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Study the heat treatment effect on the TiO_2 nano-particles prepared by sol-gel process

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Abstract
In this paper, titanium dioxide (TiO_2) nano-particles were synthesized by the sol-gel method by using Titanium tetrachloride ($TiCl_4$) solution as precursor. The effects of calcination temperature were determined. The samples were examined using X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FT-IR) analysis. X-ray diffraction measurements showed that TiO_2 nano-particles were polycrystalline with rutiles and anatase phases. The Surface morphological studies obtained from SEM micrographs. Particle size increased from 43 to 500 nm when calcination temperature was 500 ºC. In the FT-IR spectra, the peaks observed below 700 cm^{-1} due to stretching and bending vibrations of Ti–O–Ti bond.

Keywords: Titania nano-particles; Sol gel method; $TiCl_4$; FT-IR; XRD.

1. Introduction

Titanium dioxide (TiO_2) has recently attracted much attention because of its wide potential applications in environmental remediation, electronics, sensor technology, solar cell, and other related fields. It is a white pigment with very good light‐ scattering, opacifying, Ultra violet resistance and bio‐ compatibility (non‐ toxicity) properties, especially when synthesized in the rutile crystalline form. For this reason, submicron size rutile TiO_2 powders are world widely produced and exploited in the paint, ink, coatings, paper, and plastic industries. At the nanometric scale, e.g. for powders with average particle size < 100 nm, the combination of TiO_2 high surface area and enhanced semiconductor properties (especially within the anatase crystalline form) makes it an ideal candidate for a variety of innovative application field [1].
Anatase phase (tetragonal, a = b = 3.782 Å, c = 9.502 Å), rutile (tetragonal, a = b = 4.854 Å, c = 2.953 Å) and brookite phase (Orthorhombic, a = 5.436 Å, b = 9.166 Å, c = 5.135 Å) are three crystalline forms of TiO_2 As shown in Table1. Rutile crystalline phase known as most thermodynamically stable, whereas anatase and brookite phases are metastable and changed to rutile phase on heating process [2].
Sol-gel is one of the most familiar techniques used for the production and synthesis of oxide materials [3]. Sol-gel techniques processing includes producing of colloidal suspensions (“Sols”), this colloidal suspensions subsequently converted firstly to viscous gels and later to solid materials [4]. Colloidal particles are dispersed in a sol that suspended within a fluid matrix [5].

The main aim of this work including preparation of TiO_2 nanoparticles and study the characterizations of prepared TiO_2 powder and show the effect of heat treatment on the Particle size of powder.

Table 1. The Crystal structures of TiO_2 in different phases [2].

phase	Crystal structure
Rutile	Tetragonal
Anatase	Tetragonal
Brookite	Orthorhombic

2. Materials

The material used in this research was titanium (IV) chloride (TiCl4) with purity. ≥ 98.0% obtained from Fluka Chemie Company, Switzerland and Pure ethanol with purity 99.9% which was obtained from Scharlau, Spain.

The particle size of prepared TiO_2 NPs was investigated using TESCAN VEGA3 scanning electron microscope (SEM). XRD test used to characterize and determine a morphology and crystallinity of the as prepared powder. Fourier transform infrared spectroscopy (Bruker, Platinum ATR module, Germany).

3. Experemental method

The synthesis of TiO_2 nano-particles achieved by the reaction of titanium tetrachloride, ethanol (C_2H_2OH) and water in the room temperature with different amount as shown in Table 2 [6]. The magnetic stirrer used to mix the reaction mixture, which was put under a fume hood because of significant amount of Cl_2 and HCl gases evolved from this reaction. Ethanol placed in a beaker and then titanium tetrachloride ($TiCl_4$) solution added to it, the formed solution stirred for 30 min, yellow solution was obtained (Figure 1a). Distilled water was added, and the solution becomes clear and colorless with stirring for 30 min again (Figure 1b). The final sol-gel solution dried at 50 °C for 16 h (Figure 1c), then crushed by the hammering method. Eventually, the dry gel was treated at 500 °C for two hours by using box furnace to form TiO_2 (Figure 1d).

Table 2. Compounds used to prepare of TiO_2 nano-particles [6].

Compound	Amount (mL)
$TiCl_4$	5
C_2H_2OH	50
H_2O	200

(a) (b) (c) (d)

Figure 1. Preparation steps of TiO_2 nanoparticle: (a) $TiCl_4$ solution added to ethanol, (b) Distilled water was added, (c) The final sol–gel solution dried at 50 °C for 16 h, (d) after treated it at 500 °C to form TiO_2 powder.

4. Results and discussion

4.1 X-Ray diffraction pattern

XRD test used to characterize and determine a morphology and crystallinity of the as prepared powder. In this work XRD was taken for as prepared powder and annealed powders at 500 °C respectively.

Figure 2 shows XRD pattern of prepared powder obtained from $TiCl_4$ solution. The stronger peaks located at 2θ= 27.38°, 36.11°, 54.37° respond to the (110), (101), (211) planes respectively. Resulted peaks greatly agreement with the standers results data of rutile phase (ICDD 00-021-1276 TiO_2) [7], and the peaks located at 2θ= 25.38°,37.92 °,47.66 °, 62.46° respond to the (101), (004), (200) ,(204) planes correspondingly .They are in highly compatible with the stander results data of Anatase phase (ICDD 00-021-1272 TiO_2) [8]. The stronger peak results in XRD test agree to (101) plane appeared at 25.38° of diffraction pattern and this indicates the formation of TiO_2 tetragonal Anatase phase.
Figure 3 shows XRD pattern of annealing powder at 500℃ .The stronger peaks located at 2θ= 27.39°, 36.05°, 54.26° respond to the (110), (101), (211) planes correspondingly are in highly compatible with the stander results data of Rutile phase (ICDD 00-021-1276 TiO_2) [7], and the peaks located at 2θ=25.27°, 38.59°, 48.00° respond to the (101), (112), (200) planes correspondingly are in highly compatible with the standard results data of (ICDD 00-021-1272 TiO_2) [8].

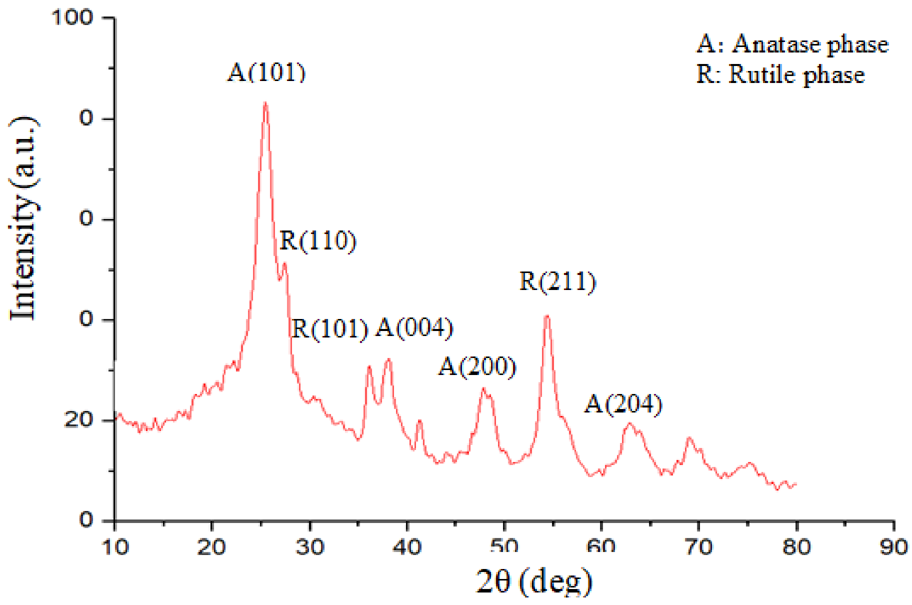


Figure 2. X-ray diffraction of prepared TiO_2 nano-particles.

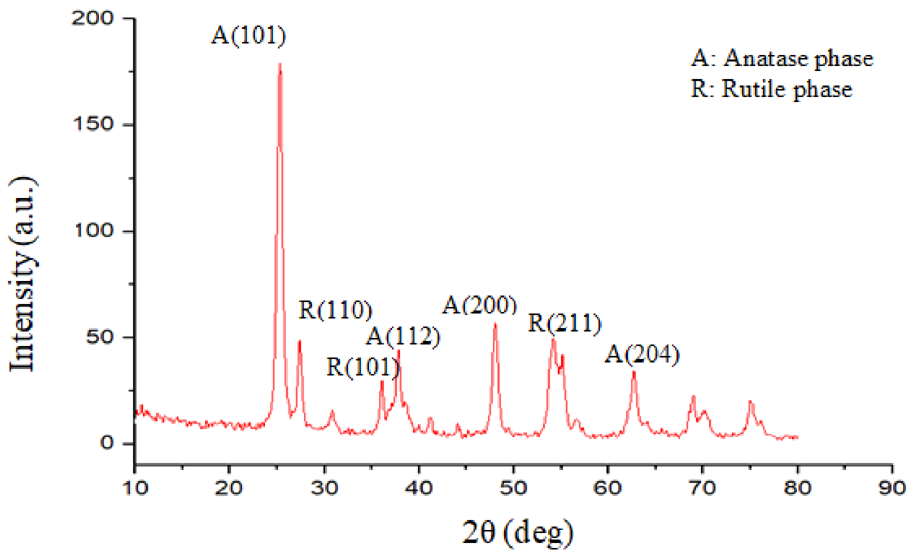
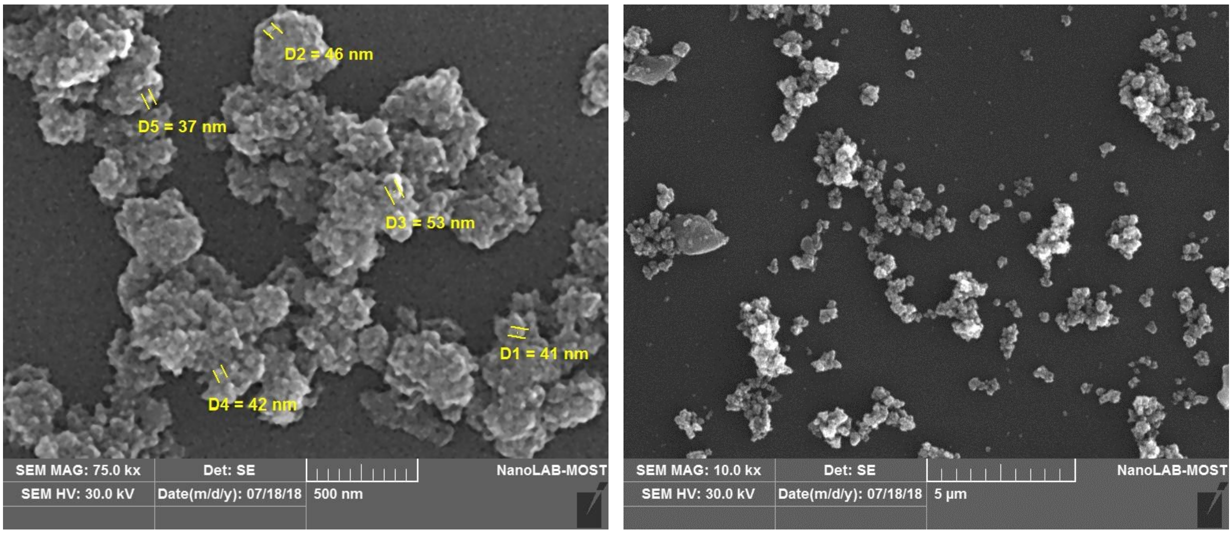


Figure 3. X-ray diffraction pattern of TiO_2 powder at 500 ℃.

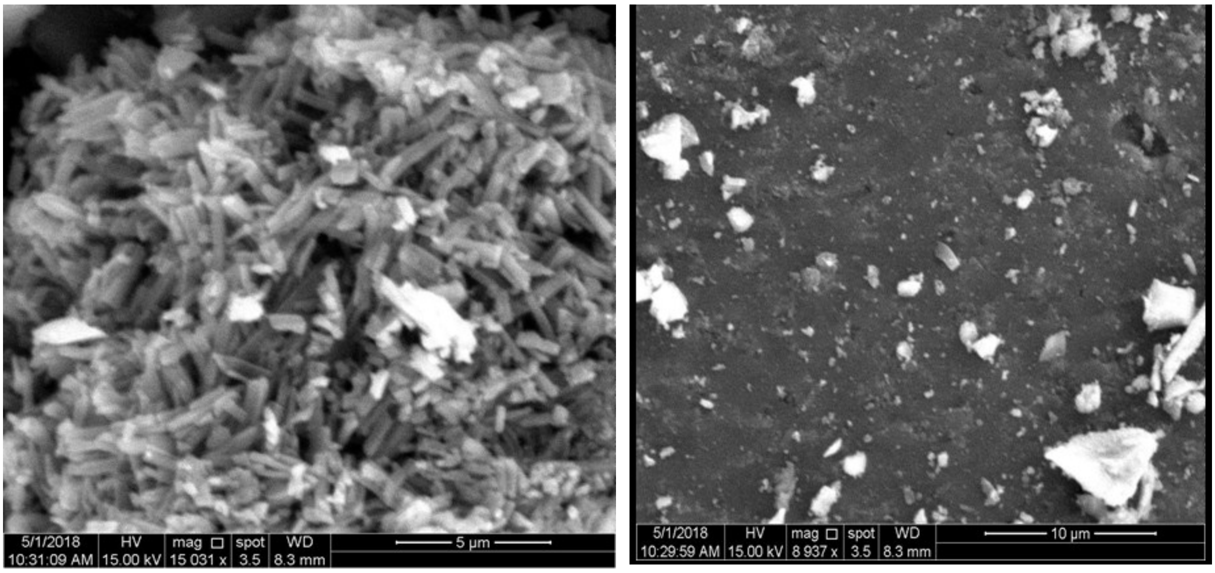
4.2 Scanning Electron Microscopy (SEM)
The topography of Titania powders (TiO_2) for prepared and annealed at 500 C° respectively observed by Scanning Electron Microscopy (SEM). TiO_2 nano-particles; prepared via Sol-Gel

method, exhibited irregular morphology due to the agglomeration of primary particles. Figure 4 which confirm that prepared TiO_2 powder is spherical in shape and regularlydistributed and there are uniform clusters of TiO_2. The average particle size of the powder was about 43nm.
Figure 5 indicates that particle shape of annealed powder is irregular and the average particle size of TiO_2 powder was about 500 nm. The SEM investigations show that the clusters size increases. The increases in cluster size are attributed to the agglomeration of particles as a result of increasing temperature.



(a) After (b) Before

Figure 4. SEM images of TiO_2 prepared powder [A] 500nm, [B] 5μm.



(a) (b)

Figure 5. SEM images of TiO_2 powder Annealing at 500 C° [A] 5μm, [B] 10μm.

4.3 Fourier transform infrared spectroscopy (FT-IR)

Chemical affinity of Pure TiO_2 NPs was study using Fourier transform infrared spectroscopy in the frequency range 4000-600 cm-1.The FT-IR spectra of the TiO_2 NPs synthesized show in Figure 6, the (Ti–O–Ti) and (Ti-O) indicated due to stretching mode bonding of TiO_2 appeared in an over saturated peak below 700 cm^{-1} [9]. A band assignment for TiO_2 NPs has already been listed in Table 3. R. Kandulna et al [10] and Z. N. Jameel et al [11] are agreement with this result.

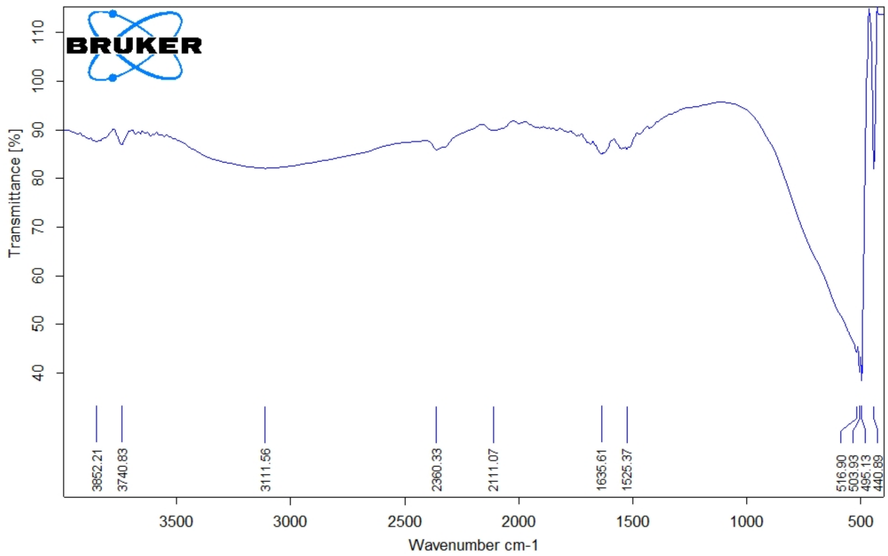


Figure 6. FT-IR for TiO_2 NPs.

Table 3. The bonds of TiO_2.

Bond	Wave numbers (Cm^{-1})
Ti-O-Ti	495.1503.9 ,3
Ti-OH	3740.8,3852.2

5. Conclusion

Sol- gel process used to prepare TiO_2 from $TiCl_4$, ethanol, and water was proved to be an efficient method, the results show that:

1. The XRD patterns confirmed tetragonal crystal structures of TiO_2 (Rutile and Anatase crystalline phase) for both dried and Annealing powder.
2. The particle size of prepared nano TiO_2 powder at 50 °C determined by using SEM was ~43 nm.
3. On the other hand the TiO_2 powder Annealing at 500°C about 500 nm particle size.
4. In the FT-IR spectra, the peaks observed below 700 cm−1due to stretching and bending vibrations of Ti–O–Ti bond.

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