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Synthesis and Characterization of Visible Light Active Fe-TiO_2 using Hydrothermal Method

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Abstract: Titanium dioxide (TiO_2) is well known due to it usage and has potential in purification methods of water and air pollution. In this study, TiO_2 nanoparticle doped with iron (Fe) was synthesized by hydrothermal method. Effect of aging time during hydrothermal treatment on the formation of TiO_2 and the performance of photocatalytic activity under visible and ultraviolet light irradiation were investigated. The structure and properties of the sample were evaluated - by X-Ray Diffraction (XRD), Energy Dispersive X-Ray (EDX), Field Emission Scanning Electron Microscope (FE-SEM) and UV-Visible Spectroscopy (UV-Vis). XRD analysis showed the studied samples consisted of anatase phase. FE-SEM images showed an agglomeration of grains with various sizes ranged 30-35 nm. Increasing aging time resulted in a narrower band gap energy and higher photocatalytic activity as compared to pure TiO_2. The result showed Fe-TiO_2 aged for 4 h provided the highest percentage (66%) of Methyl Orange (MO) degradation under visible light irradiation. The current finding suggested that, Fe-TiO_2 has high potential to degrade organic compound in water pollution

Keywords: TiO_2, hydrothermal, photocatalytic activity, optical property.

1. Introduction

The growth of worldwide industry has tremendously increased the generation and accumulation of waste by-products. This phenomenon has caused severe environmental problems that have become a major concern. Researchers all over the world have worked by various approaches to address this issue. One important technique for removing industrial waste is the use of light energy and particles sensitive to this energy to mineralize waste which aids in its removal from solution. Titanium dioxide (TiO_2) is considered very close to an ideal semiconductor for photocatalysis because of its high stability, low cost and safety toward both humans and the environment [1, 2].

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Several synthesis methods can be used to prepare high photocatalytic performance TiO_2. Spray pyrolysis, atomic layer deposition, sol-gel, hydrothermal, solvothermal, chemical vapor deposition and microwave- assisted have been explored for preparing doped and undoped TiO_2 [3-8,19]. In order to expand the absorption ability to visible light wavelength, some metal ions (Cu, Zn, Fe, Ni) and non-metal ions (C, N, S, F) have been incorporated into TiO_2 structure [9 - 11]. The incorporation of these ions is reported has possibility to improve the photocatalytic activity of TiO_2 under visible light irradiation. It is established that TiO_2 doped with metal and non-metal element within certain limits can prolong the lifetime charge carriers of TiO_2 and change the optical properties towards visible light region [12-13]. In general, the TiO_2 doped shows higher photocatalytic activities than the pure ones [2,5,13].

Fe-doping TiO_2 has attracted particular attention due to the high photocatalytic activity performance in degrading an organic pollutant under visible-light irradiation. Furthermore, Fe is deemed to be a worthy dopant because the ionic radius of Fe^{3+} (0.64 Å) is similar to that of Ti^{4+} (0.68 Å), resulting in an easier insertion of Fe^{3+} into the crystal structure of TiO_2 [12]. Previously, Ibrahim and co-workers has successfully incorporated Fe into TiO_2 using sol-gel method. They reported that the Fe addition into TiO_2 system has enhanced the ability of TiO_2 to absorb more energy under solar spectrum [14, 15].

In this present work, nanosized pure TiO_2 and Fe-TiO_2 were synthesized by adopting hydrothermal TiO_2 at 180 °C. Titanium (IV) isopropoxide (TTIP) was used as a Ti precursor while Fe (III) nitrate acted as a source of Fe dopant. The hydrothermal duration was varied from 1 to 5 h. The characteristics of the as-prepared samples were investigated using XRD, FESEM and UV-Vis. Effects of the aging time on Fe-TiO_2 properties and photocatalytic performance were investigated and discussed.

2. Materials and Method

Fe-TiO_2 was synthesized by hydrothermal method using titanium tetraisopropoxide (TTIP) and Fe (III) nitrate as a precursor of Ti and Fe, respectively. Two types of mixture named Solution A and Solution B were prepared. Solution A contained 10 ml TTIP and 30 ml isopropanol while solution B contained 30 ml isopropanol, 3 ml distilled water, 5 ml acetic acid and 0.7 g Fe (III) nitrate. After that, solution A was added drop-wisely into solution B under vigorous stirring. The resulted suspension was stirred for 2 h and moved into a teflon vessel and put in a stainless-steel autoclave in order to carry out hydrothermal process at 180 °C. The duration of hydrothermal treatment was varied from 1 to 5 h. Then, the autoclave was cooled at room temperature for an hour and the precipitates were dried at 80 °C for 12 h. The sample was grounded using a mortar to obtain TiO_2 powder. The as-prepared samples were denoted as 1Fe-TiO_2, 1Fe-TiO_2, 2Fe-TiO_2, 3Fe-TiO_2, 4Fe-TiO_2, 5Fe-TiO_2 corresponded to ageing time of 1 h, 2 h, 3 h, 4 h and 5 h, respectively. The step was repeated to produce pure TiO_2 without involving Fe (III) nitrate.

As-prepared samples were characterized by x-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and ultraviolet-visible spectrophotometer (UV-Vis). The XRD was performed on a D8 Advanced Bruker System with Cu kα radiation as the x-ray source [16, 17]. The crystallite size of the studied samples was calculated using Debye-Scherrer equation with a correction for instrumental line broadening. Morphological analysis of the samples was observed using high resolution field emission environmental scanning electron microscope (FESEM, JSM-7600F). Optical properties of samples were evaluated by Shimadzu UV-Vis spectrometer (UV- 1800) in a wavelength range of 300-800 nm.

The photocatalytic activity of as-prepared N-TiO_2 were evaluated by degradation of methyl orange (MO) under visible light. A metal halogen lamp was used as a light source and a UV-filter was employed to eliminate spectral range radiation below 400 nm. 3 mg of the as-prepared sample were dispersed and stirred in 10 ppm MO in the dark environment. After that, the solutions were irradiated up to 4 h and the aliquot samples were collected for every one-hour interval time. The concentration of degraded MO was measured by means of its corresponding to absorption intensity. The blank test was also carried out by irradiating MO solution without photocatalyst.

3. Results and Discussion

Figure 1 shows XRD pattern of the studied samples included TiO_2 and Fe-TiO_2 for various hydrothermal times. From the analysis, the peak of pure TiO_2 was matched with pattern no. JCPDS 00-021-1272, which corresponded to anatase phase [8]. This peak was also detected in with other samples. This result showed that there was no phase transformation from anatase to rutile with increasing hydrothermal time. From this analysis, the peak of anatase phase were detected at diffraction angles of 22.35°, 37.90°, 47.90°, 53.96°, 62.66° which corresponded to (101), (004), (200), (105), (211) and (204) plane, respectively. In addition, no peak associated with Fe was observed. This indicates the formation of iron-titanium solid solution where the Fe was successfully incorporated into TiO_2 structure due to the similarity of ionic radius size between Ti^{4+} (0.68 A˚) and Fe^{3+} (0.64 A˚) [12, 15].

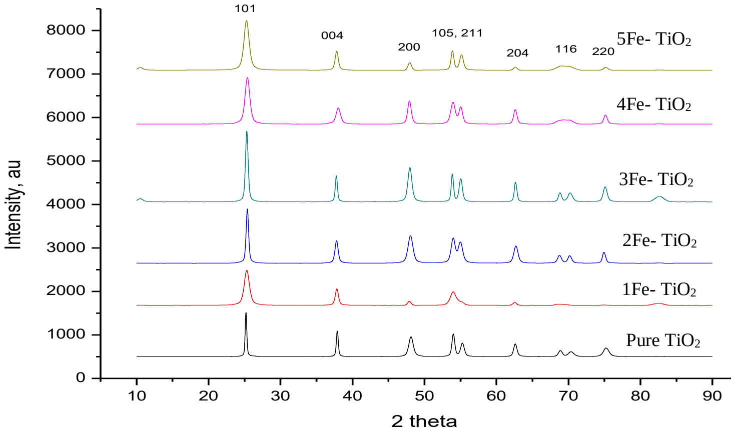


Figure 1: XRD pattern of pure TiO_2 and Fe-TiO_2 for various aging time

The calculated crystallite size of TiO_2 and Fe-TiO_2 nanoparticles was summarized in Table 1. The crystallite size was calculated using the Debye-Scherrer equation as ascribed in Eq. 1.

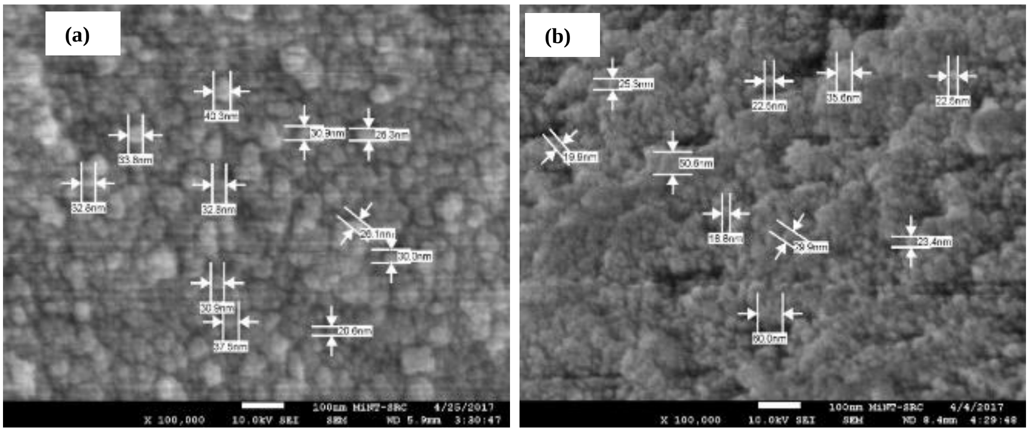
$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

where D denotes the average crystallite size (nm) K is the Scherrer constant, somewhat arbitrary value that falls in the range 0.8–1.0 (it was assumed to be 0.9 in present work); λ is wavelength of X-ray radiation (0.154 nm); θ is the diffraction angle and β is full width at half maximum (FWHM). It was found that the crystallite size was in the range of 10 nm to 21 nm. The trend showed that the crystallite size was decreased as a function of aging time.

Table 1: Crystallite size of Fe-TiO_2

Samples	Ageing time (h)	Crystallite size (nm)	Phases
Pure TiO_2	1	32.67	Anatase
1Fe-TiO_2	1	9.49	Anatase
2Fe-TiO_2	2	20.66	Anatase
3Fe-TiO_2	3	18.99	Anatase
4Fe-TiO_2	4	10.33	Anatase
5Fe-TiO_2	5	9.49	Anatase

Figure 2 exhibits the morphology of pure TiO_2 and treated Fe-TiO_2 under hydrothermal condition. The result shows that all samples were agglomerated with an average grain size, approximately 30- 35 nm. The agglomeration may be caused by several factors such as the presence of capillary absorption, solid bridge, Van der Waals and hydrogen bond [9]. Brinker and Scherer reported that the small particles inclined to agglomerate due to the high surface energy, coalescing the particles together and formed larger particles. [18].



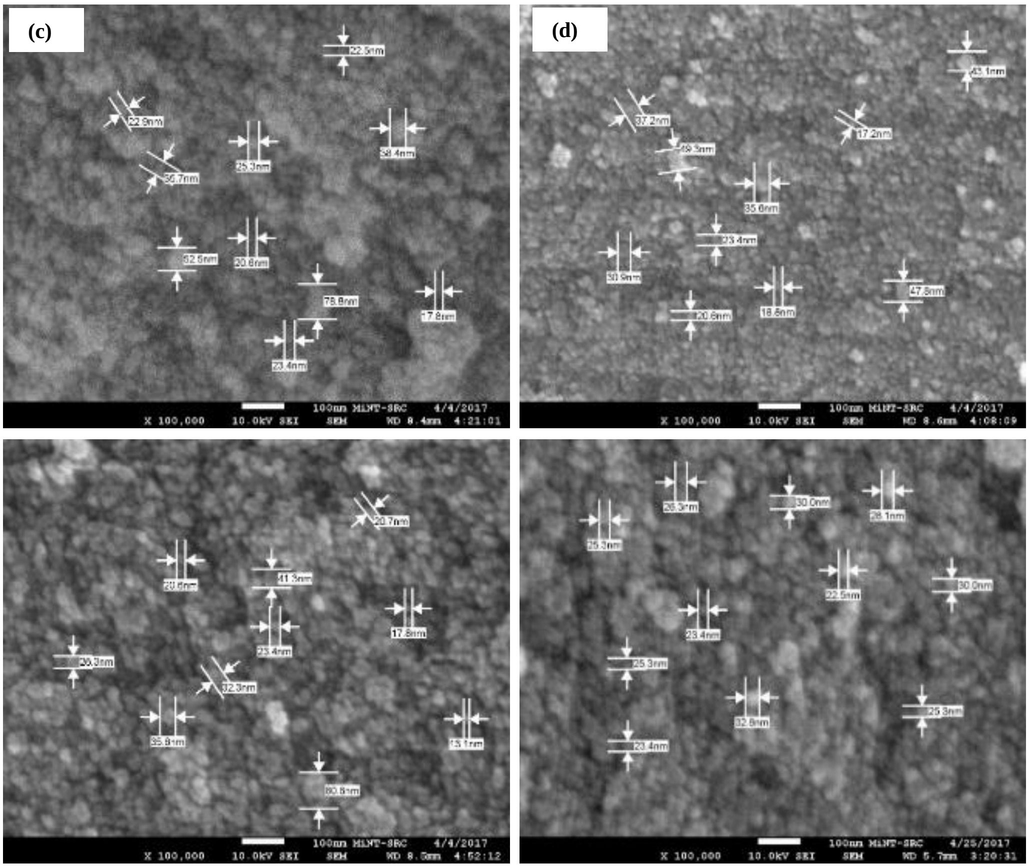


Figure 2: FESEM images for a) pure TiO_2 and b) 1Fe-TiO_2 c) 2Fe-TiO_2 d) 3Fe-TiO_2 e) 4Fe-TiO_2 and f) 5Fe-TiO_2

Figure 3 shows the result of optical absorption of TiO_2 and Fe-TiO_2 samples that were synthesized for various ageing time from 1 to 5 h. Based on the figure 3, the wavelength for TiO_2 was shifted towards visible region from 420 nm to 500 nm. This result tended to increase with increasing ageing time during hydrothermal treatment. Longer ageing time facilitates nucleation and crystal growth, resulting to the extension of optical absorption edge towards longer wavelength and narrows the bandgap energy. The addition of Fe also attributes to this phenomenon. Jasbi and Dorranian reported ageing decreased the bandgap energy due to size enlargement and phase transition [10]. In another studies by Teck & Ibrahim and Meng et al., they established that doping TiO_2 with Fe element showed better absorption in the range 400 to 600 nm [11, 15].

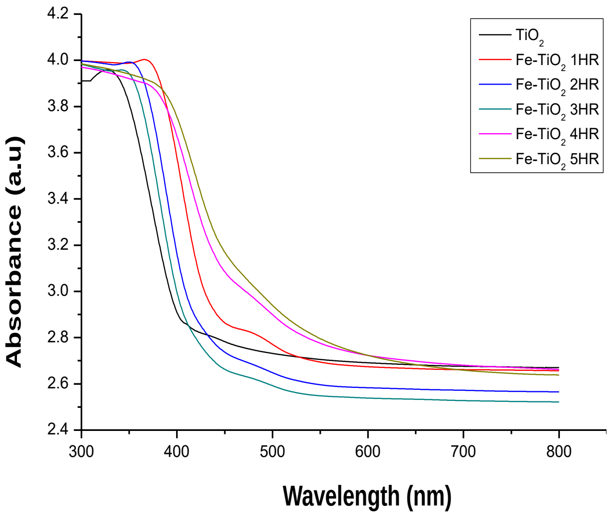


Figure 3: UV-Vis graph of sample powder TiO_2 and Fe-TiO_2 (1, 2, 3, 4, 5 hours)

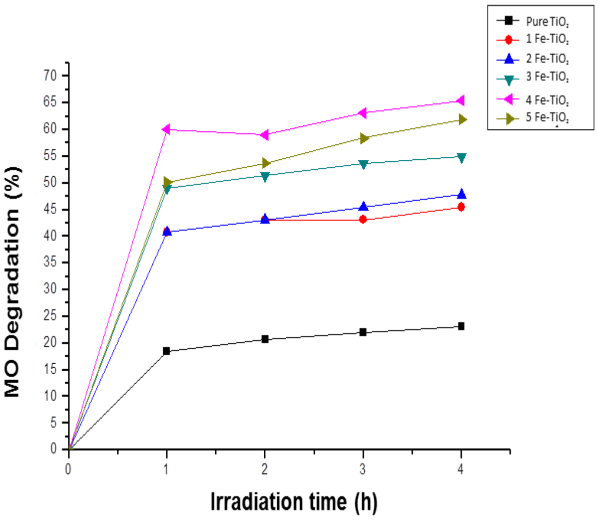


Figure 4: MO degradation under visible light irradiation

The photocatalytic performance of the as-prepared Fe-TiO_2 photocatalyst was evaluated by degrading MO solution under visible light irradiation. To achieve the adsorption equilibrium, the solution including MO and photocatalyst was stirred in the dark environment for 30 min without light irradiation. Figure 4 shows the result obtained after the photocatalytic activity which was conducted under the visible light for 4 h irradiation time. The photocatalytic activity was evaluated according to the following equation:

$$MO\ Degradation\ (\%) = \frac{C_o - C}{C_o} \times 100 \qquad (2)$$

where C_o is the original concentration of MO and C is the concentration of MO after irradiation. The performance of photocatalytic activity of Fe-TiO_2 prepared at different aging times from high to low was found as followed: 4 h> 5 h> 3h> 2 h> 1 h> pure TiO_2. The sample that was prepared for 4 h ageing time provided the highest photocatalytic activity of 66% which was virtually three times higher than pure TiO_2 (23%). From the finding, it can be said that the optimum ageing time and the extension of optical absorbance curve to visible region increased the photocatalytic performance of Fe-TiO_2. Similar results were also obtained by Esparza et al. who concluded that the doped photocatalytic materials (Fe-TiO_2) prepared by hydrothermal treatment displayed better photocatalytic activity under visible light irradiation compared to the pure TiO_2 [12]. This situation revealed an excellent synergistic effect between Fe and TiO_2. The optical profile as shown in Figure 3 supported this finding as Fe modification resulted in narrowing of the band gap, thus allowing the visible light absorption. It was believed that the Fe modification of the anatase samples successfully inhibited the recombination process and allowed more efficient photocatalytic reaction of MO degradation [16]. In short, the obtained apparent quantum efficiency values were very high, especially in the visible region.

4. Summary

Pure TiO_2 and Fe-TiO_2 were successfully synthesized by hydrothermal method, using TTIP as the precursor and Fe as the dopant. The aging time affected the characteristic and properties of the TiO2. All the photocatalysts that were produced presented in anatase phase considerably more active than the other phase. By adding Fe and varying aging time, the degradation of MO dye was significantly improved compared to pure TiO_2 under visible light irradiation. A significant improvement of 66% MO degradation of Fe-TiO_2 was attained by the sample that was aged for 4-h aging time with while pure TiO_2 provided only 23% MO degradation. This phenomenon was due to the formation of new energy level between conduction band and valance band that led to a smaller band gap energy which offered higher photocatalytic activity. From the finding, the photocatalytic of pure TiO_2 and Fe-TiO_2 can be suggested as a potential technology for environment purification

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