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To cite this article: L J Kusumawardani and Y Syahputri 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **299** 012066

IOP Conf. Series: Earth and Environmental Science **299** (2019) 012066 doi:10.1088/1755-1315/299/1/012066

Study of structural and optical properties of Fe(III)-doped TiO_2 prepared by sol-gel method

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Abstract. This study investigated the structural and optical properties of Iron(III)-doped titanium dioxide (Fe-TiO_2) 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 ($FeCl_3$). 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_2 were homogeneous with the presence of less aggregate of iron. Meanwhile, The surface area of the sample TiO_2-Fe 7.5% calculated from the BET adsorption plot is 107.096 m^2/g. This surface area is higher than the sample TiO_2-Fe 10% is 95,241 m^2. It is confirmed that iron insert to the pore of TiO_2. 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_2 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_2 with metals is widely adopted to improve the photocatalyst activity. The electronic structure of TiO_2 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[7]. 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_2. Iron (III) is a promising transition metal ion to support the purpose of this study due to similar ionic radii between Fe (0.64Å) and Ti (0.68 Å). It can be concluded that Fe ions can be easily incorporated with TiO_2 crystal lattices. Titanium dioxide modified with Fe (III) using $Fe(NO_3)_3$. $9H_2O$ as a precursor has shown efficiency in the photocatalytic process of nitrate reduction of 65.97% for 360 minutes[9]. In addition, Fe (III) - Doped TiO_2 shows magnetic properties, namely super-magnetic[15]. The effect of the synthesis method on the structural and optical properties of TiO_2-Fe was also reported[7]. The researchers explained the type of iron used in the sol-gel method. $FeCl_3$ as the Iron source reveals the smallest grain size from 120-180 nm than $Fe(NO_3)_3$. The authors in Ref. [12] reported 5% (molar ratio) Fe doped TiO_2 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[17]. TiO_2-Fe powders characterized 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 $FeCl_3$ reagent grade were purchased from Sigma Aldrich. Degussa P25 as TiO_2 standard and Ethanol 96% were purchased from Merck.
Methods. The Fe Doped 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 $FeCl_3$ with the molar ratio Fe/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 TiO_2 was formed. The nano-powder was obtained after the sample is filtered and dried overnight at room temperature. After that, TiO_2-Fe powder was annealed at 500^{o}C for 1 hour.

2.2. Characterization

Fe-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-TiO_2 powder was determined by X-ray Diffractometer (XRD). Diffraction studies were carried out using Cu Kα (l¼1.54060˚A). 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

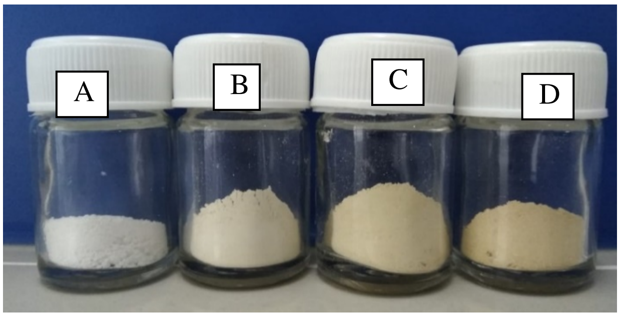

Figure 1. The Physical Appearance of Degussa P25 (A), 5% Fe doped (B), 7.5% Fe doped (C) and 10% Fe doped (D).

Fe doped TiO_2 was prepared by sol-gel method with Titanium (IV) isopropoxide as a precursor and $FeCl_3$ as a source of iron. This work aims to learn the effect of iron-doped into 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 TiO_2 indicates Fe was successfully doped into TiO_2. The prepared sample was investigated by FTIR spectroscopy. The FTIR spectra of Fe doped 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 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 cm^{-1} is assigned to Ti-O-Fe vibration. The FTIR results are in good agreement with Luu Cam Loc, at all. 2010[14].

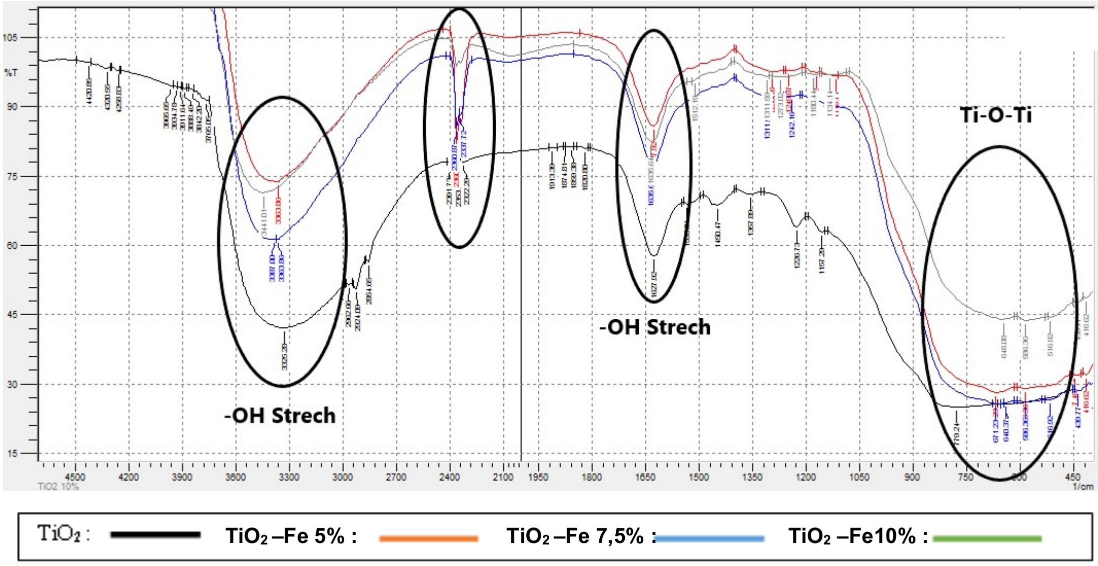

Figure 2. FTIR spectra of TiO_2 P25 Degussa and TiO_2-Fe powders.

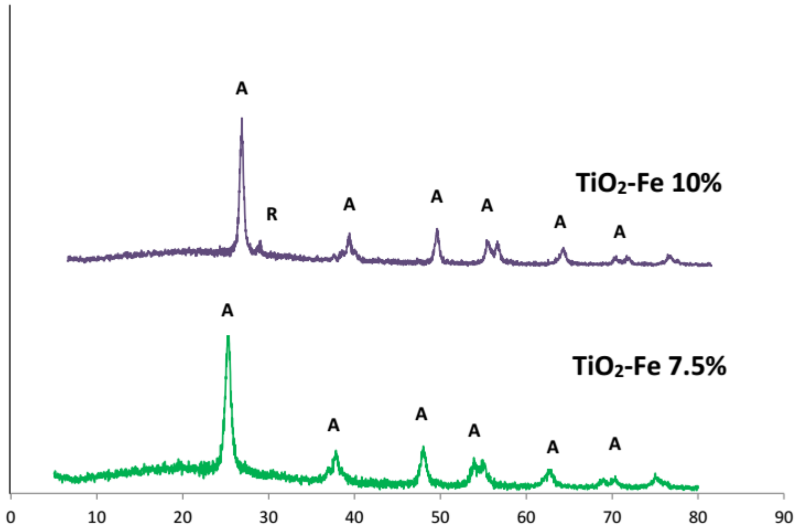

Figure 3. XRD Patterns of TiO_2-Fe Nanoparticles.

The X-ray diffraction pattern of the Fe doped TiO_2 is shown in Fig.3. Strong diffraction peak at 25° indicating TiO_2 in the anatase phase. The 2θ peaks at 27,5° confirm its rutile structure. There are no characteristic peaks of Fe_2O_3 because Fe^{3+} ions replace Ti^{4+} ions in the crystal framework of 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.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

where λ is a wavelength of X-Ray, β is FWHM (full width at half maximum), θ is diffraction angle, d is d-spacing and D is particle diameter size.

Table 1. Crystallite Size of TiO_2-Fe 7,5% and 10%.

Samples	Crystallite Size (nm)
TiO_2-Fe 7,5%	14.72
TiO_2-Fe 10%	68.08

The prepared sample was investigated by Field Emission Scanning Electron Microscopy (FESEM). Morphology of Fe doped 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 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 TiO_2-Fe 7.5% calculated from the BET adsorption plot is 107.096 m^2/g. This surface area is higher than the sample TiO_2-Fe 10% is 95,241 m^2. It is confirmed that iron insert to the pore of TiO_2.

Table 2. Morphological characteristic of Fe doped TiO_2.

	Amount percentage of iron in 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

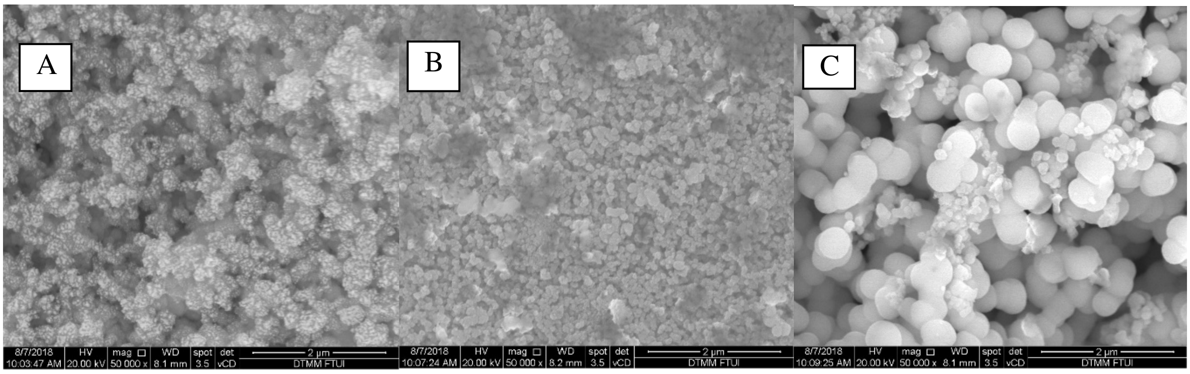

Figure 4. Morphology of TiO_2-Fe 5%, (b) TiO_2-Fe 7,5% (c) TiO_2-Fe 10%.

The analysis of UV-vis diffuse reflectance spectra (DRS) is shown in Figure. 5. The light absorption of un-doped TiO_2 in the visible region is not significant, whereas iron-doped 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 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 TiO_2 at the Fe/Ti molar ratio (5%) has good optical properties, Its method used Iron (III) Chloride 6-Hydrate and $C_{12}H_{28}O_4Ti$ as a precursor. Therefore, It concludes that the method and precursor of TiO_2: Fe synthesis influence on their structural and optical properties.

Table 3. Value Band Gap of TiO_2 Standard versus TiO_2- Fe.

Sample	Band Gap, E (eV)
TiO_2-Fe 5%	2,35
TiO_2-Fe 7,5%	2,29
TiO_2-Fe 10%	2,30
TiO_2 P25 Degussa	3,20

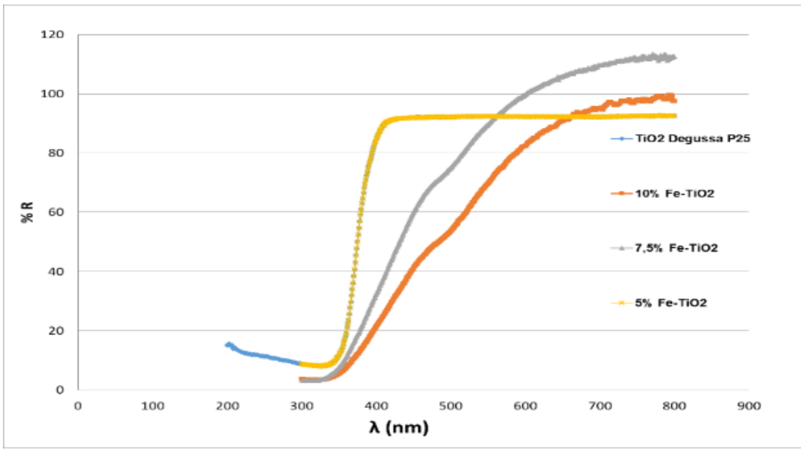

Figure 5. Diffuse Reflectance Spectra of TiO_2 P25 Degussa and TiO_2-Fe.

3. Conclusions

In summary, The Fe doped TiO_2 was successfully synthesized by the simple sol-gel method using $FeCl_3$ as an iron source. The XRD results revealed that the coexistence of rutile and anatase phase at 10% Fe-loaded 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 cm^{-1} and the Ti-O-Fe in TiO_2 framework was appeared at 2200 – 2300 cm^{-1}. Iron was successfully trapped in TiO_2. The FESEM surface morphology showed that 10% Fe-loaded 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 TiO_2 because the surface area of 10% Fe doped 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 TiO_2 will give optimum the photocatalytic activity.

Acknowledgement
This research was financially supported by Directorate of Research and Community Service From Ministry of Research and Higher Education Republic of Indoesia. We acknowledge Inong Thari Novacdalya for her help in analysis.

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