Investigation of the role of pH on structural and morphological properties of titanium dioxide nanoparticles

S A Sadiq, Z Waseem, S Hanif, S Riaz, K Hayat, A I F Batool, Y Jamil, M Y Naz and H Anwar*

Advanced Nanomaterials and Devices Laboratory, Department of Physics, University of Agriculture Faisalabad, 38040 Faisalabad, Pakistan.

*E-mail: Hafeez.anwar@gmail.com

Abstract. In the present research work, titanium dioxide (TiO$_2$) nanoparticles were synthesized by sol-gel method in which titanium tetraisopropoxide (TTIP) used as a precursor and the effect of pH on their structural and morphological properties was investigated systematically. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the prepared samples. The acidity-alkalinity of the gel was adjusted to different pH values (1, 4, 7 and 10) by using respective media, i.e. HCl and NH$_3$OH. The results showed that from strong acidic media to strong basic media, the average particle size was found to increase from 14 nm at pH 1 to 20 nm at pH 10, whereas the average particle size was 19 nm at pH 7. All peaks in XRD patterns perfectly indexed to the stable anatase tetragonal phase except sample at pH 1, where some traces of rutile phase was also present. XRD results showed the formation of single phase high purity nanoparticles. TiO$_2$ nanoparticles showed homogeneous morphology with low agglomeration at pH 7 and pH 10.

1. Introduction

The last four decades have witnessed a great interest in the characterization of titanium dioxide nanoparticles for their beneficial use in a large number of applications such as cosmetics, ceramics, solar cells, pollution-reduction and analytical devices. Titanium dioxide is one of the most promising nanomaterials because it is highly stable, low-cost and is believed to be non-toxic. Titanium dioxide has been synthesized by different methods including hydrothermal method [1] direct oxidation, sol-gel method [2, 3] and chemical vapour deposition [4]. Among them sol-gel method is one of the common method because of its good chemical homogeneity. It is a well-known fact that the specific surface area and the surface-to-volume ratio is increased remarkably with the decrease in the size of the material. High surface area caused by the small size of the particle is highly advantageous and beneficial to many TiO$_2$ based applications and devices [5]. Zhang and Banfield presented a useful and productive report on structural characteristics, mechanical and thermodynamic properties of nanocrystalline TiO$_2$ [6]. Ibrahim and Sreekantan [7] identified that in the formation of titanium dioxide structure, pH plays an important role. Results showed that anatase structure was formed at lower acidic condition and rutile phase was formed at higher acidic condition. They explained from SEM images that at pH 1 TiO$_2$ powder showed rod like shape while sample prepared at pH 3 and 5 were spherical in shape. They also observed that particle size was smaller at higher pH. Degree of crystallinity of anatase is pH dependent and lower acidity enhanced the crystallinity also promotes formation of big crystallite size. They prepared titanium dioxide (TiO$_2$) nanoparticles through sol-gel method using titanium tetraisopropoxide as a precursor.
They investigated the effect of pH and reaction morphology on the preparation of TiO$_2$ nanoparticles. The experimental results showed that morphology of titanium dioxide was in nanopowder form when NH$_4$OH catalyst was used and in case of HCl, it showed a granular or bulk form. The pH of the prepared solution has great influence on the particle size of titanium dioxide nanoparticles \cite{8, 9}.

In this research work, a simple and cost effective method for the preparation of titanium dioxide nanoparticles at different pH through sol-gel method was used in which titanium tetraisopropoxide used as a precursor. All samples were characterized by using different techniques i.e. scanning electron microscopy (SEM) and X-ray diffraction (XRD). Then effect of pH on their structural and morphological properties was investigated.

2. Experimental procedure
Titanium dioxide nanoparticles were synthesized by sol-gel method at different pH conditions and their structural and morphological properties were observed. Titanium dioxide nanoparticles were prepared from titanium tetraisopropoxide, ethanol, hydrochloric acid and distilled water. In this work, titanium tetraisopropoxide used as a precursor and hydrolysis of titanium tetraisopropoxide was carried out at different pH values through a respective media i.e. NH$_4$OH and HCl. In First step, solution A was prepared when 5.5 ml titanium tetraisopropoxide (TTIP) and 54.8 ml ethanol were mixed together and placed on magnetic stirrer for continuous stirring (300 rpm). In second step, solution B contained a homogenous mixture of 1.68 ml hydrochloric acid and 19 ml of distilled water. Then the solution B was allowed to mix with already prepared solution A of titanium tetraisopropoxide (TTIP) in ethanol under continuous stirring. The resultant solution of titanium tetraisopropoxide (TTIP), ethanol, hydrochloric acid and distilled water were kept under constant stirring for further 20 hours. At this stage, pH of solution was found to be 1 and was measured by using Eutech pH meter. The prepared solution was filtered and after filtration, the material was dried in an oven Model (Shel-Lab) at 80 °C for 1 hours. The dried sample was ground to fine powder using agate pestle and mortar. The particles obtained after grinding were calcined in furnace Model (SNOL-LHM01) at 500 °C for 4 hours.

Thus, first sample A of titanium dioxide nanoparticles having pH value 1 was ready for characterization. The next three samples namely sample B, sample C and sample D of titanium dioxide nanoparticles with pH values of 4, 7 and 10, respectively. These samples were prepared in the similar manner with only difference that their pH was adjusted by gradual addition of suitable amount of NH$_4$OH or HCl. Synthesis process is shown in figure 1.

![Figure 1. Schematic of preparation of TiO$_2$ nanoparticles.](image-url)
3. Characterization

Powder X-ray diffraction was used to determine the average particle size and crystal phase of titanium dioxide nanoparticles. XRD patterns of TiO$_2$ nanoparticles were recorded using PANalytic X'Pert PRO with $\lambda=1.54056$ Å which is the wavelength characteristic of the Cu- $K_\alpha$ radiation operated at 15 kV. The average crystallite size (Scherrer’s Equation), lattice parameters, volume of unit cell and X-ray density were measured by using equation (1), equation (2), equation (3) and equation (4).

$$ T = \frac{0.9\lambda}{\beta \cos \theta} $$

(1)

$$ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} $$

(2)

$$ V_{cell} = a^2c \sin 60 $$

(3)

$$ D = \frac{ZM}{N_A V_{cell}} $$

(4)

where $T$ is the crystal size, $\beta$ is the line width (FWHM), $\theta$ is the diffraction angle and the $\lambda$ is the wavelength of X-ray radiation. $Z$ is the number of molecules per unit cell, $M$ is the molar mass of the titanium oxide, $N_A$ is Avogadro number, $V_{cell}$ is the volume of the unit cell. The morphological and structural properties of titanium dioxide nanoparticles were determined by JEOL JSM 5910 scanning electron microscope. The samples were mounted on specimen stub by using double sided carbon tape and a thin film of gold was deposited in order to have good results.

4. Results and discussion

XRD patterns of the all samples (A, B, C, D) synthesized by sol-gel method at different pH values (1, 4, 7 and 10) and calcined at 500 °C for 4 hours were showed in figure 2. All the peaks can be perfectly indexed to the stable anatase tetragonal phase of TiO$_2$ single crystal structure with the lattice constant $a=b=3.8$ Å and $c=9.50$ Å, indicating the high purity and crystallinity of the obtained samples. For example, sample B of titanium dioxide prepared at pH 4 exhibit diffraction peaks in the range of 2θ, 25.43, 37.88, 48.08, 54.05, 55.05, 62.7, 70.37 and 75.27, indexed to (hkl) planes (101), (004), (200), (105), (211), (204), (220) and (215), showing that the sample comprises of pure anatase phase of TiO$_2$. Concerning the presence of the anatase phase, the structure is body-centered-tetragonal. Moreover, it can be seen from table 1 that the values of densities of all the four prepared samples were nearly equal to 3.9 g/cm$^3$, which can be taken another obvious evidence of the fact that prepared samples have anatase phase. It is also noticed that pH affects particles size and degree of crystallinity. A trace of rutile was found in sample prepared at pH 1 at 27º corresponding to rutile phase (110). In this case, it is found that high acidity in medium solution favours the formation of rutile phase while lower acidity favours anatase formation [10]. This mechanism could be explained using the concept of partial charge model [11].

4.1. Effects of pH on the particle size of TiO$_2$

Figure 2 shows the XRD patterns of the particles prepared at different pH conditions. The sharp peaks of crystalline anatase appeared in all the XRD patterns of the all specimens. The most intense peak was (101) at the value of 2θ round about 25º peak of anatase in all samples, whereas, for sample prepared at pH = 1, (110) peak for rutile phase at 2θ = 27.67 was present. The average particle size of sample A at pH 1 (strong acidic end) was 14 nm. At neutral condition pH 7, particle size of sample C was 19 nm. Similarly, at highly basic end (pH =10) particle size of sample D was found to be 20 nm. The variation in crystallite size as per increase in pH values is contrary to literature [12]. According to previously reported literature, average particle size decreased with increasing pH values, i.e., from acidity to alkalinity. These observed and calculated facts suggested that there is a strong correlation between pH and average particle size [13].
Figure 2. XRD patterns of titanium dioxide nanoparticles synthesized through sol-gel method with different pH values for sample with (A) pH 1, (B) pH 4, (C) pH 7 and (D) pH 10.

The lattice parameters did not show any significant change at different pH value, indicating that the interaction of hydrochloric acid with the TiO$_2$ nanoparticles has been occurred only at the surface of the nanoparticles. Various structural parameters calculated from XRD data were shown in table 1.

Table 1. Various structural parameters extracted from XRD data at different pH values.

| Samples | pH | Average particle size (nm) | Lattice constant (Å) | Volume of titanium dioxide (Å$^3$) | Density of titanium dioxide (g/cm$^3$) | Phase |
|---------|----|---------------------------|----------------------|----------------------------------|--------------------------------------|-------|
| A       | 1  | 14                        | 3.79 9.50            | 136.46                           | 3.89                                 | Anatase with traces of rutile |
| B       | 4  | 12.5                      | 3.78 9.50            | 135.74                           | 3.91                                 | Anatase |
| C       | 7  | 19                        | 3.81 9.50            | 138.0                            | 3.84                                 | Anatase |
| D       | 10 | 20                        | 3.80 9.50            | 137.18                           | 3.87                                 | Anatase |

4.2. Effect of pH on the morphology of TiO$_2$

The surface morphology of TiO$_2$ nanoparticles is shown in figure 3. Titanium dioxide nanoparticles prepared at acidic conditions showed an agglomerated and aggregated nanoparticles of irregular shape as shown in figure 3(a) and (b). TiO$_2$ nanoparticles showed uniform morphology with low agglomeration at neutral and higher basic condition in figure 3(c) and figure 3(d). It is found that the morphology markedly depends on the pH of precursor solution.
5. Conclusion

Effect of pH on morphological and structural properties of titanium dioxide (TiO$_2$) nanoparticles were investigated through scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. From these investigations, it can be concluded that TiO$_2$ were prepared at different pH conditions (1, 4, 7 and 10) and calcined at 500 °C had different average particle size and morphologies. The average particle size was found to be increase with increasing pH values ranging from 14 nm to 20 nm. All peaks in XRD patterns can be perfectly indexed to the stable anatase tetragonal phase; except sample prepared at pH 1 that showed some rutile traces. The results show the high purity and crystallinity of the obtained samples. Agglomerated and irregular to uniform morphology was found with increasing pH values.

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References

[1] Rasalingam S, Wu C-M and Koodali R T 2015 *ACS applied materials & interfaces* 7 4368.
[2] Nabi G, Khalid N, Tahir M B, Rafique M, Rizwan M, Hussain S, Iqbal T and Majid A 2018 *Journal of Inorganic and Organometallic Polymers and Materials* 28 1552.
[3] Senić Ž, Bauk S, Vitorović-Todorović M, Pajić N, Samolov A and Rajić D 2011 *Scientific Technical Review* 61 63.
[4] Lopez L, Daoud W A, Dutta D, Panther B C and Turney T W 2013 *Applied Surface Science* 265 162.
[5] Ahmed M, El-Katori E E and Gharni Z H 2013 *Journal of Alloys and Compounds* 553 19.
[6] Zhang J, Yu J, Zhang Y, Li Q and Gong J R 2011 *Nano Letters* 11 4774.
[7] Ibrahim S A and Sreekantan S 2011 Effect of pH on TiO2 nanoparticles via sol-gel method. In: *Advanced Materials Research: Trans Tech Publ* pp 184.
[8] Lim C S, Ryu J H, Kim D-H, Cho S-Y and Oh W-C 2010 *Journal of Ceramic Processing Research* **11** 736.

[9] Prasad S and Madhavan J 2013 *Synthesis* **5** 2970.

[10] Chen Z, Wang F, Balachandran S, Li G, Liu P, Ding Y, Zhang S and Yang M 2018 *Nanotechnology* **29** 125602.

[11] Li L, Yan J, Wang T, Zhao Z-J, Zhang J, Gong J and Guan N 2015 *Nature communications* **6** 5881.

[12] Tsega M and Dejene F 2017 *Heliyon* **3** e00246.

[13] Devi G S, Kumar K S and Reddy K S 2015 *Particulate Science and Technology* **33** 219.