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## Study of structural and optical properties of Fe(III)-doped TiO<sub>2</sub> prepared by sol-gel method

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# Study of structural and optical properties of Fe(III)-doped TiO<sub>2</sub> prepared by sol-gel method

L J Kusumawardani<sup>a</sup> and Y Syahputri<sup>a</sup>

<sup>a</sup>Department of Chemistry, Universitas Pakuan, Bogor, 16143, Indonesia

\*E-mail: linda.wardani@unpak.ac.id

**Abstract.** This study investigated the structural and optical properties of Iron(III)-doped titanium dioxide (Fe-TiO<sub>2</sub>) powders which were synthesized by sol-gel method with a post-annealing temperature at 500°C. Iron(III)-doped titanium dioxide was prepared from Titanium (IV) Isopropoxide and Iron (III) Chloride (FeCl<sub>3</sub>). Iron (III) Chloride was added in different concentration (5, 7.5 and 10 % w/w). The synthesis powders were characterized by FTIR, Diffuse Reflectance Spectroscopy (DRS), Field Effect Scanning Electron Microscopy (FESEM), X-ray Diffraction (XRD) and BET. FESEM analysis showed the morphology of 10 % (w/w) Fe doped TiO<sub>2</sub> were homogeneous with the presence of less aggregate of iron. Meanwhile, The surface area of the sample TiO<sub>2</sub>-Fe 7.5% calculated from the BET adsorption plot is 107.096 m<sup>2</sup>/g. This surface area is higher than the sample TiO<sub>2</sub>-Fe 10% is 95,241 m<sup>2</sup>. It is confirmed that iron insert to the pore of TiO<sub>2</sub>. DRS Analysis revealed the light absorption in the visible region was increased with increasing the iron concentration up to 10% (w/w).

## 1. Introduction

The problem of TiO<sub>2</sub> for a photocatalytic process is a relatively large band gap (3.0 eV for the rutile phase and 3.2 eV for the anatase phase). The doping of photocatalyst, especially TiO<sub>2</sub> with metals is widely adopted to improve the photocatalyst activity. The electronic structure of TiO<sub>2</sub> nanoparticles doped with various metals creates the new chemical compositions, modifies their optical properties, affects the crystallization process and influences the photocatalytic efficiency of titania<sup>1</sup>. This is explained by the ability of the modified titania samples to reduce the band gap energy value and the recombination rates of photo-electron pairs induced by hole under sunlight radiation compared to pure TiO<sub>2</sub>. Iron (III) is a promising transition metal ion to support the purpose of this study due to similar ionic radii between Fe (0.64 Å) and Ti (0.68 Å). It can be concluded that Fe ions can be easily incorporated with TiO<sub>2</sub> crystal lattices. Titanium dioxide modified with Fe (III) using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a precursor has shown efficiency in the photocatalytic process of nitrate reduction of 65.97% for 360 minutes<sup>2</sup>. In addition, Fe (III) - Doped TiO<sub>2</sub> shows magnetic properties, namely super-magnetic<sup>3</sup>. The effect of the synthesis method on the structural and optical properties of TiO<sub>2</sub>-Fe was also reported<sup>4</sup>. The researchers explained the type of iron used in the sol-gel method. FeCl<sub>3</sub> as the Iron source reveals the smallest grain size from 120-180 nm than Fe(NO<sub>3</sub>)<sub>3</sub>. The authors in Ref. [12] reported 5% (molar ratio) Fe doped TiO<sub>2</sub> nanoparticles were prepared by a sol-gel method exhibited good optical properties.

This work aims to investigate titanium dioxide nanoparticles with different amount of Fe (5, 7.5 and 10% w/w) by sol-gel method. In this research Titanium (IV) Isopropoxide used as Titanium precursor, while Iron (III) Chloride as a source of iron. The Sol-gel method was chosen because the stoichiometry of the proposed process is controllable. In addition, the powders synthesized by this method are highly



pure and the required equipment is not expensive<sup>17</sup>.  $\text{TiO}_2$ -Fe powders characterized  $\text{TiO}_2$ -Fe powders obtained by Diffuse Reflectance Spectroscopy (DRS), Fourier Transformed Infrared (FTIR), FESEM, X-ray diffraction (XRD) and BET.

## 2. Experimental

### 2.1. Materials and Methods

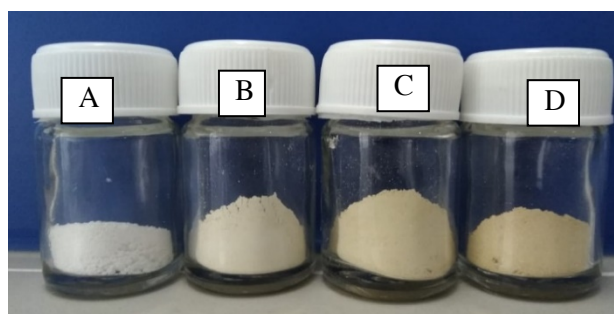
**Materials.** Titanium (IV) Isopropoxide (TTIP) 97 % and  $\text{FeCl}_3$  reagent grade were purchased from Sigma Aldrich. Degussa P25 as  $\text{TiO}_2$  standard and Ethanol 96% were purchased from Merck.

**Methods.** The Fe Doped  $\text{TiO}_2$  nano-powder was prepared by sol-gel method using Titanium (IV) Isopropoxide (TTIP) as Titanium Precursor. Briefly, 4.5 ml of TTIP and 21 ml of ethanol were mixed with 3.5 ml of distilled water and addition of  $\text{FeCl}_3$  with the molar ratio  $\text{Fe}/\text{TTIP}$  equal 5%, 7.5% and 10% (w/w). For obtaining sol, the solution was stirred at room temperature for 4 hours. During the stirring, the Fe doped  $\text{TiO}_2$  was formed. The nano-powder was obtained after the sample is filtered and dried overnight at room temperature. After that,  $\text{TiO}_2$ -Fe powder was annealed at  $500^\circ\text{C}$  for 1 hour.

### 2.2. Characterization

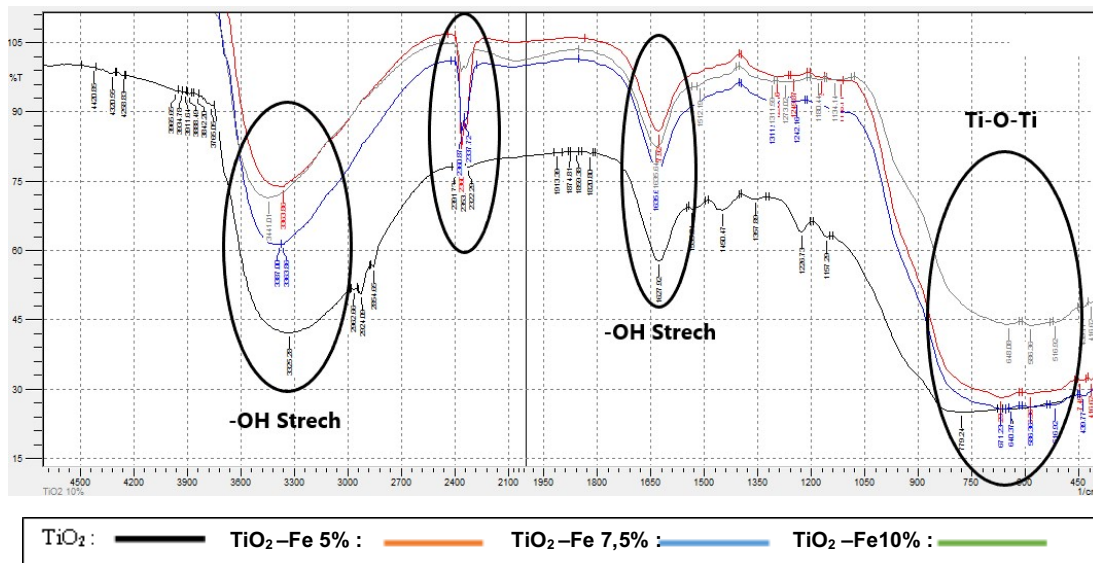
Fe- $\text{TiO}_2$  powder characterized by Fourier Transform Infrared (FTIR) to determine the various functional groups present in a nanoparticle. Specific surface areas of the samples were determined by Brunauer Emmet Teller (BET) adsorption method. The microscopic analyses of the samples were done by Field Emission Scanning Electron Microscope (FESEM). The crystallinity of Fe- $\text{TiO}_2$  powder was determined by X-ray Diffractometer (XRD). Diffraction studies were carried out using  $\text{Cu K}\alpha$  ( $1.54060^\circ\text{\AA}$ ). The crystallite sizes of the as-prepared samples were calculated using Scherer's formula. Further optical characterization of the nanopowder was done by Diffuse Reflectance Spectroscopy (DRS). The reflectance spectra were taken over the range of 800-200 nm.

### Results

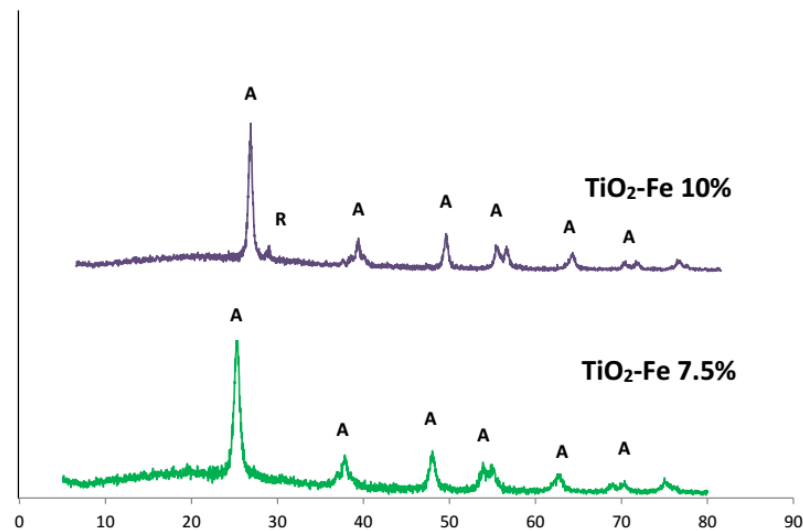


**Figure 1.** The Physical Appearance of Degussa P25 (A), 5% Fe doped (B), 7.5% Fe doped (C) and 10% Fe doped (D).

Fe doped  $\text{TiO}_2$  was prepared by sol-gel method with Titanium (IV) isopropoxide as a precursor and  $\text{FeCl}_3$  as a source of iron. This work aims to learn the effect of iron-doped into  $\text{TiO}_2$  and to investigate the photocatalytic activity and bandgap by characterization of the obtained powder by FTIR, FE-SEM, XRD, BET, and DRS. Figure 1. Shows the brown color from Fe doped  $\text{TiO}_2$  indicates Fe was successfully doped into  $\text{TiO}_2$ . The prepared sample was investigated by FTIR spectroscopy. The FTIR spectra of Fe doped  $\text{TiO}_2$  are shown in Figure 2. The absorption band at  $3200 - 3600$  is assigned to the -OH group. The absorption band at  $400 - 800 \text{ cm}^{-1}$  has sharp peaks after the calcination process. It indicates Ti-OH bonds was fully converted to Ti-O-Ti. The absorption band at  $2200 \text{ cm}^{-1}$  is assigned to Ti-O-Fe vibration. The FTIR results are in good agreement with Luu Cam Loc, et al. 2010<sup>14</sup>.



**Figure 2.** FTIR spectra of  $\text{TiO}_2$ , P25 Degussa and  $\text{TiO}_2\text{-Fe}$  powders.



**Figure 3.** XRD Patterns of  $\text{TiO}_2\text{-Fe}$  Nanoparticles.

The X-ray diffraction pattern of the Fe doped  $\text{TiO}_2$  is shown in Fig.3. Strong diffraction peak at  $25^\circ$  indicating  $\text{TiO}_2$  in the anatase phase. The  $2\theta$  peaks at  $27.5^\circ$  confirm its rutile structure. There are no characteristic peaks of  $\text{Fe}_2\text{O}_3$  because  $\text{Fe}^{3+}$  ions replace  $\text{Ti}^{4+}$  ions in the crystal framework of  $\text{TiO}_2$ . Adding Iron has not altered the framework structure but affect the crystallite size. Particle size has been estimated by using the Scherer formula and calculated in Table 1. The crystallite size of 7.5% iron content is relatively small than 10% because there is a rutile phase after adding 10% (w/w) Fe which is increasing the size of particles.

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where  $\lambda$  is a wavelength of X-Ray,  $\beta$  is FWHM (full width at half maximum),  $\theta$  is diffraction angle,  $d$  is  $d$ -spacing and  $D$  is particle diameter size.

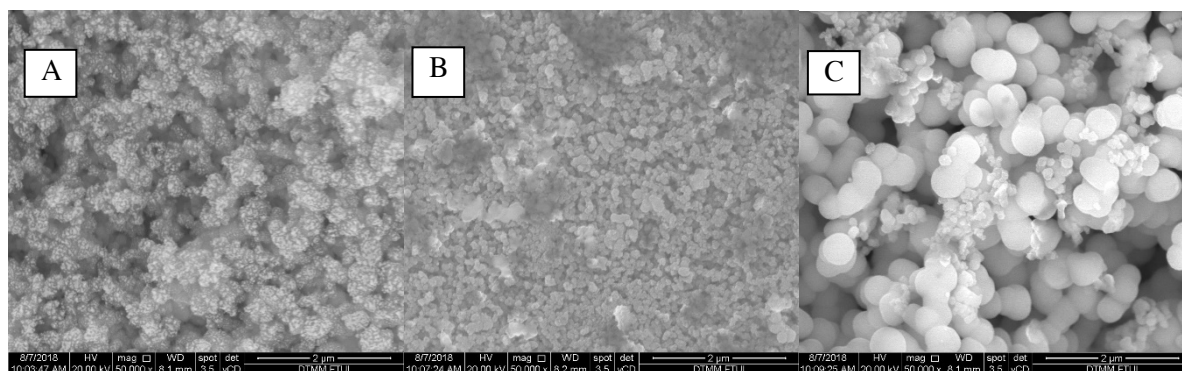
**Table 1.** Crystallite Size of  $\text{TiO}_2$ -Fe 7,5% and 10%.

Samples	Crystallite Size (nm)
$\text{TiO}_2$ -Fe 7,5%	14.72
$\text{TiO}_2$ -Fe 10%	68.08

The prepared sample was investigated by Field Emission Scanning Electron Microscopy (FESEM). Morphology of Fe doped  $\text{TiO}_2$  revealed by FESEM is shown in Figure.4. The analysis is summarized in the term of shape and distribution in Table.2. The samples of 10 % (w/w) Fe doped  $\text{TiO}_2$  were homogeneous with the presence of less aggregate of iron. This condition is supported by surface area measurements using BET for a prepared sample. The surface area of the sample  $\text{TiO}_2$ -Fe 7.5% calculated from the BET adsorption plot is 107.096  $\text{m}^2/\text{g}$ . This surface area is higher than the sample  $\text{TiO}_2$ -Fe 10% is 95,241  $\text{m}^2$ . It is confirmed that iron insert to the pore of  $\text{TiO}_2$ .

**Table 2.** Morphological characteristic of Fe doped  $\text{TiO}_2$ .

	Amount percentage of iron in $\text{TiO}_2$ (%Fe (w/w))		
	5%	7,5%	10%
Shape distribution	Spherical irregular, more aggregates	Quite Spherical regular, more aggregates	Spherical regular, and less aggregates

**Figure 4.** Morphology of  $\text{TiO}_2$ -Fe 5%, (b)  $\text{TiO}_2$ -Fe 7,5% (c)  $\text{TiO}_2$ -Fe 10%.

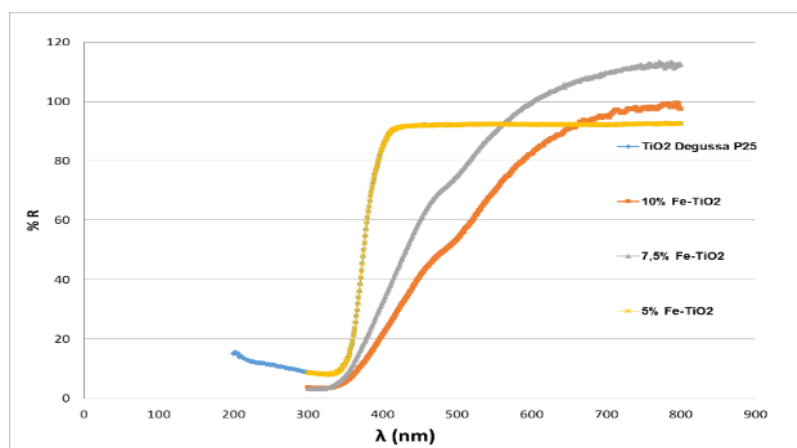
The analysis of UV-vis diffuse reflectance spectra (DRS) is shown in Figure. 5. The light absorption of un-doped  $\text{TiO}_2$  in the visible region is not significant, whereas iron-doped  $\text{TiO}_2$  shows an enhancement of light absorption in this region. The light absorption in the visible region was increased with increasing the iron concentration. Particularly 10% Fe Doped, absorption was observed in the range 400–600 nm. The percent (%) reflectance sample compared to a  $\text{TiO}_2$  P25 Degussa. Based on the spectra have been obtained, the value of the band gap is determined by calculating the Kubelka-Munk equation according to:

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

$F(R)$  is the Kubelka–Munk function,  $R$  the ratio of the intensities of radiation reflected in a diffuse manner from the sample and from the known sample,  $K$  represents the absorption coefficient of radiation and  $S$  is the scattering factor. The value of the energy gap is summarized in Table 3. DRS showed that the 10% Fe doping in titania has the lowest the band gap energy decreased from 3,2 to 2,3 eV. It slightly different result from the authors in Ref. [12] showed Fe doped  $\text{TiO}_2$  at the Fe/Ti molar ratio (5%) has good optical properties, Its method used Iron (III) Chloride 6-Hydrate and  $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$  as a precursor. Therefore, It concludes that the method and precursor of  $\text{TiO}_2$ : Fe synthesis influence on their structural and optical properties.

**Table 3.** Value Band Gap of  $\text{TiO}_2$  Standard versus  $\text{TiO}_2$ - Fe.

Sample	Band Gap, E (eV)
$\text{TiO}_2$ -Fe 5%	2,35
$\text{TiO}_2$ -Fe 7,5%	2,29
$\text{TiO}_2$ -Fe 10%	2,30
$\text{TiO}_2$ P25 Degussa	3,20



**Figure 5.** Diffuse Reflectance Spectra of  $\text{TiO}_2$  P25 Degussa and  $\text{TiO}_2$ -Fe.

### 3. Conclusions

In summary, The Fe doped  $\text{TiO}_2$  was successfully synthesized by the simple sol-gel method using  $\text{FeCl}_3$  as an iron source. The XRD results revealed that the coexistence of rutile and anatase phase at 10% Fe-loaded  $\text{TiO}_2$  was shown in XRD patterns. The XRD results also proved that the crystallite size increase with the increase of Fe content. The FTIR measurement, a vibration of Ti-O was seen at  $400 - 800 \text{ cm}^{-1}$  and the Ti-O-Fe in  $\text{TiO}_2$  framework was appeared at  $2200 - 2300 \text{ cm}^{-1}$ . Iron was successfully trapped in  $\text{TiO}_2$ . The FESEM surface morphology showed that 10% Fe-loaded  $\text{TiO}_2$  had uniform size and also less aggregate. With the help of BET measurements, it was confirmed that iron successfully inserts to the pores of  $\text{TiO}_2$  because the surface area of 10% Fe doped  $\text{TiO}_2$  is less than others. DRS Analysis revealed that the light absorption in a visible region was increased with increasing the iron concentration up to 10% (w/w). Considering all the measurement results, the 10% Fe loaded  $\text{TiO}_2$  will give optimum the photocatalytic activity.

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### References

- [1] Beeldena A 2006 *An environmentally friendly solution for air purification and self-cleaning effect: the application of TiO<sub>2</sub> as photocatalyst in concrete*. Belgium.
- [2] Benedix R *et al.* 2000 *Progress in Inorganic Chemistry* 54 47.
- [3] Cullity BD and Stock SR 2001 *Element of X-ray diffraction*, 3rd Ed, Prentice Hall Inc., New Jersey, p. 169-171.
- [4] Di Paola A, Ikeda S, Marcì G, Ohtani B and Palmisano L 2001 *International Journal of Photoenergy* 3 171.
- [5] Grätzel M 2001 *Nature* **414** 338
- [6] Hoffmann MR, Martin ST, Choi W and Bahnemann DW 1995 *Chem. Rev.* 95 69.
- [7] Hreniak A, Katarzyna G, Bartosz B, Andrzej S, Jacek C and Agnieszka I 2015 *Optical Materials* 46 45.
- [8] Irkham 2013 Studi Preparasi TiO<sub>2</sub> Nanotube Terimobilisasi untuk Degradasi Fotokatalitik Paraquat Diklorida Menggunakan Reaktor Alir. *Skripsi FMIPA UI Depok, Indonesia*.
- [9] Kobwittaya K and Sirivithayapakorn S 2014 *APCBEE Procedia* 10 321.
- [10] Kokila P, Senthilkumar V and Prem Nazeer K 2011 *Scholars Research Library, Archives of Physics Research*. 2(1) 246.
- [11] Li S *et al.* 2010. Nitrogen-doped TiO<sub>2</sub> nanotube arrays with the enhanced photoelectrochemical property. *Hainan Superior Resources*.
- [12] Nasralla, Yeganeh, M, Astuti Y, Piticharoenphu S, Shahtahmasebi N, Kompany A, Karimipour M, Mendis BG, Poolton and Šiller L 2012 *Transactions F: Nanotechnology* 20 1018.
- [13] Amy LL, Guangquan L and Yates JT 1995 *Surface Science Center Rev.* 95 735.
- [14] Loc LC, Tuan NQ and Thoang HS 2010 *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **1** 015008.
- [15] Karen O, Agnieszka H, Andrzej S, Dominika GK and Agnieszka I 2015 *Processing and Application of Ceramics* 9(1) 43.
- [16] Rashad MM, Elsayed EM, Al-Kotb MS and Shalan AE 2013 *Journal of Alloys and Compounds*. 581 71.
- [17] Somayeh S and Faranak A 2015. *J Nanostruct Chem*.
- [18] Sorolla MG *et al.* 2012 *Journal of Environmental Sciences* **24(6)** 1125.
- [19] Tjitrosoedirdjo *et al.* 1984 Pengelolaan gulma di perkebunan. *Gramedia*, Jakarta, Indonesia.