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Synthesis and Characterization of Titanium Dioxide Nanoparticles under Different pH Conditions

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ABSTRACT

Ethanol as a solvent, a precursor of titanium isopropoxide and a stabilizer of either hydrochloric acid or ammonium hydroxide was used to prepare a titanium dioxide aqueous solution. The aqueous solutions with different values of pH and the morphology of the resultant reaction of the nanoparticles of titanium dioxide were investigated. The X-ray diffraction showed that at low temperatures and with acidic solutions, rutile structures are more favorable to grow on titanium dioxide synthesized, while at low and average temperatures and with base solutions, anatase phase is more pronounced. The crystalline form and the re-confirmation of the crystallite size growth were observed by the scanning electron microscopy. The atomic force microscopy was used to confirm the relation between the roughness and thickness with the pH level.

Keywords: TiO$_2$ nanoparticle, hydrolysis, TTIP, pH

دراسة ووصف لجزيئات نانوية لثنائي اوكسيد التيتانيوم تحت ظروف مختلفة للرقم الحامضي

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الخلاصة

تم تحضير محلول ثنائي اوكسيد التيتانيوم بخلط الايثانول كمذيب وايزوبروبوكسايد التيتانيوم كبادئ وحامض الهيدروكلوريك وهيدروكسيد الامونيوم كمثبتات عند تصنيع المحلول المائي. تم فحص المحاليل المائية برقم حامضي مختلف و التشكيل الناتج عن التفاعل للجزيئات النانوية لثنائي اوكسيد التيتانيوم المحضرة. تم ايجاد تأثير الرقم الحامضي على تشكيل التفاعل اعتمادا على كمية العامل المساعد. أظهر حيود الأشعة السينية لن تركيب الروتايل هو ألمفضل في المحلول الحامضي وعند درجة حرارة واطئة. اما طور الاناتيس فهو الاكثر تفضيلا في محلول قاعدي وعند درجات حرارة منخفضة ومتوسطة. تم استخدام المجهر الالكتروني لملاحظة الشكل البلوري والنمو البلوري. تم تأكيد العلاقة بين الخشونة والسمك مع الرقم الحامضي باستخدام المجهر الذري.

الكلمات الرئيسية: جزيئات نانوية لثنائي اوكسيد التيتانيوم, التحلل المائي, الرقم الحامضي

1. INTRODUCTION

Nanocrystalline metal oxides have gained a lot of attention because of their unique properties. Titanium dioxide (TiO_2) powder is an important nanomaterial and has been used in many industrial applications, e.g. fillers, catalyst supports, photo-catalysts, and pigments. The powders possess interesting catalytic, optical, and dielectric properties, **Barbe, et al., 1997, Monticone, et al., 2000, Boujday, et al, 2004, Carp, et al, 2004 and Ruiz, et al., 2004**. Titanium dioxide has various crystalline structures which are used in solar cells, air purifier catalysts, photovoltaic materials, gas and humidity sensors and antireflection coatings, **Han, et al., 2006, Samuela, et al., 2005 and Chen, et al., 2006**. Titanium dioxide has 6 polymorphs of anatase, rutile, brookite, TiO_2-B, TiO_2-H and TiO_2-II, **Shieh, et al., 2008**. Among these polymorphs, rutile with tetragonal structure (space group p42/mmm), anatase with tetragonal structure (space group I41/amd) and brookite with orthorhombic structure (space group Pcab) are more important because of their higher stability and useful properties. Rutile, the only thermodynamically stable phase at normal pressure and room temperature, have a lower band gap energy (3 eV) in comparison with brookite and anatase phases (3.2 eV) which are metastable and can be transformed into rutile phase by calcination processing at 600-800˚C, **Tang, et al., 2000 and Ruiz, et al., 2004**.

This material's final properties depend on the size, morphology and crystalline phase of the prepared TiO_2 nanopowder. There are several processes that have been developed to prepare TiO_2 nanostructured material with interesting properties. These are: liquid process (sol-gel), **Trung, et al, 2003** and **Sugimotom, et al., 2002**, solvothermal, **Kim, et al., 2003**, hydrothermal, **Ruiz, et al., 2004** and **Nian,** and **Teng, 2006**, solid-state processing routes (mechanical alloying/milling), **Kim, et al., 2004**, mechano-chemical, **Guimaraes, et al., 2006**, thermal plasma, **Oh, and Ishigaki, 2008** and other routes such as laser ablation, **Matsubara, et al., 2003**. To prepare nano-TiO_2 powder, the sol-gel method is used. The sol-gel process used to prepare nanopowder of TiO_2 with interesting properties needs to control some parameters. In the peptization process, the reaction can be carried out on a molecular level. This can be done either by heating the solution or by using peptization agent, **Look, and Zukoski, 1992**. The final size of the nanoparticles of TiO_2 is influenced to a great extent by the pH of the prepared solution, **Sugimoto, et al., 2003**. Therefore, the optimization of the preparation conditions can control the size and the size distribution of synthesized powder. In this research work, optimization of the preparation conditions is studied so a narrow size distribution of the TiO_2 powders with a nanometer scale can be provided using controlled pH of the solution.

2. EXPERIMENTAL WORK

2.1 Materials

The reagents used in this work were of analytical grade purity. No additional purification is needed. Tetraisopropoxide (purity, 97 %), Ti $[OC_3H_7]_4$ was supplied by Sigma-Aldrich company and was used as a starting material and. Both ammonium hydroxide [NH_4OH] and hydrochloric acid [HCl] were supplied by High Media, while ethanol (99%) was supplied by Merck. In all standard solutions, de-ionized water was used.

2.2. Preparation of TiO_2 Nanoparticles

The precursor solution was made of a mixture of 5 ml titanium tetra-isopropoxide, TTIP in addition to 15 ml ethanol. The hydrolysis catalyst used was a solution of distilled water, with a volume of 250 ml. Using HCl and NH_4OH may be used to adjust the pH of the solution as shown in **Table 1**. When both the solutions were mixed together under strong stirring, the gel

preparation process started. The hydrolysis of TTIP gave a solution of turbid nature and this was heated up to 60–70 ∘C for a time of 16 hours, i.e. peptization. After the peptization process, the solution volume decreases to 50 cm^3, then a suspension was produced. The prepared precipitates were washed three times with de-ionized water. Then three times with ethanol. The product was left to be dried for 12 hours at 100°C. Finally, the prepared powder was annealed at a temperature range of 200 to 700°C for the duration of three hours.

The process of hydrolysis and condensation of titanium alkoxides in aqueous media were used to prepare the nanometer TiO_2 colloids in the nanometer. Alkoxides are hydrolyzed and then polymerized to form a network of three-dimensional oxide in the presence of water. These reactions can be represented by equations (1) and (2):

Hydrolysis:

$$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH \qquad (1)$$

Condensation:

$$Ti(OH)_4 \rightarrow TiO_2 \cdot nH_2O + (2-n)H_2O \qquad (2)$$

R could be an ethyl, or i-propyl, or n-butyl, etc. Nucleation of the stable hydroxide $Ti(OH)_4$ cannot happen. This is due to the strong acidity of tetravalent cations. The water molecules from reaction (2) have always a partial charge of positive nature. According to this, olation and oxolation can go ahead simultaneously during the process of nucleation and growth. This will lead to an oxide of $TiO_2 \cdot nH_2O$ of amorphous type. Here n is the number of water molecules and it depends on the conditions of experiments. Rutile or anatase phases formation by the precipitation of TiO_2 depends on the experimental procedure. Adjusting the initial water concentration and the pH could control the stage of deoxilation prior to the olation. The precipitation of TiO_2 anatase nanoparticles will be formed as a result of this control leads the experimental procedure.

2.3. Characterization of TiO₂ Nanoparticles

X-ray diffraction (XRD) was used to report the composition of the crystal phase and the crystallite size of the TiO_2 nanoparticles was recorded using Cu Ka radiation with a voltage of 40 kV type Shimadzu SRD 6000, Japan. The particles morphology and structure were investigated using scanning electron microscopy FEI NOVA NANO SEM device (www.daypetronic.com). The specific surface area (BET) was also determined with Thermo Analyzer/USA.

3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) in **Fig. 1** belongs to the patterns of the prepared powder samples in the initial solution using different values of pH. This figure shows distinguished peaks at 25.4°. Also, the particle size and degree of crystallinity are affected by the value of pH. The sample prepared at pH 1 which corresponds to the anatase phase (110), shows a trace of rutile at 27.3°. This shows that the formation of the rutile phase is favored in the high acidity solution, while the anatase formation will be favored lower acidity. Also, the results show that the formation of rutile is favored by high acidity. The idea of partial charge model may explain this mechanism according to **Aruna, et al., 2000**.

At strong acidity condition the hydrolysis of titanium cation occurred, as given by this model $[Ti(OH)(OH_2)_5]^{3+}$ of stable type will be formed. These forms could not condense, because of the hydroxo group that has a positive charge. If the acidity is not low enough so that the stabilization of the precursors occur, new types of $[Ti(OH)_2(OH_2)_5]^{2+}$ will be formed by de-protonation.

According to **Ellis and Sykes, 1972**, the condensation of these species may not happen probably. This is because of intra-molecular oxolation to $[TiO(OH_2)_5]^{2+}$ that happens spontaneously. When the activity of the solution is sufficient enough, so that further de-protonation to $[TiO(OH)(OH_2)_4]^+$ is allowed, the condensation to both of anatase and rutile phases begins. This can be subjected to intra-molecular of deoxolation $[TiO(OH)_3(OH_2)_3]^+$ depending on the exact value of pH. For lower pH values, deoxolation does not happen. Oxolation will lead to the linear growth that happens along the equatorial plane of cations. According to this reaction, rutile formation happens because of the oxolation between resulted linear chains. At higher values of pH, and as deoxolation occurs, the condensation process can proceed. This happens in an apical direction. A skewed chain of anatase structure will be formed. So, and according to this study, it is believed that the pH values affect the resulting crystal structure is, **Aruna, et al., 2000** and **Henry, et al., 1992**. Rutile formation is promoted by higher acidity, while lower acidity will promote anatase formation.

Fig. 2 shows the XRD patterns of the calcined powder of TiO_2 at different temperatures (400, 500, 600 and 700°C) and at pH = 4. At 400 and 500°C, it is clear that all the coordinates of the peaks of prepared samples were accepted the three strong standard peaks of titanium dioxide (anatase) (2θ of 25.281,3.52 d spacing), (2θ of 37.8 2.378 d spacing), and (2θ of 48.049 -1.8 d spacing) the peaks of samples were identified by comparison with (JCPDS) file No. (21.1272) according to 2θ and d spacing. This emphasized the structure of anatase at 2θ = 25.4. It is noticeable that no peak assigned to the rutile phase, 2θ = 27.36, is shown by the diffractograms.

Scherrer's equation can be used to estimate the TiO_2 average crystallite size:

$$D = K\lambda / \beta\cos\theta \qquad (3)$$

In this equation, K represents the Scherer constant, λ is the wavelength of X-ray, β is the peak width of half maximum, and θ is the angle of Bragg diffraction. Equation (4) is used to find the content of anatase and rutile of all TiO_2:

$$X = 1/(1 + 0.8 \, IA/IR) \qquad (4)$$

where,
X represents the fraction of rutile in the powders by weight, IA is the X-ray integrated intensity of the strongest peaks of anatase at 2θ = 25.3°, (101) plane, and IR is the X-ray integrated intensity of the strongest peaks of rutile at 2θ = 27.5°, (110) plane the weight percentage (Wt %) and crystalline size of anatase and rutile phases as shown in **Table 2**.

Fig. 3 shows the transformation of anatase to rutile as a function of both the pH level and temperature. In strong acid, it is noticed that the temperature of the rutile ratio is moved to a low value of 400-500°C. This may be due to that the particles in strong acid have high surface energy. Accordingly, the rutile ratio will increase rapidly and this depends on the lower level of pH in addition to higher temperatures. At the higher levels of pH, it also increases slowly. An assumption is made in that the anatase phase is to be eliminated following the large particles of rutile phase with poor agglomeration. At higher temperatures and during the process of particle growth, aggregation takes place.

The formation of various phases of the powders of TiO$_2$ is shown in **Table 3**. It is shown as a function of pH and the temperature of calcination, where: Am represents the amorphous, A represents the anatase, and R represents the rutile. As the temperature was increased, the anatase phase was converted to the rutile phase. This could be attributed to the crystallite growth which is promoted thermally. In particular, the HCl catalyst activates to a large degree the phase transformation of amorphous Ti(OH)$_4$ to anatase TiO$_2$ and also the anatase TiO$_2$ to rutile. From the other side, the NH$_4$OH catalyst did not activate the transformation of phases and the crystallization of the particles. This shows that somewhere from 400 to 700°C, the nucleation process and the growth of the rutile phase have been begun. It may be assumed that the pH value of acid affected the growth of rutile crystals.

The size of crystalline of prepared nanoparticles of TiO$_2$ in the different pH is shown in **Fig. 4**. The smallest crystallites are obtained in the solution of pH =1, or the acidic solution, from the hydrolysis of TTIP and the dried powder at 100 ∘C.

In **Fig. 5**, it can be seen the crystalline size of TiO$_2$ as a function of the temperatures of calcination. As the temperature, is increased to 200°C and then to 400°C, the formed crystallites size has increased. This could be because of the growth of the crystallite that is thermally promoted. An increase in the size of the crystallites of anatase from 7.8 to 38.2 nm was noticed when the temperature of calcination has been increased to 700°C. At this temperature, sharp rutile peaks are also noticed in the XRD in addition to anatase. The formed rutile with the larger size and the remained particles of anatase showed quite different behavior than rutile. This implies that both the processes of nucleation and growth of rutile phase were promoted at a temperature from 400 to 700°C according to **Li, et al., 2000**.

The SEM micrographs of the prepared particles of TiO$_2$ are shown in **Fig. 6** and **Fig. 7**. These are given at different pH and a calcination temperature of 100°C. Spherical particles of the prepared powder with poor agglomeration and aggregation are shown in **Fig. 6**, for the acidic solution of pH = 1. On the other hand, in a base solution of pH = 9, the as-prepared powder consists of non-spherical particles and is highly agglomerated, as shown in **Fig. 7**.
The nucleation and growth procedures of TiO$_2$ nanoparticles controlled the formation of the grain size and morphology. These are strongly related to the values of pH in the synthesized solution of TiO$_2$. At pH range of 1 to 4, elongated and granular morphology starts to appear on the deposited TiO$_2$. For pH = 9, sphere-shaped and relatively rough are found.

The development of the grain sizes and morphology were controlled by the nucleation and development methodology of TiO$_2$ nanoparticles which is unequivocally identified with the pH in TiO$_2$ integrated arrangement. At pH 9, the crystallites are observed to be non-circle molded and generally harsh while a granular and lengthened morphology begins to show up on the stored TiO$_2$ with pH extend (1 to 4). As appeared in **Fig. 8 (a)** and **(b)**, it was shown that as the pH of the TiO$_2$ arrangements diminishes, it enhances the crystallinity of the movies and lessening the crystallites measure as acquired from XRD and SEM investigation as shown in **Fig. 8** where AFM results are given.

4. CONCLUSIONS

The process of hydrolysis of the titanium isopropoxide solution of alcoholic nature, followed by the peptization of the formed suspension up to a temperature of 60–70 ∘C for 16 hours can be used to prepare nanocrystalline TiO$_2$ powder. The formation of the TiO$_2$ structure is affected to a large degree by the values of pH. The anatase structure is promoted by lower acidity, while the rutile phase is promoted by higher acidity. The anatase extent of crystallinity depends on pH.

Lower values of acidity enhance the crystallinity. Also, the formation of large crystallite size is promoted by lower values of pH. The phase transformations of amorphous $Ti(OH)_4$ to anatase TiO_2 and anatase to rutile were significantly activated by HCl catalyst. On the other hand, the phase transformation and the crystallization of the particles were not activated by the NH_4OH catalyst.

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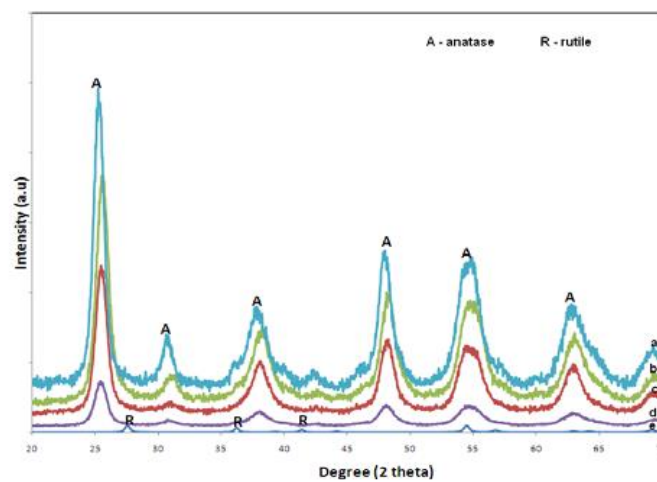
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Table 1. Nanoparticles crystallite size variation with different amount of catalyst (acid and base) and variation with the amount of water.

Experiment	Amount of precursor (ml)	Amount of ethanol (ml)	Amount of H_2O (ml)	Amount of acid and base (ml)	Crystalline size (nm)
1	5	15	2.5	0.5 HCl	6-9
2	7	15	2	0.25 HCl	8-13
3	5	15	2.5	0.25 NH$_4$OH	8-16
4	7	15	2	0.5 NH$_4$OH	4-16

Figure 1. XRD patterns of nanocrystalline titania samples prepared by sol-gel method with various pH condition as (a) pH 9, (b) pH 7, (c) pH 4, (d) pH 3 and (e) pH 1.
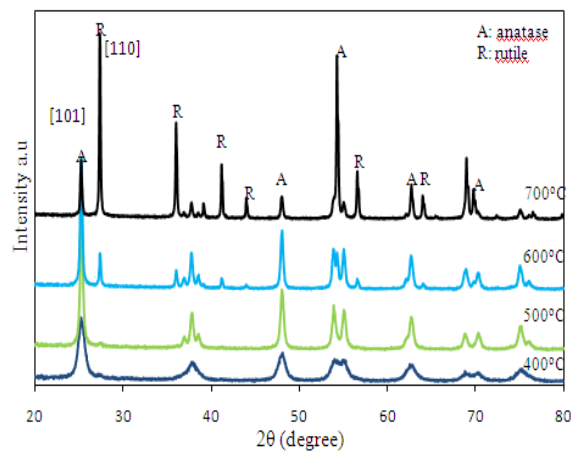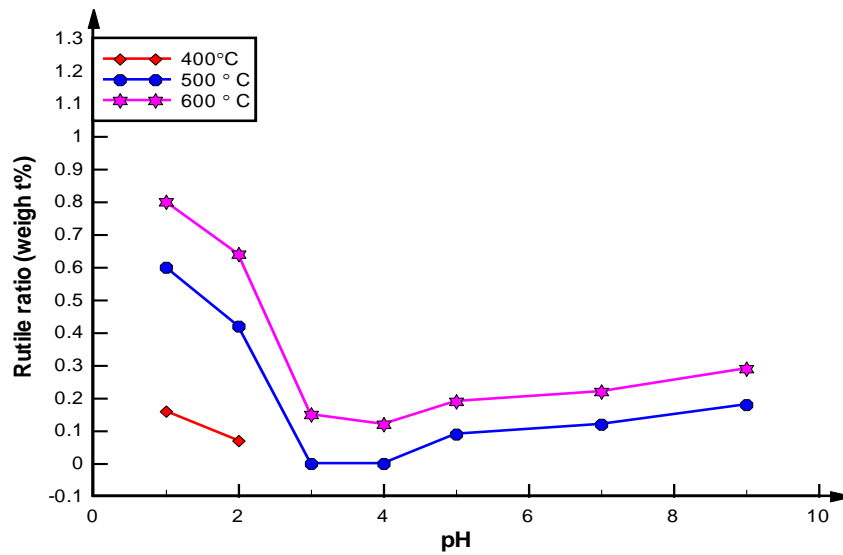

Figure 2. XRD pattern of the TiO$_2$ powder at pH=4 and various calcining temperatures.

Table 2. Weight percentage Wt % and crystalline size of anatase and rutile phases.

T (ºC)	Anatase phase Wt % d(nm)		Rutile phase Wt% d(nm)	
400	100	7	-	-
500	77	17	23	20
600	42	20	58	23
700	20	25	80	32

Figure 3. Calculated rutile weight fractions of the TiO_2 powders as a function of pH.

Table 2. Formation of various phases for the TiO_2 powders as a function of pH and calcination temperature.

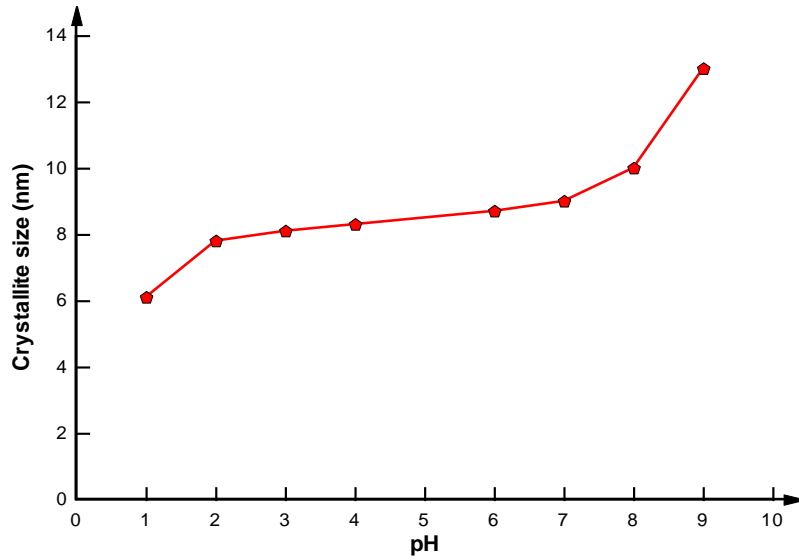| pH	Dried (100)	Calcination Temperature, ºC			
		400	500	600	700
9	Am*	A	A+R	A+R	A+R
7	Am	A	A+R	A+R	A+R
4	Am	A	A	A+R	A+R
3	Am	A	A	A+R	A+R
2	Am	A+R	A+R	A+R	A+R
1	Am	A+R	A+R	A+R	A+R

*Am: Amorphous, A: Anatase, R: Rutile

Figure 4. Crystalline size variation of prepared powders at different pH.
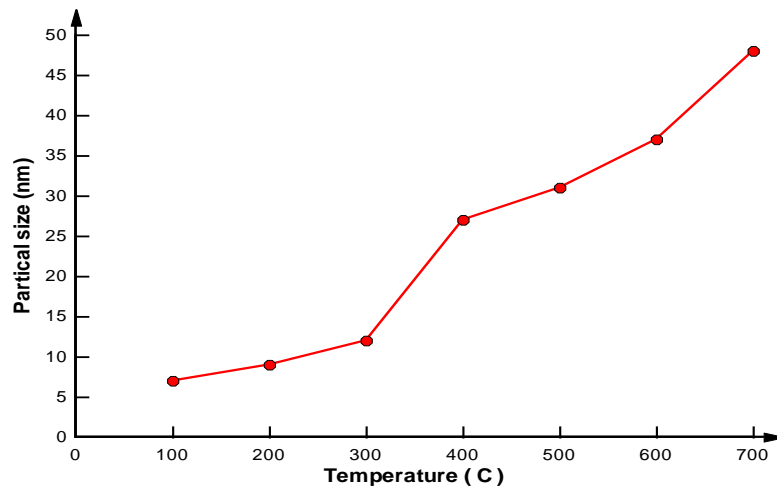

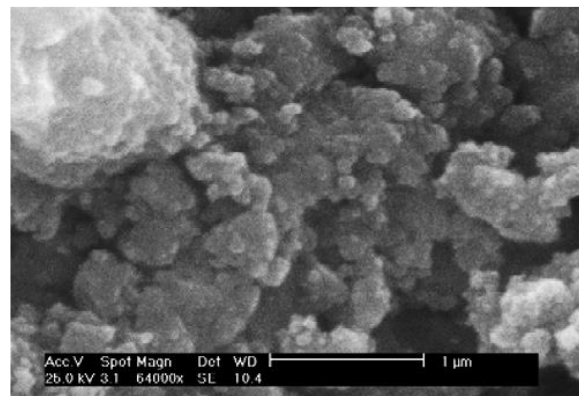**Figure 5**. Crystalline size variation of prepared powders at different temperatures.

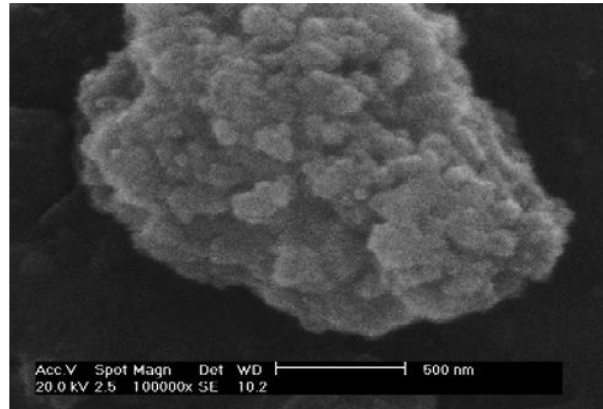**Figure 6**. SEM micrographs of dried powders at 100 ∘C:(pH=1).

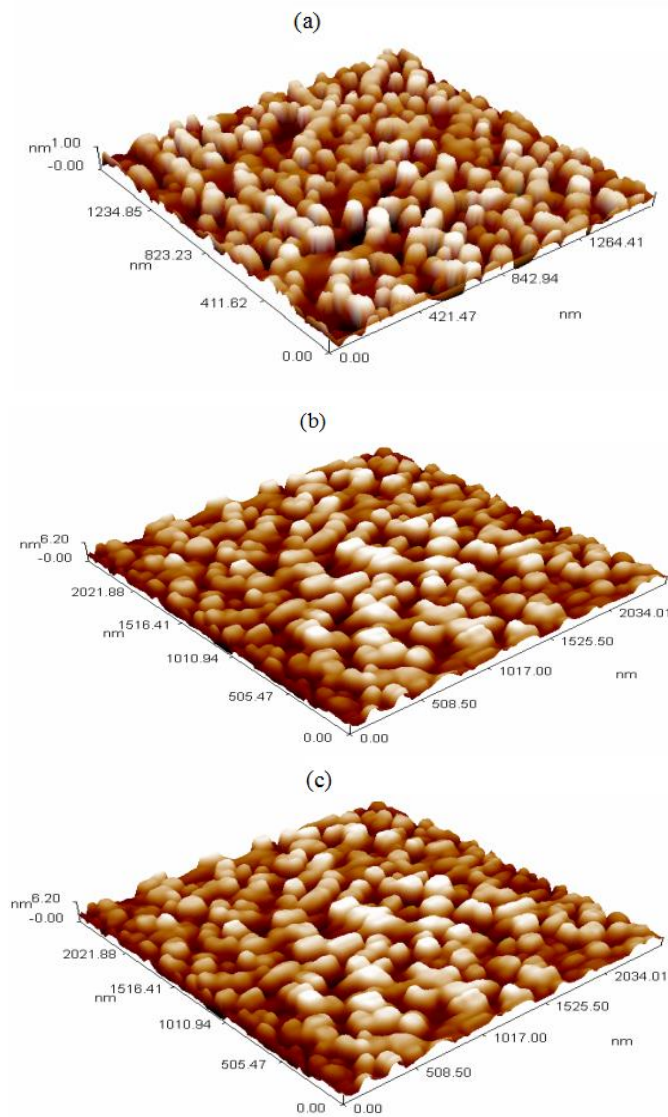**Figure 7.** SEM micrographs of dried powders at 100 ◦C: (pH=9).

Figure 8. The AFM images of TiO_2 with temperature 400ºC (a) pH=1, (b) pH=4 (c) pH=9.