Synthesis and material characterization of TiO$_2$ nanoparticles doped with iron (Fe)

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Abstract. Titanium dioxide (TiO$_2$) doped with iron (Fe) atom are investigated using X-Ray diffraction, field emission scanning electron microscopy (FESEM), and photocatalysts measurements. Fe-TiO$_2$ nanoparticles with different concentration of iron were formed using the conventional co-precipitation technique from two different chemical solutions. The precursors of TiO$_2$ were prepared using titanium tetrachloride (TiCl$_4$) of 50 ml, and iron trichloride (FeCl$_3$) was used as a dopant source. X-ray diffraction results show that diffraction pattern have two phases structures anatase and rutile phase structures where the intensity of the rutile structures are superior to that the anatase phase intensities. The results from FESEM micrograph indicate that the agglomerations were taken place, forming into clusters. Irradiation of ultraviolet (UV) with varying the time from 30 minutes to 120 minutes to the Fe-doped TiO$_2$ nanoparticles using methylene blue shows that the absorption intensity reduces as time irradiation increased. The results indicate that the TiO$_2$ nanoparticles doped with iron are suitable as photocatalysts.

1. Introduction

Nanoparticles are particles having the size in the nanometer scale, which ranges from 1-100 nanometers. The nanoparticles have characteristics superior in physical and chemical properties than the bulk. The main cause of the physical and chemical properties of nanoparticles is increasing fraction of atomic surfaces due to reduced particle size. One of the much-studied of the nanoparticles is TiO$_2$. TiO$_2$ nanoparticle is a n-type semiconductor material that is widely used in environmental purification due to its long-term stability, the photo energy with high oxidation, and non-toxic [1-4]. However, TiO$_2$ have shortcomings in terms of absorption in UV range because it has a wide bandgap of 3.0 eV for rutile and 3.2 eV for anatase [1,5]. Therefore, there is several restrictions of using TiO$_2$ for further application under ultra violet light (UV). In order to improve the absorption of the TiO$_2$ in UV-range, iron ion was used as a dopant in TiO$_2$ nanoparticles to reduce the band gap of TiO$_2$.

In the present study, we fabricate the TiO$_2$ nanoparticles doped with iron using the co-precipitation method by combining of two different chemical compounds TiCl$_4$ as precursor and FeCl$_3$ as a dopant at the same time [6]. The co-precipitation method is used because it is relatively simple, inexpensive, and...
requires a fairly short time. TiO$_2$ nanoparticles doped with iron were used to investigate the structural characteristics such as the crystallite size and the strain using the x-ray diffraction (X-RD) measurements. We performed the field emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM) to observe the surface morphology. Since the nanoparticles of Fe-doped TiO$_2$ is used as a photocatalyst, the UV-Vis absorption experiment was performed to irradiated for different time interval using UV light to a methylene blue in which the Fe-doped TiO$_2$ was present.

2. Experimental setup
Nanoparticles of titanium dioxide (TiO$_2$) doped iron (Fe) with a doping concentration of 1% and 2% was prepared by weighing 0.211 grams of FeCl$_3$ using digital scales and 5mL of TiCl$_4$. FeCl$_3$ solid was subsequently dissolved into 200mL of water that has been filtered twice, and it was added with HCL (37%) slightly so FeCl$_3$ soluble in water. Then 5mL of TiCl$_4$ solution is cooled and then added dropwise into a solution containing FeCl$_3$ by means of constant stirring for 2 hours using a magnetic stirrer. After 2 hours stirring, it was continued stirring at 500°C for 16 hours in order to find the homogenous solution. The precipitate obtained was dialyzed until the reaction of Cl negative ions was reduced and dried by using a furnace at a temperature of 100°C during 5 hours.

Structural properties of TiO$_2$ doped with iron nanoparticles such as the crystallite size and strain were determined using the Debye-Scherrer and William-Hall method where the data was derived from X-ray diffraction (X-RD) measurements. In order to confirm the results from the X-RD measurements, X-ray fluorescence (X-RF) was used to estimate the oxide and element content in the samples. Field emission scanning electron microscopy (FESEM) was performed to look at the surface morphology of the samples, and these results will be confirmed with High-resolution transmission electron microscopy (HRTEM). Since the TiO$_2$ nanoparticles doped with iron is a potential candidate for photocatalytic, therefore we used the methylene blue (MB) that was irradiated with the ultraviolet (UV) to observe the degradation of the absorption intensity of MB in which Fe-doped TiO$_2$ was present.

3. Results and discussion
3.1. X-RF and X-RD
X-ray fluorescence (X-RF) measurements were carried out before to take experimental data of X-ray diffraction (X-RD) observing the oxide and the element content in Fe-doped TiO$_2$ nanoparticles. The measurement of X-RF was carried out for counting the oxide and element content such as Fe$_2$O$_3$ and Fe in the Fe-doped TiO$_2$ nanoparticles using ARL Quant’x EDXRF analyzer. The results of the oxide content were tabulated in Table.1. This table shows the oxide and element content in the samples. As shown in Table.1, the iron oxide (Fe$_2$O$_3$) and element content of Fe into TiO$_2$ nanoparticles doped iron increased from 0.24% to 0.71% as the ratio of Fe/Ti increased from 1% to 2%. However, the titanium dioxide content in the samples slightly decreased from 98.84% to 98.07%.

| Dopant Ratio (Fe/Ti) (%) | Oxide content (%) | Element content (%) |
|-------------------------|------------------|---------------------|
|                         | TiO$_2$ | Fe$_2$O$_3$ | others | Ti     | Fe     | others |
| 1                       | 98.84   | 0.24       | 0.92    | 98.50  | 0.32   | 1.18   |
| 2                       | 98.07   | 0.71       | 1.22    | 97.47  | 0.93   | 1.60   |

Figure.1 shows the X-RD diffraction patterns of Fe-doped TiO$_2$ nanoparticles at the different ratio of Fe/Ti 1% and 2%. The diffraction peak of the samples indicates the rutile and anatase phase structures that were clearly observed in which the rutile phase is dominant phase structures compare to the anatase phase. The anatase phase structure was observed at 2$\theta$ = 27.73, and 48.65° corresponding to the plane of (011) and (020), respectively. For the rutile phase structures, the diffraction peak was observed at 2$\theta$ = 27.36, 36.21, 41.29, 43.73, 54.22, and 56.19° that corresponds to the plane of (110), (101), (111), (120), (020), (210), and (220), respectively. Also, it shows from the X-RD diffraction peak that the iron-
doped does not completely activated into the samples since there was the oxide content (Fe$_2$O$_3$) in the diffraction curves emerging at diffraction peak of $2\theta = 32.44^\circ$. The diffraction peak intensity of the oxide (Fe$_2$O$_3$) increase as the ratio of Fe/Ti concentration increased from 1% to 2%, indicating the activation of iron-doped into the samples. These results are well confirmed from the X-ray fluorescence in which the oxide element content was obviously detected, although the concentration of oxide content is very small. These results are quite surprising because it is expected that the iron ion can be incorporated completely with titanium (Ti) due to a similar the ionic radii between Fe (0.68 Å) and Ti (0.64 Å) [7]. However, the results from X-RD indicate that not all iron is substituted the titanium.

Figure 1. X-ray diffraction (X-RD) curves of TiO$_2$ nanoparticles with various iron-doped concentrations

Table 2. The structure parameters of Fe-doped TiO$_2$ nanoparticles at different ratio of Fe/Ti

| Ratio (Fe/Ti) | (hkl)   | Scherrer Method [8] | William Hall Plot-Method [9] Uniform Deformation Method (UDM) |
|--------------|---------|---------------------|---------------------------------------------------------------|
|              |         | Size (nm) | Strain | Size (nm) | Strain |
| 1%           | (110)   | 14.264    |        |           |        |
|              | (101)   | 19.336    |        |           |        |
|              | (111)   | 19.897    | 0.00702| 18.88     | 0.00695|
|              | (210)   | 14.554    |        |           |        |
|              | (220)   | 12.372    |        |           |        |
| 2%           | (110)   | 12.955    |        |           |        |
|              | (101)   | 17.886    |        |           |        |
|              | (111)   | 18.167    | 0.00712| 18.31     | 0.00367|
|              | (210)   | 15.169    |        |           |        |
|              | (220)   | 14.908    |        |           |        |

The crystallite size ($D$) and the strain ($\varepsilon$) of TiO$_2$ nanoparticles doped iron were calculated from the X-ray diffraction measurements results using the Debye-Scherrer equation [8],

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)\

where $\lambda$ (1.5406 Å) is the x-ray wavelength radiation of Cu Kα, $\beta$ is the full width at half-maximum (FWHM) of the diffraction peak, and $\theta$ is the Bragg angle, respectively. The structures parameters of the samples are tabulated in Table 2. To estimate the structural parameters, it is assumed that not all the
diffraction peaks take into account to calculate the crystallite size and the strain of the samples. Since the rutile phase structures are dominant in the diffraction curves compare to anatase phase structures, thereby the diffraction peak corresponding to the anatase is neglected in this case. According to the Debye-Scherrer equation, the crystalline size of TiO$_2$ doped iron at a concentration of 1% is approximately 16.08 nm. For iron-doped concentration of 2%, the crystallite size (D) of the sample is around 15.82 nm. In order to confirm the structural parameters of the samples, the William-Hall (UDM) was also used to determine the crystalline size and the strain using the equation [9]

$$\beta_{hkl} \cos \theta = \frac{k\alpha}{D} + (4\varepsilon \sin \theta)$$

(2)

For William-Hall calculation method, it is assumed that the strain is uniform all crystallographic direction where the material properties are not depend of the direction [9]. Based on the equation (2), the term of $\beta_{hkl} \cos \theta$ is plotted against $(4\sin \theta)$ will result to the slope and $y$-intercept of the fitted line. The slope corresponds to the strain and the $y$-intercepts represent to the crystalline size of the samples, respectively. The William-Hall plot of the fitted line of the equation (2) for the TiO$_2$ doped iron was depicted in Figure.2 at different ratio of Fe/Ti. Based on the fitted line, the crystalline size of the samples is 18.88 and 18.31 nm at iron concentration of 1%, and 2% respectively. For the case of the strain, it decreases from 0.00695 to 0.00367. The crystallite size and the strain results that were estimated from the William-Hall method are slightly different with the Debye-Scherrer method due to the different number of parameters used. However, both the Debye-Scherrer and William-Hall method have positive strain indicating that the strain tensile present during the synthesis of the samples. This strain decrease as the concentration of the iron increased. It is expected that it will change to the negative strain that is compressive strain as the concentration of the iron is further increased.

Figure 2. The William-Hall (UDM) calculation of TiO$_2$ nanoparticles doped with iron at a different concentration of 1% and 2%. From the linear fitting, $y$-intercept corresponds to the crystalline size and the slope represents the strain.

3.2. Surface morphology
The surface morphology of the TiO$_2$ nanoparticles doped with iron was performed using the field emission scanning electron microscopy (FESEM). Figure 2a and 2b show the SEM images with the different magnification of the Fe-doped TiO$_2$, respectively. It is obviously seen in this figure the formation of the spherical shape morphology on its surface. They are distributed denser and a little empty space when the SEM magnification is 50,000 times. However, we observe a less distribution of the spherical shape and more empty space generating in these samples when the SEM magnification is 40,000 times. In addition to this, Figure 2a and 2b reveal that there is an agglomeration of the spherical
shape take place in the samples, and they tend to generate a cluster as seen in Figure 2a. Also, it is interesting to see that all the spherical shape on its surface grown by sharp nanorods.

Subsequently studies on high resolution TEM was conducted to observe more advance in the surface morphology of the samples in which many sharp nanoroads observed in SEM images were generated during the synthesis of the samples. Figure 2c and 2d display HRTEM images of the Fe-doped TiO$_2$ with different magnifications. It is obviously observed that nanoparticles of Fe-doped TiO$_2$ are agglomerated like-nanoflowers forming in the surface of the samples. The agglomeration of nanoflowers are consists of the nanoroads which are very sharp generating its surface which are also clearly seen in the Figure 2D. Similar surface morphology were observed in the previous studies [10] using the similar precursor that is the combination of chemical compound FeCl$_3$ and TiCl$_4$. Also in ref [11,12], they reported that the agglomeration like-flower consists of nanoroads were clearly seen in the HRTEM images. The formation of nanoroads can be explained by prolonged aging at elevated temperature. In this study, they use a hydrothermal method using the precursor of titanium tetrabutoxide.

![Figure 3](image)

**Figure 3.** (a), (b) Field emission (FESEM) images of nanoparticles Fe-doped TiO$_2$ with different magnification, (c), (d), HRTEM images of Fe-doped TiO$_2$ nanoparticles varying in magnification.

### 3.3. Photocatalysts

Figure 4 presents the UV-Vis absorption spectra of photodegraded methylene blue (MB) solution irradiated by ultraviolet light with the different time interval of irradiation in the appearance of the TiO$_2$ nanoparticles doped iron. Also, we observed three different maxima intensity appearing at the wavelength of 244, 291, and 661 nm, respectively. The absorption position is shifted to a lower wavelength from 661 nm to 647 nm when the irradiation time interval increased. In addition to this, the peak intensity at $\lambda_{\text{max}}$ at 661 nm decreased significantly after the MB was irradiated with the UV light during 120 minutes. These results indicate that there is decolourization of methylene blue (MB) which
results from the absorption of the nanoparticles doped iron. Based on the photodegraded of MB, the Fe-doped TiO$_2$ nanoparticles is potentially used as photocatalysts.

**Figure 4.** The UV-Vis absorption spectra of methylene blue solution irradiated with the ultraviolet light in the presence of TiO$_2$ nanoparticles doped with iron at different time interval irradiation.

### 4. Conclusion

TiO$_2$ nanoparticles doped with iron have been successfully fabricated with different concentration of iron using the co-precipitation method. The structural characterization of the samples that were observed by means X-RD shows that Fe-doped TiO$_2$ having two phases structures; rutile and anatase phases where the rutile phases are dominant compared to the anatase phase. Also, the oxide content (Fe$_2$O$_3$) can be detected by the X-RD measurement, although its concentration is very low, as shown the X-RF measurement. The results from X-RD measurement indicate that the iron does not completely incorporate via substitution or interstitial with Ti, although the ionic radii of Fe and Ti are similar. From FESEM and HRTEM measurements, the surface morphology of the Fe-doped TiO$_2$ nanoparticles shows an agglomeration of spherical shape forming like nanoflowers which is consists of sharp nanorods on its surface. Based on the UV-Vis absorption measurement, it shows that the intensity of methylene blue in the presence of Fe-doped TiO$_2$ decreased significantly after irradiated with the UV light during 120 minutes. The results from UV-Vis absorption indicates the TiO$_2$ doped with iron is potentially used as photocatalysts.

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