Influence of annealing on Fe-doped TiO2 powders using co-precipitation technique

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Influence of Annealing on Fe-Doped TiO_2 Powders Using Co-precipitation Technique

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Abstract. The influence of thermal annealing to TiO_2 nanopowders doped with Fe atoms was investigated using co-precipitation method. Fe-doped TiO_2 nanopowders were prepared using a cold titanium tetrachloride ($TiCl_4$) and $FeCl_3$. The samples were annealed at various temperatures from 200ºC to 500ºC during 60 minutes. Based on the X-Ray Diffraction results showed that the grain size of Fe:TiO_2 nanopowders increased as annealing temperature was increased. This was due to the reducing of FWHM values in the X-RD spectra. FTIR results showed that the spectra were observed at 3417 cm^{-1}, 2358 cm^{-1}, 1645 cm^{-1}, and 518 cm^{-1} indicating the bond functional groups of O-H bond, C-O bond, O-H bond, and Fe-O bond, respectively. The agglomeration of Fe:TiO_2 nanopowders into a large cluster were observed with scanning electron microscopy (SEM) when the samples were annealed at 500ºC.

INTRODUCTION

Nanopowders or nanocrystalline titanium dioxide is well known multifunctional nanoparticle because its stability and non-toxicity [1]. TiO_2 can be applied in optical filters, antireflection coatings, sensors and catalysts [2]. This wide range of the application of TiO_2 is due to its unique electronic and structural properties. TiO_2 can be classified into three crystalline phases: anatase, rutile, and brookite. Rutile is the most stable phase and it is usually obtained after annealing at temperature above 500ºC [3]. Also, TiO_2 is in the visible light region and its band gap is 3.0 eV for rutile and 3.2 eV for anatase crystalline phase. TiO_2 can be greatly improved by doping with metal ions, such as nickel, chromium, iron, vanadium, and zinc etc. [4]. Doping opens up the possibility of changing the electronic structure of TiO_2 nanoparticles, altering their chemical composition and optical properties.

Iron has been considered an appropriate candidate to iron because the radius of Fe^{3+} is around 0.64 Å which is similar to that of Ti^{4+}(0.68 Å). Therefore, it can be easily that Fe might be to incorporated with the crystal lattice of TiO_2 [5]. One of the interests of Fe-doped TiO_2 is its potential application in spintronic and magneto-optic devices. The band gap of iron is 2.6 eV, so, it will reduce the width of the energy gap of TiO_2 and increase the efficiency of absorbing visible light [6]. In addition to this, Fe doped TiO_2 can be used in spintronic devices [7], which would allow for the creation of systems that would consume less energy.

In this work, we investigate the influence of thermal annealing of TiO_2:Fe nanopowders for application in sensor and catalysts. TiO_2:Fe. For this purpose, nanopowders Fe-doped TiO_2 were prepared using a chemical compound $FeCl_3$ and $TiCl_4$. The nanopowders samples were annealed in the temperature range of 200ºC until 500ºC for 60 minutes. Several experimental techniques were used to characterize TiO_2:Fe such as X-ray diffraction to observes the structural of the samples, Fourier Transform Infra Red (FTIR) was used to observe the functional group of the Fe-doped TiO_2 nanopowders.

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EXPERIMENTAL

Nanopowders of titanium dioxide (TiO_2) doped by Iron (Fe) atoms with a doping concentration of 2% were prepared by a conventional co-precipitation method using 0.211 grams of iron trichloride ($FeCl_3$)and 5mL of titanium tetrachloride ($TiCl_4$). $FeCl_3$ solid was subsequently dissolved in 200 ml of water that has been filtered twice and added HCl (37%) slightly so $FeCl_3$ soluble in water. Then 5ml of $TiCl_4$ solution is cooled and then added drop wise into a solution containing $FeCl_3$ by a constant stirring for 2 hours. After stirring 2 hours at room temperature, the obtained dispersion was heated at 50°C for 16 hours with a constant stirring. The precipitate obtained dialyzed until the reaction of Cl negative ions is reduced and dried by using a furnace at a temperature of 100° C for 5 hours. The nanopowders of TiO_2:Fe were annealed with various temperature from 200°C to 500°C during 60 minutes. After annealed the samples were characterized using x-ray diffraction (Shimadzu XRD 7000) to determine the crystallite size using the Scherrer formulation. Scanning Electron Microscopy (SEM) was performed to identify the morphological structure of TiO_2:Fe nanopowders that formed after the synthesis process, and Fourier Transform Infra Red (FTIR - Shimadzu prestig 21) was used to determine the functional groups of the samples.

RESULTS AND DISCUSSION

X-ray diffraction patterns of the Fe-doped TiO_2 powders that were annealed at different temperatures from 200°C to 500°C during 60 minutes are presented in Fig.1. The X-RD patterns reported in ICDD files for rutile TiO_2 (ICDD File No: 96-900-4142) are also presented in these figures. It can be seen from these figures that, all the powders are well crystalline material. From this figures, the peak intensity was observed at the diffraction angle of 27.48°, 36.02°, 39.27°, 41.37°, 44.05°, 54.32°, and 56.71° which were corresponded to the plane of (110), (101), (200), (111), 120), (210), and (220) respectively. These planes are corresponded to rutile crystal structure. In addition to this, the peak intensity of these planes becomes stronger after annealing at high temperature. The anatase structure of TiO_2:Fe were also observed in these figures, but its intensity is smaller than the TiO_2:Fe rutile structure. Therefore, in these nanopowders the rutile structures are dominant compared to the anatase structures in terms of their intensity. These results are quite different compared to the previous studies, where they were observed the transformation phase structures from rutile crystal structure to anatase crystal structure after annealing at 800°C [8]. Also, another previous study showed that TiO_2:Fe was in rutile structures.

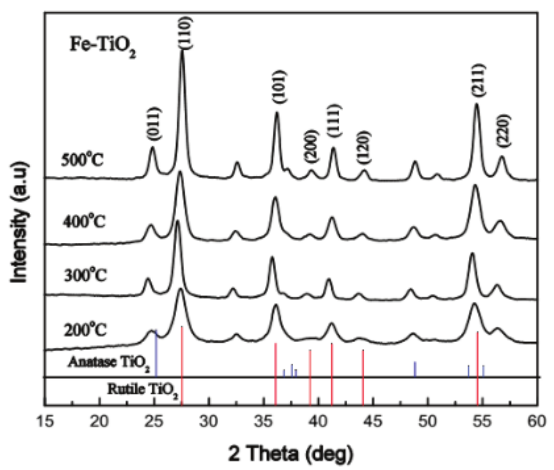


FIGURE 1. The x-ray diffraction pattern of TiO_2:Fe nanopowders after annealing with various temperature from 200°C to 500°C for 60 minutes. Also it is included the X-RD pattern of TiO_2 rutile crystalline phases as a comparison.

Based on the X-RD results, the crystalline size of the nanopowders can be estimated using the Debye-Scherrer formulation

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

Where k is a geometrical factor taken to be 0.9, β is the full width at half-maximum (FWHM) of the (110), (101), and (211) diffraction peak, λ =1.541Å is the X-ray diffraction, and θ is the diffraction angle of the prominent peak for the rutile structure (2θ ~ 27.4, 36.1, 54.2). Using these values, the diameter of TiO_2:Fe nanopowders after annealing at 200°C is in the range from 7 to 10 nm. The crystallite size of the samples increased in the range from 15 to 20 nm after annealing the samples at 500°C. The increase in crystallite size of the samples after annealing is probably due to an agglomeration take place during annealing, thereby the size of the particles increase. Table.1 shows a lattice parameter and the crystallite size of Fe-doped TiO_2 nanopowders.

TABLE 1. The lattice parameter values and the crystallite size of Fe-doped TiO_2 nanopowders.

Annealing Temperature (°C)	TiO_2 (Rutile)	TiO_2 (Anatase)	2θ (deg)	FWHM	D(nm)	Average of D (nm)
200°C	Tetragonal a=b # c (a=4.59 Å, c=2.96 Å)	Tetragonal a=b # c (a=3.79 Å, c=9.54 Å)	27.37	1.16	7.7	8.3
			36.09	0.90	9.9	
			54.24	1.24	7.3	
300°C	Tetragonal a=b # c (a=4.62 Å, c=2.97 Å)	Tetragonal a=b # c (a=3.79 Å, c=9.52 Å)	27.34	0.91	9.9	9.7
			36.03	0.76	12.5	
			54.29	0.94	6.9	
400°C	Tetragonal a=b # c (a=4.62 Å, c=2.99 Å)	Tetragonal a=b # c (a=3.78 Å, c=9.51 Å)	27.11	0.67	13.8	13.4
			35.75	0.55	13.8	
			54.01	0.68	12.5	
500°C	Tetragonal a=b # c (a=4.59 Å, c=2.96 Å)	Tetragonal a=b # c (a=3.80 Å, c=9.58 Å)	27.52	0.59	15.3	17.4
			36.17	0.50	19.7	
			54.42	0.61	17.2	

The FT-IR spectra of Fe-doped TiO_2 (2 wt % Fe) nanopowders that were annealed from 200°C to 500°C during 60 minutes are displayed in Figure.2. As shown in this figure, the transmittance band at 3417 cm^{-1} was seen due to the presence of the stretching vibrations of the O-H groups of H_2O molecules adsorbed on the surface of TiO_2. This band was gradually increased after annealing at 400°C and 500°C, and then it slightly increased after annealing at 500°C. The stretching vibrations of the O-H groups were also observed at 1645 cm^{-1} [9]. The presence of some weak transmittance bands between 3850 and 3530 cm^{-1}, 780 and 470 cm^{-1} were observed. The transmittance peak at 667 and 518 cm^{-1} were observed which attributed to different vibrational modes of TiO_2. Anatase and rutile structures of TiO_2 exhibit certain strong FT-IR absorption bands in the region of 800-650 cm^{-1} [10]. In addition to this, the broad band appears at below 1150 cm^{-1} is due to Ti-O-Ti vibration [11]. Based on the FT-IR results, all the transmittance peak of Fe-doped TiO_2 nanopowders can be summarized in Table.2.

TABLE 2.The transmittance band of Fe-Doped TiO_2 Nanopowders

The transmittance band (cm^{-1})	Functional Groups
3417 [9]	O-H
1645 [9]	O-H
667 [10]	Ti-O-Ti
518 [10]	Ti-O

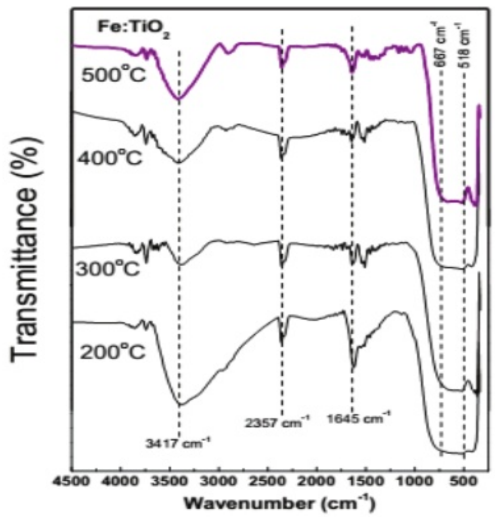
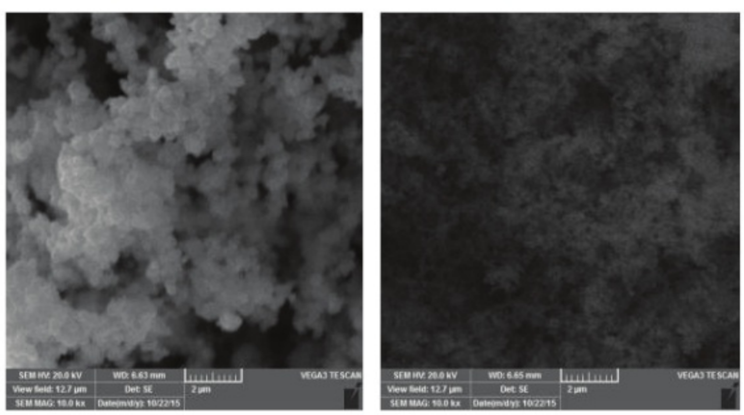


FIGURE 2. FT-IR spectra of Fe-doped TiO_2 (2 wt % Fe) powders after annealing with various temperature from 200°C to 500°C during 60 minutes

Figure 3 shows the scanning electron microscopy (SEM) micrographs of the TiO_2:Fe nanopowders with 2 wt % Fe which were annealed at different temperature of 400°C and 500°C during 60 minutes. It was clearly seen from Fig 3a that after annealing at 400°C, the Fe-doped TiO_2 nanopowders consists of nano-sized particles with spherical shape in agglomerated powders. It was seen from the Figure 3b that after annealing the samples at temperature of 500°C, the nano-particles tend to form a large cluster; thereby it was not clearly observed the grain boundary of the particles. As a result, the size of the particles becomes larger in comparison to the samples that annealed at 400°C. These results were confirmed in the X-ray diffraction measurement that there was an increase in the particle size of the powders when the powders were annealed at high annealing temperature, although SEM did not give results the particles size.



(a) (b)

FIGURE 3. SEM micrographs of TiO_2:Fe nanopowders with 2 wt % Fe after annealing at (a) 400°C and (b) 500°C.

SUMMARY

We have studied the influence of annealing to Fe-doped TiO_2 nanopowders using co-precipitate method. The X-ray diffraction results showed that the increase of diameter size of the particles was observed clearly after annealing. The X-RD results were confirmed in the SEM results, in which high annealing temperature, the particles tends to agglomerate into a large cluster, so that the diameter of the particles increase. FT-IR results showed that the transmittance spectra appear at different band that indicate the different types of the band occurring in the samples. The spectra were observed at 3417 cm^{-1}, 1645 cm^{-1}, and 518 cm^{-1} indicating the band functional groups of O-H band, O-H band, and Ti-O-Ti band, respectively.

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