

Effect of Fe-doped TiO₂ nanoparticle derived from modified hydrothermal process on the photocatalytic degradation performance on methylene blue

Zhijie Li^a, Wenzhong Shen^b, Wensen He^a, Xiaotao Zu^{a,*}

^a Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu 610041, PR China

^b State Key Laboratory of Heavy Oil, China University of Petroleum, Dongying 257061, PR China

Received 28 September 2007; received in revised form 23 November 2007; accepted 23 November 2007

Available online 7 January 2008

Abstract

Anatase Fe-doped TiO₂ nanoparticles with 10–15 nm particles sizes were directly prepared with amorphous TiO₂ nanoparticles and Fe(NO₃)₃·9H₂O by hydrothermal method. The TiO₂ crystallite grain sizes decreased with the increase of Fe contents. When Fe contents increased, the diffuse reflectance spectra of Fe-doped TiO₂ nanoparticles displayed a red shift in the band gap transition. And the absorbing band edge moved to visible range when the Fe contents were more than 2 mol%. XPS analysis showed that Fe³⁺ was not on the surface of TiO₂ nanoparticles, but inserting into the matrix interior. As a result, the photoactivity degradation of MB on Fe-doped TiO₂ nanoparticles decreased.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Titania; Nanoparticles; Hydrothermal; Methylene blue; Photocatalyst

1. Introduction

Nano-sized titania has attracted increasing attention because of its wide application in many fields, such as photocatalysts, anti-UV agent, ceramics, inorganic membranes, sensors, solar energy conversion and so on [1,2]. In particular, recently numerous works have been carried out to display its photocatalytic activity due to its promising performance in degrading various organic and inorganic environmental pollutants [3,4]. It has been reported that the addition of Pt [5], Cr³⁺ [6], Cu²⁺ [7], Fe³⁺ [8–14] or other cation into anatase titania can improve its photoactivity. Among them, Fe-doped TiO₂ system is considered as a potential candidate for photocatalyst, and it has reported that the photocatalyst improved with optimal Fe content [8,9,11].

Various methods have used to synthesize Fe-doped TiO₂ nanoparticles, such as sol–gel method [9,11], impregnation [10] and hydrothermal method [8,13,14]. Among these, hydrother-

mal method is an important method to synthesize titania nanoparticles. Janes et al. [14] prepared Fe-doped TiO₂ powders by hydrolysis of titanium alkoxide in an aqueous solution of iron (II) following hydrothermal processing. Zhu et al. [8] also prepared it with titanium tetra-*tert*-butoxide and FeCl₃ by hydrothermal process. In the hydrothermal treatment, grain size, particle morphology, crystalline phase, and surface chemistry can be controlled via processing variables. The process of preparing Fe-doped TiO₂ nanoparticles determines its physico-chemical and photocatalytic properties and the effect mechanisms of Fe are not yet fully elucidated. So changing the hydrothermal conditions to investigate the effect of Fe³⁺ on TiO₂ is necessary.

In the present work, Fe-doped TiO₂ nanoparticles were directly prepared with amorphous TiO₂ nanoparticles and Fe(NO₃)₃·9H₂O by hydrothermal method. It was founded that photoactivity degradation of MB decreased with the content of Fe decreased, which was different with the former reports [8,9,11]. This was due to that Fe³⁺ was not on the surface of TiO₂ nanoparticles, but inserting into the matrix interior of TiO₂ nanoparticles.

* Corresponding author. Tel.: +86 28 83201939; fax: +86 28 83201939.
E-mail address: xiaotaozu@yahoo.com (X. Zu).

2. Experimental

2.1. Synthesis of samples

2.1.1. Preparation of amorphous TiO₂

At 25 °C, with magnetic stirring, the solution of 2.5 ml titanium *n*-butoxide and 25 ml C₂H₅OH was dropped to the solution of 13 ml H₂O and 13 ml C₂H₅OH in 30 min to form a white suspension. After stirred for 30 min, it was filtered and washed by C₂H₅OH. Finally, the product was dried at 110 °C and was grinded. Then the amorphous TiO₂ nanoparticles were obtained.

2.1.2. Preparation of Fe-doped anatase TiO₂

0.0946 g Fe(NO₃)₃·9H₂O, 2 g amorphous TiO₂ and 50 ml H₂O were added into a Teflon-lined autoclave to hydrothermal react at 200 °C for 24 h. The resulted product was filtered and dried at 110 °C. Then 1 mol% Fe-doped TiO₂ was obtained. Samples with different Fe contents (0%, 0.1%, 0.5%, 1.0%, 2.0%, 5.0% and 10.0% (M/M)) were also prepared by the same process through varying the content of added Fe(NO₃)₃·9H₂O.

2.2. Characterization of samples

The crystalline phase particles were determined using X-ray diffraction (XRD) performed on a D/max2500 diffractometer (40 kV, 30 mA, Cu K α radiation). The morphology of particles was observed by transmission electron microscope (TEM, Hitachi-600-2). The BET surface area was calculated by nitrogen adsorption at 77 K on Tristar3000 (Micromeritics, Co.). The concentration of Fe was measured by inductively coupled plasma optical emission spectrometer (ICP, AtomScan 16). The element composition and the chemical state of particle surface were determined by X-ray photoelectron spectroscopy (XPS, PHI5300X, PerkinElmer Physics Electronics, Mg K α as radiation source). UV–vis diffuse reflectance spectra (DRS) were measured on Shimadzu UV-2101 apparatus, equipped with an integrating sphere, using BaSO₄ as reference.

2.3. Photodecomposition of methylene blue (MB)

The photochemical reactor was consisted of a cylindrical jacketed quartz tube with 5.0 cm in diameter and 27 cm in length. A 300 W highly pressure mercury vapor lamp with a wavelength at 365 nm was placed inside the reactor. The light source assembly was placed concentrically inside the 300 ml Pyrex glass container of 6.0 cm in diameter and 28.5 cm height filled with 250 ml MB solution. The distance between the source and bottom of the vessel was 1.5 cm to aid for better stirring using a magnetic stirrer. To keep the temperature of the solution during the reaction, water was circulated through the annulus of the jacket quartz tube. The MB concentration was 100 ppm with a catalyst loading of 0.5 kg/m³. Before irradiation, the suspension aqueous solution was stirred continuously in dark for 30 min to ensure adsorption/desorption equilibrium. The adsorption equilibrium concentration was used as the initial value for the further

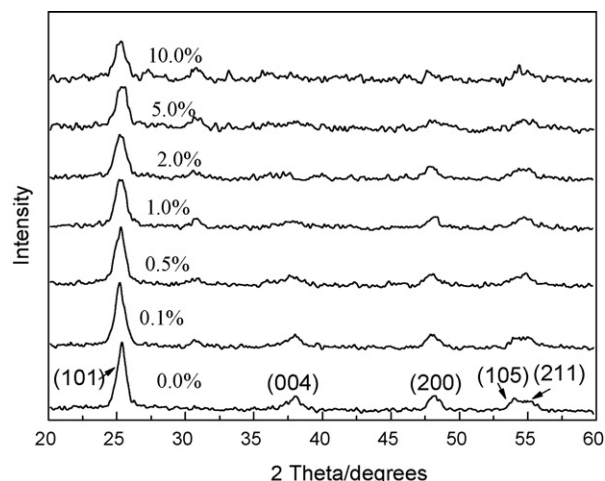


Fig. 1. XRD patterns of Fe-doped TiO₂ nanoparticles with different Fe content.

kinetic treatment of the photodecomposition processes. Samples were collected from the mixture solution at regular intervals and centrifuged to analyze by Shimadzu UV-2101 apparatus to determine the concentration of MB.

3. Results and discussion

3.1. The crystalline phase of particles

The XRD patterns of Fe-doped TiO₂ nanoparticles are shown in Fig. 1. It could be seen that all samples were anatase phase. In addition, no characters peaks of iron oxides phases appeared for all samples, which meant that iron oxide existed as amorphous phase. This suggested that iron distribution was possibly continuous in the particles. At the same time, Fig. 1 suggested a decrease of crystallinity of the Fe-doped TiO₂ nanoparticles in comparison with the undoped TiO₂, indicated by the decrease in the intensity of TiO₂ peaks. It suggested that the addition of Fe³⁺ could occupy regular lattice site of TiO₂ and distorted crystal structure of the host compound. The crystalline grain sizes of TiO₂ calculated by Scherrer formula decreased from 15.2 to 10.7 nm when the Fe content increased from 0.0% to 10.0%.

3.2. The morphologies of nanoparticles

The TEM images of undoped TiO₂ and 5.0% Fe-doped TiO₂ nanoparticles are showed in Fig. 2. The nanoparticles were spherical with narrow size distribution. The average particles sizes were about 15 and 12 nm for undoped TiO₂ and 5.0% Fe-doped TiO₂ nanoparticles, respectively. The Fe-doped TiO₂ nanoparticles owned smaller sizes and were more dispersed and uniformed than undoped TiO₂. Both narrow size distribution of nanoparticles and excellent dispersibility were in favor of photoactivity and anti-UV agent. The specific surface area of samples decreased when Fe content increased. It was 113 m² g⁻¹ for undoped TiO₂, but it was 111 and 108 m² g⁻¹ for 1% and 5% Fe-doped TiO₂ nanoparticles, respectively. It was inconsistent with the fact that the particle sizes decreased when Fe contents

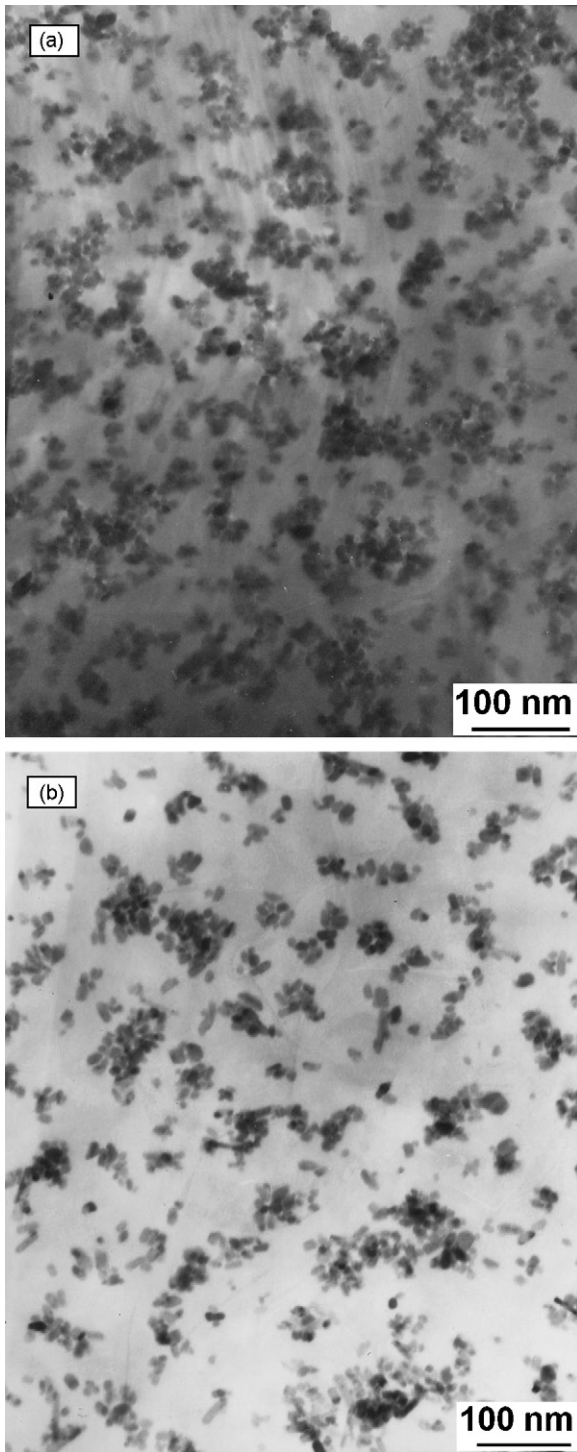


Fig. 2. TEM images of samples (a) undoped TiO_2 and (b) 5.0% Fe-doped TiO_2 nanoparticles.

increased. The decrease of particles sizes should resulted to larger specific surface area. It might be that the surface of Fe-doped TiO_2 nanoparticles smoother than undoped TiO_2 , so the specific surface area decreased. Compared with those prepared by sol–gel method [11] and by hydrothermal process with titanium tetra-*tert*-butoxide and FeCl_3 [8], the prepared Fe-doped TiO_2 nanoparticles had a smaller sizes and larger specific surface area.

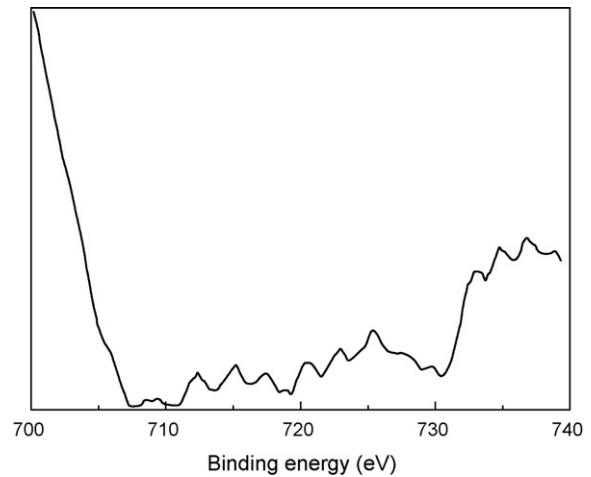


Fig. 3. The XPS spectra of 5.0% Fe-doped TiO_2 nanoparticles.

3.3. XPS analysis

The molar concentration of Fe was 5.0% measured by inductively coupled plasma optical emission spectrometer (ICP) in 5.0% Fe-doped TiO_2 nanoparticles. But in XPS spectrum of 5.0% Fe-doped TiO_2 nanoparticles (see Fig. 3), it was found that the Fe 2p characteristic peaks around 711 eV did not appeared [15]. It meant that there was no Fe on the surface calculated from the integral area. So, the results of ICP and XPS indicated that Fe^{3+} must be inserted into the matrix interior of TiO_2 nanoparticles. The ionic radius of Ti^{4+} is 0.068 nm, and the Fe^{3+} is 0.064 nm, so the Fe^{3+} ions could substitute Ti^{4+} to form stable solid solutions. The less amounts of iron calculated from these XPS data had also been found in the Fe-doped titania prepared by sol–gel method [16].

3.4. UV–vis diffuse reflectance spectra (DRS)

The UV–vis diffuse reflectance spectra of samples with different Fe contents are depicted in Fig. 4. The spectra of Fe-doped TiO_2 nanoparticles displayed a red shift in the band gap transi-

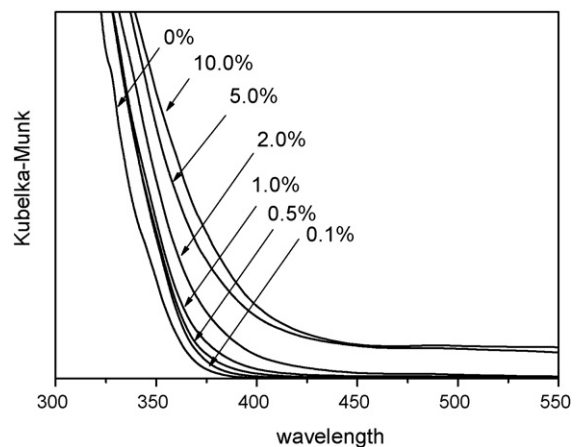


Fig. 4. The UV–vis diffuse reflectance spectra of samples with different Fe contents.

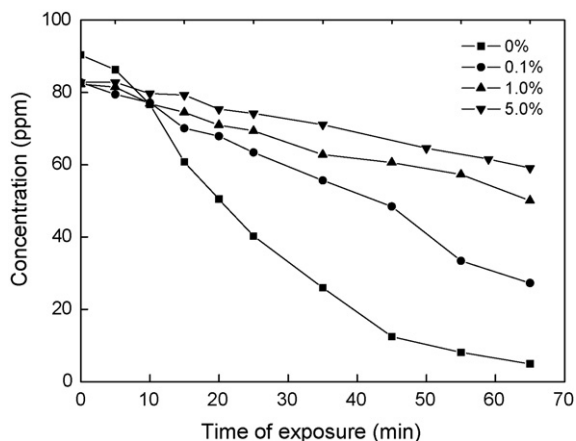


Fig. 5. Kinetics of the photocatalytic decomposition of MB on Fe-doped TiO₂ nanoparticles with different Fe contents.

tion with the increase of Fe content. It has been reported that the shift resulted from the incorporation of iron ions into the TiO₂ nanoparticles prepared by sol–gel method [9,11]. Red shifts of this type could be attributed to the charge-transfer transitions between the iron ion d electrons and the TiO₂ conduction or valence band. The Fe-doped TiO₂ composite nanoparticles showed more excellent absorption in the longer wavelength range (UVA: 320–400 nm) than TiO₂ nanoparticles, which was favorable for anti-UV agent. And when the Fe content was more than 2.0%, the absorbing band edge moved to visible range. On the other hand, there should be no separated phase of iron oxide because its characteristic broadband centered at 500 nm was not appeared, even in the spectra of 10% Fe-doped TiO₂ nanoparticles [17]. It also proved that the iron doped with TiO₂ nanoparticles rather than existed as iron oxide.

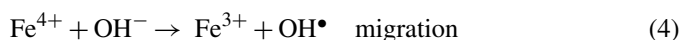
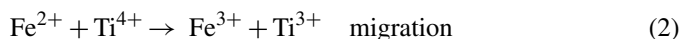
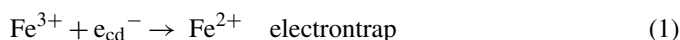
3.5. Photodecomposition of methylene blue (MB)

The photocatalytic decomposition kinetics of MB on samples is given in Fig. 5. Before reaction, 9.5% MB was adsorbed by the undoped TiO₂, but only approximately 17.4% MB was adsorbed by the Fe-doped TiO₂. It could be seen in Fig. 5 that the concentration of MB could be decreased to 5 ppm in 65 min on undoped TiO₂. But the Fe-doped TiO₂ nanoparticles had lower photocatalytic activity than undoped TiO₂ nanoparticles. It only decreased to 27.8, 50.5 and 59.1 ppm after 65 min reaction for 0.1%, 1.0% and 5.0% Fe-doped TiO₂ nanoparticles. The photoactivity of samples decreased when Fe content increased. It was different with the former reports that the addition of Fe remarkably improved the photocatalytic activity. M.S. Nahar [9] reported that, at the 0.5 wt% doping amount of Fe-doped TiO₂, the rates under UV light were 1.4 times greater than undoped TiO₂. And Zhou et al. [12] reported that a small amount of Fe³⁺ ions in TiO₂ powders could enhance their photocatalytic activity. The photocatalytic activity of Fe-doped TiO₂ powders exceeded that of Degussa P25 by a factor of more than two times at an optimal atomic ratio.

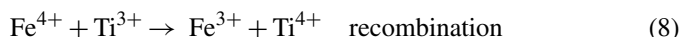
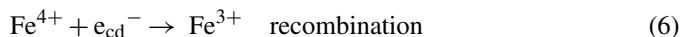
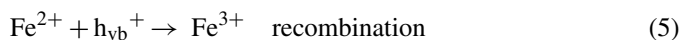
The specific surface areas, particle size and the crystallinity must be considered in comparison the photocatalytic activity

among these samples. Because all samples were in anatase phase and the specific surface area was similar, the variation in photocatalytic activity could not originate from the difference of crystal phase and specific surface area. The smaller average particles sizes of the Fe-doped TiO₂ nanoparticles should be in favor of high photocatalytic activity, but this was inconsistent with experimental results. So, the addition of Fe³⁺ should only be responsible for the resulted low photocatalytic activity.

It is generally assumed that a higher photoactivity for Fe-doped TiO₂ is possible in comparison with the undoped material, principally because Fe³⁺ can act as both hole and electron traps to enhance lifetimes of electrons and holes according to the following reactions [8]:



In most case h_{vb}^+ and OH^\bullet are the main active species in photoactivity process. However, as Fe³⁺ inserted into the matrix interior of TiO₂ composite nanoparticle, the role of the iron ions was different. Doped Fe³⁺ was isolated far from the surface with a much lower chance of transferring trapped charge carriers to the interface. As a result, the Fe were more likely to act as recombination centers for the electron–hole pair than as trap sites for eventual charge transfer at the interface, according to the following reactions:



Thus, Fe-doped TiO₂ composite nanoparticles derived from modified hydrothermal process showed decreased photoactivity.

Another important application of TiO₂ nanoparticles was anti-UV agent. It could effectively offer broadband shield for both parts of the terrestrial UV radiation. And it was chemically inert, non-toxic and non-irritating. However, because of its photoactivity, it could accelerate photodegradation reaction of some organic ingredients in these products. As anti-UV agent, it was necessary to decrease the photoactivity of TiO₂ nanoparticles. So, the low photoactivity of the prepared Fe-doped TiO₂ nanoparticles was in favor of anti-UV agent.

4. Conclusions

In summary, spherical Fe-doped TiO₂ nanoparticles with 10–15 nm particles sizes could be directly prepared by hydrothermal method. The diffuse reflectance spectra of Fe-doped TiO₂ nanoparticles displayed a red shift in the band gap transition with the increase of Fe content. XPS analysis showed the Fe was not on the surface of TiO₂ nanoparticles, but inserting

into the matrix interior. As a result, the photoactivity degradation of MB on Fe-doped TiO₂ nanoparticles decreased. It was different with the former reports that the addition of Fe remarkably improved the photocatalytic activity. So, the process of preparing Fe-doped TiO₂ nanoparticles by hydrothermal method determines its photocatalytic properties.

References

- [1] L. Miao, P. Jin, K. Kaneko, A. Terai, N. Nabatova-Gabain, S. Tanemura, Preparation and characterization of polycrystalline anatase and rutile TiO₂ thin films by rf magnetron sputtering, *Appl. Surf. Sci.* 212 (2003) 255–263.
- [2] N. Perkas, O. Palchik, I. Brukental, I. Nowik, Y. Gofer, Y. Kolytyn, A. Gedanken, A mesoporous iron-titanium oxide composite prepared sonochemically, *J. Phys. Chem. B* 107 (2003) 8772–8778.
- [3] T. Sreethawong, Y. Suzuki, S. Yoshikawa, Photocatalytic evolution of hydrogen over nanocrystalline mesoporous titania prepared by surfactant-assisted templating sol–gel process, *Catal. Commun.* 6 (2005) 119–124.
- [4] W. Ho, J.C. Yu, J. Yu, Photocatalytic TiO₂/glass nanoflake array films, *Langmuir* 21 (2005) 3486–3492.
- [5] S. Kim, S. Hwang, W. Choi, Visible light active platinum-ion-doped TiO₂ photocatalyst, *J. Phys. Chem. B* 109 (2005) 24260–24267.
- [6] T.J. Kemp, R.A. McIntyre, Transition metal-doped titanium(IV) dioxide: characterisation and influence on photodegradation of poly(vinyl chloride), *Polym. Degrad. Stabil.* 91 (2006) 165–194.
- [7] I. Tseng, J.C.S. Wu, H. Chou, Effects of sol–gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction, *J. Catal.* 221 (2004) 432–440.
- [8] J. Zhu, W. Zheng, B. He, J. Zhang, M. Anpo, Characterization of Fe-TiO₂ photocatalysts synthesized by hydrothermal method and their photocatalytic reactivity for photodegradation of XRG dye diluted in water, *J. Mol. Catal. A* 216 (2004) 35–43.
- [9] C.Y. Wang, D.W. Bahnemann, J.K. Dohrmann, A novel preparation of iron-doped TiO₂ nanoparticle with enhanced photocatalytic activity, *Chem. Commun.* (2000) 1539–1540.
- [10] M.S. Nahar, K. Hasegawa, S. Kagaya, S. Kuroda, Comparative assessment of the efficiency of Fe-doped TiO₂ prepared by two doping methods and photocatalytic degradation of phenol in domestic water suspensions, *Sci. Technol. Adv. Mater.* 8 (2007) 286–291.
- [11] J.A. Navio, J.J. Testa, P. Djedjeian, J.R. Padron, D. Rodriguez, M.I. Litter, Iron-doped titania powders prepared by a sol–gel method. Part II. Photocatalytic properties, *Appl. Catal. A* 178 (1999) 191–203.
- [12] M. Zhou, J. Yu, B. Cheng, Effects of Fe-doping on the photocatalytic activity of mesoporous TiO₂ powders prepared by an ultrasonic method, *J. Hazard. Mater. B* 137 (2006) 1838–1847.
- [13] M. Kang, Synthesis of Fe/TiO₂ photocatalyst with nanometer size by solvothermal method and the effect of H₂O addition on structural stability and photodecomposition of methanol, *J. Mol. Catal. A* 197 (2003) 173–183.
- [14] R. Janes, L.J. Knightley, C.J. Harding, Structural and spectroscopic studies of iron (III) doped titania powders prepared by sol–gel synthesis and hydrothermal processing, *Dyes Pigments* 62 (2004) 199–212.
- [15] C. Wang, D.W. Bahnemann, J.K. Dohrmann, A novel preparation of iron-doped TiO₂ nanoparticles with enhanced photocatalytic activity, *Chem. Commun.* 16 (2000) 1539–1540.
- [16] J.A. Navio, G. Colon, M. Macias, C. Real, M.I. Litter, Iron-doped titania semiconductor powders prepared by a sol–gel method. Part I. Synthesis and characterization, *Appl. Catal. A* 177 (1999) 111–120.
- [17] M.I. Litter, J.A. Navio, Photocatalytic properties of iron-doped titania semiconductors, *J. Photochem. Photobiol. A* 98 (1996) 171–181.