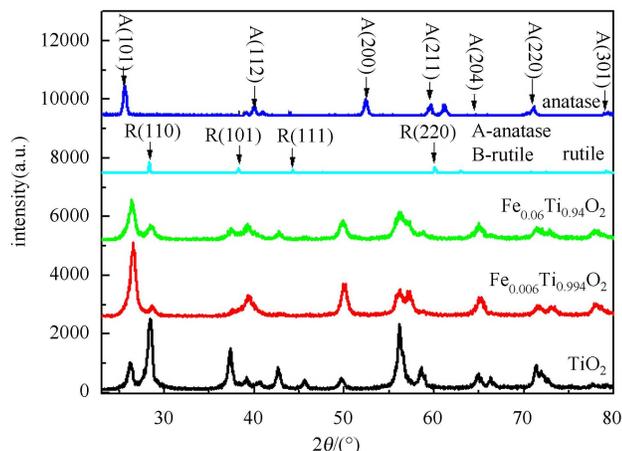


Fig. 1. XRD patterns of anatase and rutile and Fe_xTi_{1-x}O₂ nanoparticles ($x=0, 0.6\%$ and 6%).

Figure 2 displays Ti K-edge EXAFS Fourier transforms (FTs) spectra of anatase, and Fe K-edge EXAFS FTs spectra of Fe_{0.006}Ti_{0.994}O₂ and Fe_{0.06}Ti_{0.94}O₂ and their fits. As references, the Fe K-edge spectra of Fe, FeO, Fe₂O₃, Fe₃O₄, and the Ti K-edge EXAFS spectrum of rutile are also shown in Fig. 2. The FT features of Fe_{0.006}Ti_{0.994}O₂ and Fe_{0.06}Ti_{0.94}O₂ nanoparticles are very close to anatase TiO₂ powders, with the first coordination peaks of both Fe K-edge and Ti K-edge at ~ 1.4 Å, a value corresponding to Fe-O and Ti-O coordination shells. The second single coordination peaks at 2.3 Å correspond to the Fe-O-Ti and the Ti-O-Fe coordination shells. These peaks are clearly different from those of Fe, FeO, Fe₂O₃, and Fe₃O₄ systems. Therefore, we may rule out the presence of Fe, FeO, Fe₂O₃, and Fe₃O₄. This also indicates that Fe ions in Fe-doped TiO₂ nanoparticles replace Ti atoms in the TiO₂ lattice within the doping concentration from 0.006 to 0.06. It is also important to underline that, compared to anatase, the first peak in the Fe_xTi_{1-x}O₂ samples presents a shift of ~ 0.1 Å toward high R. This result points out an expansion of the bond length of the Fe-O bond respect to that of Ti-O. In addition, we can see that the weaker intensity of the second coordination peaks suggest that these samples have a specific Fe-O-Ti structure containing many structural defects, which are extremely important in enhancing the photocatalytic activity of these nanoparticles [16, 17].

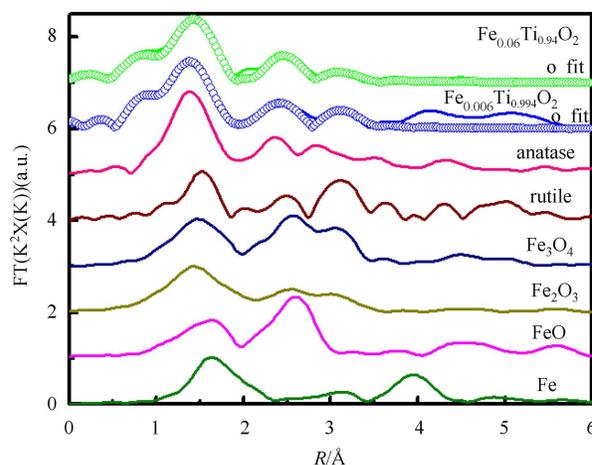


Fig. 2. The radial structural functions obtained by the FTs of Fe K-edge EXAFS spectra and their fits, for Fe_{0.006}Ti_{0.994}O₂ and Fe_{0.06}Ti_{0.94}O₂, and the radial structural functions of the Ti K-edge EXAFS spectra of anatase (theoretical) and rutile (theoretical), as well as Fe K-edge FTs EXAFS of Fe, FeO, Fe₂O₃ and Fe₃O₄.

In order to obtain additional quantitative structural information, we fit the main peak corresponding to Fe-O and Ti-O pairs. Data obtained using the basic EXAFS

Table 1. Structural parameters around Fe atoms in the synthesized titania samples.

sample	coordination	coordination numbers (N)	$R/\text{\AA}$	$\sigma^2/\text{\AA}^2$
theoretical	Ti-O	4	1.92	
TiO ₂ anatase	Ti-O	2	1.97	
Ti _{0.994} Fe _{0.006} O ₂	Fe-O	3.9±0.1	1.94±0.01	0.0065±0.0001
	Fe-O	1.9±0.1	1.99±0.01	0.0064±0.0002
Ti _{0.94} Fe _{0.06} O ₂	Fe-O	3.9±0.1	1.96±0.01	0.0073±0.0003
	Fe-O	1.8±0.1	2.03±0.01	0.0073±0.0002

formula are shown in Fig. 2 [18]. The best fit of the structural parameters obtained for these samples are summarized in Table 1 and the results of the fit are shown as empty circles in Fig. 2. As shown in Table 1, we can see that both Fe-O bond lengths in the Ti_{0.994}Fe_{0.006}O₂ are ~ 0.02 Å longer than the Ti-O bond lengths of the anatase TiO₂ phase, pointing out that Fe ions replace Ti ions and expand the cluster of the nearest oxygen atoms [9]. With a doping content increasing from 0.6% to 6%, both Fe-O bond lengths expand, in agreement with XRD data. Moreover, because Fe doping enhances the distortion, this phase is a thermodynamically less stable phase [19].

The ionic radius of Fe³⁺ (0.64 Å) is smaller than that of Ti⁴⁺ (0.68 Å), and from the standard XAFS spectra, we can see that the length of the Ti-O bond of rutile is longer than that of anatase, so the Fe ions replace the Ti ions for the doping samples, leading to the distortion of the local structure for anatase as relatively smaller than that for rutile, and eventually making the doping system more stable.

To investigate the optical absorption characteristic of Fe-doped TiO₂ nanoparticles, UV-Vis absorption spectra were also collected. As shown in Fig. 3, the light absorption edges of 0.6% and 6% Fe-doped TiO₂ are 490 nm and 613 nm, respectively, with a remarkable red shift to the visible range compared to the spectrum of pure TiO₂ (387 nm). At the same time, the absorption intensity of visible radiation increases when the iron doping content increased from 0.6% to 6%.

With the increase of Fe ions, the absorbance in the visible region is enhanced, a behavior associated with the Fe ion occupancy in the Ti sites of the TiO₂ lattice. Thus an interaction among d electrons of Fe and the TiO₂ conduction or valence band occurs [20] eventually narrowing the energy gap of the titanium oxide through the formation of new intermediate energy levels [21, 22].

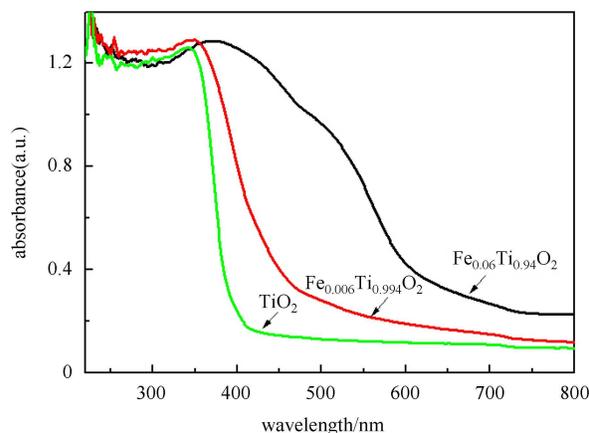


Fig. 3. UV-Vis absorption spectra of Fe_xTi_{1-x}O₂ nanoparticles for $x=0, 0.6$ and 6%.

4 Conclusion

The local structure of Fe doped TiO₂ nanoparticles prepared by a sol-gel method have been investigated by XRD and XAFS, combined with UV-Vis to monitor their absorption characteristics. XRD patterns show that all Fe-doped TiO₂ samples qualitatively have the anatase TiO₂ structure. Moreover, detailed Fe and Ti K-edge EXAFS experiments further reveal that Fe atoms replace Ti atoms in the anatase lattice. Doping with iron leads to the formation of the structural defects and, probably, a lot of intermediate energy levels that may narrow the energy gap, being the mechanism responsible for the red shift observed in the spectra of these materials in the UV-Vis region.

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References

- 1 Hashimoto K, Irie H, Fujishima A. *Jpn. J. Appl. Phys.*, 2005, **44**: 8269
- 2 GOU Y Q, CHEN D Y, SU Z X. *Appl. Catal. A: General*, 2004, **261**: 15
- 3 Di Paola A, Garcia-Lopez E, Ikedab S. *Catal. Today*, 2002, **75**: 87
- 4 Choi W, Termin A, Hoffmann M R. *J. Phys. Chem.*, 2004, **98**: 13669
- 5 Yamashita H, Harada M, Misaka J, Takeuchi M, Neppolian B, Anpo M. *Catal. Today*, 2003, **84**: 191
- 6 ZHU J F, ZHENG W, HE B, ZHANG J L, Anpo M. *Mol J. Catal. A*, 2004, **216**: 35
- 7 ZHANG X W, ZHOU M H, LEI L C. *Catal. Commun.*, 2006, **7**: 427
- 8 Anpo M, Takeuchi M. *J. Catal.*, 2003, **216**: 505
- 9 Kato H, Kudo A. *J. Phys. Chem. B*, 2002, **106**: 5029
- 10 ZHU J F, DENG Z G, CHEN F, ZHANG J L, CHEN H J, HUANG J Z, ZHANG L Z, Anpo M. *Appl. Catal. B*, 2006, **62**: 329
- 11 Choi W, Termin A, Hoffmann M R. *J. Phys. Chem.*, 1994, **98**: 13669
- 12 ZHU S Y, SHI T F, LIU W H, WEI S Q, XIE Y N, FAN C Z, LI Y Z. *Physica B*, 2007, **396**: 177
- 13 WU Z, ZHANG J, Ibrahim K, XIAN D C, LI G, TAO Y, HU T D, Bellucci S, Marcelli A, ZHANG Q H, GAO L, CHEN Z Z. *Appl. Phys. Lett.*, 2002, **80**: 2973
- 14 Yadav B C, Verma N, Singh S. *Opt. Laser Technol.*, 2012, **44**: 1681
- 15 Stern E A, Newville M, Ravel B, Rehr J J, Yacoby Y, Haskel D. *Physica B*, 1995, **208**: 154
- 16 LIU F D, Kiyotaka Asakura, HE H, LIU Y C, SHAN W P, SHI X Y, ZHANG C B. *Catal. Today*, 2011, **164**: 520
- 17 LIU F D, Kiyotaka Asakura, XIE P Y, WANG J G, HE H. *Catal. Today*, 2013, **201**: 131
- 18 PAN Z Y, SUN Z H, XIE Z, XU J H, Kojima I, WEI S Q. *J. Phys. D: Appl. Phys.*, 2006, **39**: 2796
- 19 Stengl V, Bakardjieva S. *J. Phys. Chem. C*, 2010, **114**: 19308
- 20 YU J G, XIANG Q J, ZHOU M H. *Appl. Catal. B*, 2009, **90**: 595
- 21 ZHU J, REN J, HUO Y, BIAN Z, LI H. *J. Phys. Chem. C*, 2007, **111**: 18965
- 22 CONG Y, ZHANG J, CHEN F, Anpo M, HE D. *J. Phys. Chem. C*, 2007, **111**: 10618