

Preparation and Characterization of TiO₂ Nanocrystals using Titanium Isopropoxide

M. H. Mangrola and V. G. Joshi

Department of Physics

Veer Narmad South Gujarat University, Surat-395007, Gujarat, India

Email: mhmangrola@gmail.com, joshi_vibhuti@yahoo.com

B. H. Parmar

Department of Physics

Government Science College, Valod-394640, Gujarat, India

Email: bhparmar2000@yahoo.com

(Received December 22, 2011)

Abstract: Titanium dioxide (TiO₂) nanoparticles were prepared by hydrolysis of Titanium Isopropoxide (TTIP) and aqueous solution with constant pH and then peptizing the resultant suspension gel (White-Blue) and calcinations of the gel at various temperatures. Two samples prepared with different concentration of the water. The resultant powder has been examined by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Analysis (EDAX) and Photoluminescence (PL). It has been found that the powders calcinated at 100⁰C are consist of anatase fine crystalline phase with a crystalline size of 14 nm to 15 nm. The resultant TiO₂ nanocrystals are found to have uniform size and morphology. At 800⁰C, calcinated powders are consist mixture of anatase and rutile phase in both the samples. A very fine network texture made from uniform nanoparticle has been confirmed by scanning electron microscope analysis. The composition of the presence of various elements in TiO₂ nanocrystal has been studied by EDAX. The photoluminescence emission spectra are taken at different excitation wavelength. It is observed that the emission spectra shift when the excitation wavelength is increased.

Key Words: TiO₂ nanocrystal, Anatase and Rutile Phase, XRD, SEM, EDAX, PL.

1. Introduction

Much recent research focused on controlling the size, shape, crystal structure and surface properties of semiconducting oxide materials. TiO₂ is one of the most widely studied materials, because it has interesting optical,

dielectric, and catalytic properties and many industrials and research application such as pigments, photo catalysts¹⁻⁸.

Titanium dioxide (TiO_2) powders have been obtained either directly from titanium bearing minerals or by precipitation from solution of titanium salts or alcoxide. Hydrolysis is one of common process to produce TiO_2 with different phases like anatase, rutile and brookite. Rutile is a thermodynamically stable phase possessing smaller band gap energy (3.0eV) than the anatase phase⁹ (3.2eV). The most common form is rutile which is also the most stable form. Anatase and brookite both convert to rutile upon heating Rutile, anatase and brookite all contain six coordinated titanium¹⁹.

So far several techniques were reported for synthesizing titania nanoparticles/crystals through controlled nucleation and growth processes in dilute Ti (IV) solution. Among them are the sol gel, hydrothermal and peptization methods. All method strongly effects on the crystallizations behavior and characterization of the final powder^{1, 9-16}.

In this work we employed the hydrolysis and peptization method for obtaining fine TiO_2 with uniform size and morphology and observed the impacts of crystallization and size distribution with different calcination temperature of the obtained TiO_2 powder.

2. Experimental Section

2.1 Materials: The materials used are Titanium Isopropoxide (TTIP, 97%, Sigma Aldrich), Isopropanol (99%), NH_4OH , HNO_3 , Ethanol and Double deionized water. All the materials are of analytical grade and are used as received if mentioned otherwise.

2.2 Synthesis process: In this work the two samples A & B are prepared. Precursor solution (for Sample A) mixture of 5-7 ml titanium Isopropoxide (TTIP) with 15-17 ml Isopropanol has been taken. A 250 ml solution of double deionized water has been used as the solvent for hydrosolysis catalyst. Precursor solution (for Sample B) mixture of 12-15 ml TTIP with 30 ml Isopropanol has been taken. A 600 ml solution of double deionized water has been used as the solvent for hydrolysis catalyst. The pH

value was maintained at 2 throughout the process in both samples by adding HNO₃ and NH₄OH.

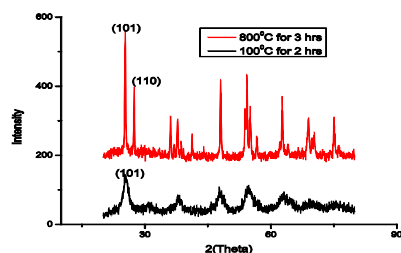
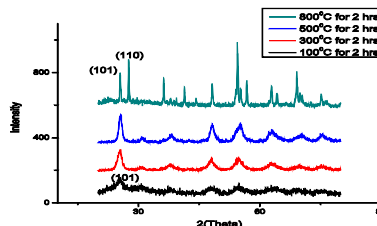
The gel preparation process started when both solutions were mixed together under vigorous stirring at constant temperature between 65⁰C and 70⁰C for 20 hours. Substantial gel formation has been observed. The resultant suspension observed to as white-blue and opaque with high viscosity. The prepared precipitates were washed several times by ethanol to remove all the impurities and byproducts and calcinate at 100⁰C for 2 hours. Sample A again calcinate at 800⁰C for 3 hours and Sample B again calcinate at 300, 500 and 800⁰C for 2 hours each. After the calcinate only dry powder is remain which appears light Yellow colour in both sample.

3. Characterization

X-ray powder diffraction (XRD) analysis was performed on a Phillips XPert Pro parameters (anode materials copper target ($\lambda_{CuK\alpha} = 1.5406 \text{ \AA}$). The diffractometer used 40 kV and 30 mA. Scanning took place between 20⁰ and 80⁰ (2 θ) with a 0.0500 step size and an acquisition time of 3s per step. The morphology of the products was explored by using scanning electron microscope (Leo 1430 VP). Powder samples were put over aluminum stub and coated with layer (~4-8 nm) of Au before analyzing by SEM. Energy Dispersive X-ray Analysis (EDX or EDAX) taken for the element concentration and qualitative analysis and photoluminescence analysis is taken only for sample A calcinate at 800⁰C.

4. Result and Discussion

4.1 X-ray Diffraction Analysis: In this work, two samples have been prepared by same process with different concentration of water and found different results in both the sample. The XRD data of the sample A and sample B at 100⁰C for 2 hours (Fig. 1(a) & Fig.1 (b)) is characteristic of anatase TiO₂ phase. The XRD peaks become higher at the precursor stage of both the samples and the sharpness and height of the peak increases further with the calcination temperature. Comparing with other TiO₂ XRD data at same diffraction angle^{1, 9-16}. In this case we have observed higher and sharp peaks.

Fig.1 a XRD data of TiO₂ powder of sample AFig.1 b XRD data of TiO₂ powder of sample B

The XRD data of the samples calcinated at 100⁰C shows anatase phase of TiO₂. In some of the references, the phase conversion i.e. anatase to rutile has been reported^{1,20} at the 600⁰C. While our experimental results shows the phase conversion in both the samples at 800⁰C instead of 600⁰C. Figure 1 (a & b) shows that at 800⁰C the peak of rutile phase is more predominant and only two-three peaks for anatase phase are obtained. In other words the mixer of rutile and anatase phase is observed in both samples calcinate at 800⁰C. It can be inferred from the XRD data that if it is provided more high annealing temperature (above 800⁰C) than only rutile phase will appear. The rutile and anatase phase is conformed from the peak of XRD data. The (101) plane diffraction peak for anatase phase and (110) plane diffraction peak for rutile phase. The other peaks and crystallinity of both samples at different temperature have been studied by comparing the data in the references^{8, 14-17}. All the XRD peaks of compound were defined with the help of refinement using a program XPowder (XPowder Ver. 2010.01.10 Pro.). The refinement data confirmed a tetragonal structure. The refined lattice parameters for the sample A, for anatase phase are $a=b=3.8057 \text{ \AA}$ and $c=9.5046 \text{ \AA}$ and cell volume is 137.69 and for rutile $a=b=4.5881 \text{ \AA}$ and $c=2.9617 \text{ \AA}$ and cell volume is 62.34. For the sample B, for anatase phase are $a=b=3.7990 \text{ \AA}$ and $c=9.4705 \text{ \AA}$ and cell volume is 136.68 and for rutile $a=b=4.5769 \text{ \AA}$ and $c=2.9519 \text{ \AA}$ and cell volume is 61.84. There is a good agreement between observed and calculated d-values is shown in table-1 for anatase and table-2 for rutile.

Table 1. Comparison between d-obs. and d-cal. for anatase phase of the sample (A & B) calcinate at 100⁰C.

Sample A				Sample B			
2(Θ)	d(obs)	d(cal)	hkl	2(Θ)	d(obs)	d(cal)	hkl
25.43	3.5104	3.5243	(101)	25.33	3.5140	3.5243	(101)
38.03	2.3645	2.3787	(004)	37.53	2.3849	2.3787	(004)
47.03	1.8948	1.8971	(200)	48.13	1.8892	1.8971	(200)
54.63	1.6788	1.6705	(121)	54.68	1.6774	1.6705	(121)
63.18	1.4706	1.4631	(016)	69.18	1.3570	1.3592	(007)
69.03	1.3595	1.3592	(007)	74.83	1.2657	1.2665	(215)

Table 2. Comparison between d-obs. and d-cal. for rutile phase of the sample (A & B) calcinate at 800⁰C.

Sample A				Sample B			
2(Θ)	d(obs)	d(cal)	hkl	2(Θ)	d(obs)	d(cal)	hkl
25.28	3.5208	3.5163	(101)	25.48	3.5137	3.5292	(101)
27.43	3.2495	23.2417	(110)	27.63	3.2364	3.2417	(110)
36.13	2.4842	2.4827	(011)	36.28	2.4745	2.4827	(011)
37.83	2.3765	2.3787	(004)	41.38	2.1805	2.1832	(111)
41.23	2.1881	2.1832	(111)	48.23	1.8855	1.8971	(020)
48.03	1.8929	1.9029	(200)	54.53	1.6816	1.6842	(121)
54.28	1.6888	1.7001	(105)	56.78	1.6202	1.6209	(220)
62.68	1.4811	1.4766	(002)	62.78	1.4769	1.4766	(002)
69.13	1.3578	1.3572	(031)	69.28	1.3552	1.3572	(031)
75.08	1.2643	1.2646	(215)	75.28	1.2614	1.2647	(215)

The Debye-scherrer formula is used to calculate the crystalline size from the broadening of the corresponding X-Ray spectral peaks. This is generally accepted method to estimate the mean crystalline size of nanoparticles.

$$B = k\lambda/s \cos\Theta,$$

where; s is the crystallite size, λ is the wavelength of the X-ray radiation ($\text{CuK}\alpha = 0.15406 \text{ nm}$), k is a constant taken as 0.94, θ is the diffraction angle and B is the line width at half maximum height.

When the calcination temperature of samples is raise up to 500 °C, the rutile phase shows quite different behaviour and shows somewhat larger crystalline size as compared to the anatase. It is also observed that the

calcination temperature effects on the crystalline size of the samples which has been confirmed by the calculation of the crystalline size using Debye-Scherrer formula. The calculations are shown in table-3.

Table 3. Comparative crystalline size

Sample A		Temperature	Sample B	
Anatase	Rutile		Anatase	Rutile
17	---	100 ⁰ C	14	---
---	---	300 ⁰ C	16	---
---	---	500 ⁰ C	21	---
67	84	800 ⁰ C	67	72

A graph of temperature Vs Crystalline size shows the proportionality between crystalline size and calcination temperature (Fig.2). The crystalline size on anatase phase in the samples at 100⁰C is very narrow. The data in Table1 shows that the rutile nuclei have strong tendency to grow against the temperature as compare to anatase.

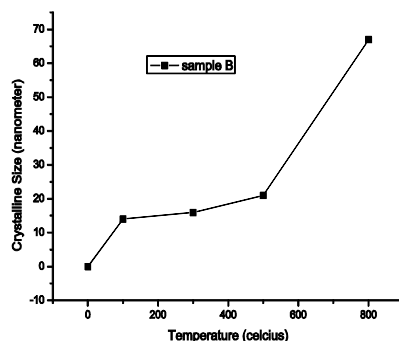


Fig.2 Crystalline size Vs Temperature

4.2 Scanning Electron Microscope Analysis: Fig. 3 shows the SEM micrographs of TiO₂ nanoparticles prepared at different calcination temperatures. As shown in Fig.3 (a, b, c d & e) there is a poor agglomeration in TiO₂ powder. The processed of aggregation keep on repeating as the calcinations temperatures increases.

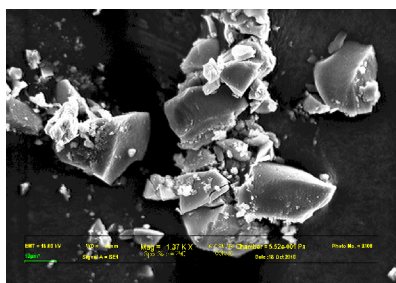


Fig.3 a Micrograph of the samples A calcinate at 100°C

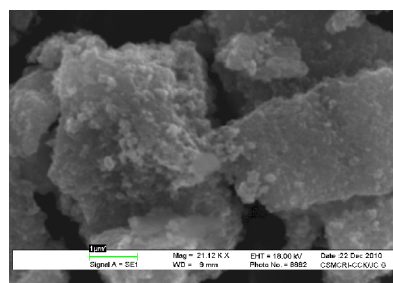


Fig.3 b Micrograph of the samples A calcinate at 800°C

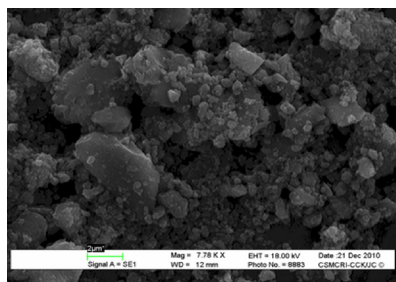


Fig.3 c Samples B calcinate at 300°C ;

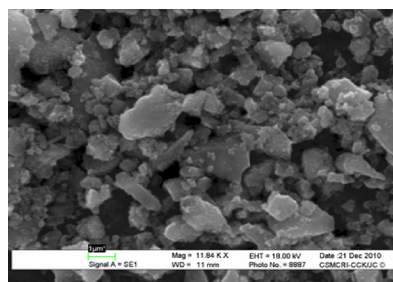


Fig.3 d Samples B calcinate at 500°C

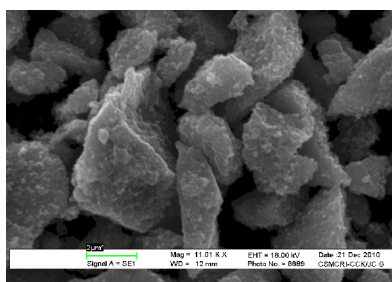


Fig.3 e Samples B calcinate at 800°C

Above SEM micrograph shows that the particle size become larger in both samples as calcination temperature increased.

4.3 Energy Dispersive X-Ray Analysis: As shown in Fig.4 (a, b, c & d) the EDAX data of the both samples calcinate at different temperature. EDAX data shows the composition of element present in TiO_2 powder. EDAX data conform the purity of the samples i.e. no extra impurity in the sample.

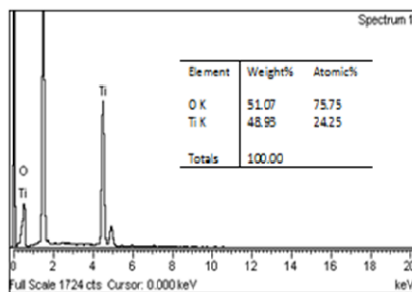


Fig.4 a EDAX data of the samples A calcinate at 800°C

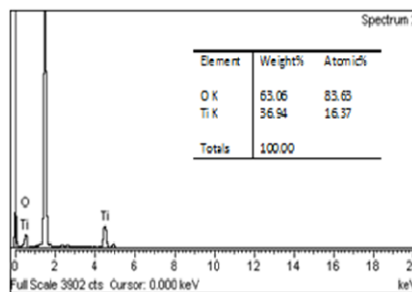


Fig.4 b EDAX data of the samples B calcinate at 300°C

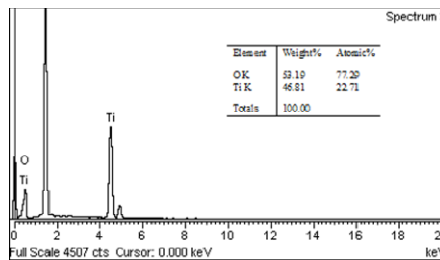


Fig.4 c EDAX data of the samples B calcinate at 500°C

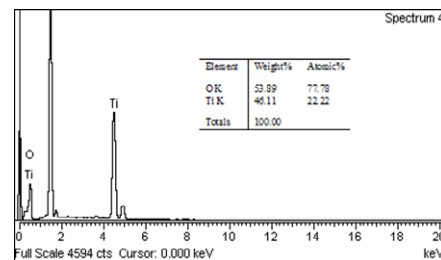


Fig.4 d EDAX data of the samples B calcinate at 800°C

Above EDAX data shows that the calcination temperature effect on the atomic percentage of the titanium and oxide.

4.4 Photoluminescence Analysis

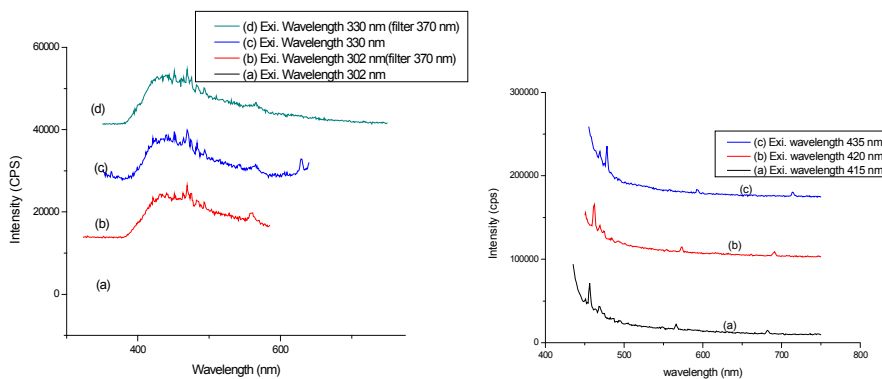
Fig.5 (a & b) Photoluminescence Analysis of TiO₂ powder calcinated at 800°C (Sample A).

Fig. 5 (a & b) shows the PL spectra of the TiO₂ nanocrystals at room temperature. There is a wide photoluminescence band in the wavelength from 350 nm to 500 nm has been observed at the excitation wavelength of 302 nm and 330 nm as shown in figure 5(a). Our results shows that there is no shifting in emission spectra at these excitation wavelength of 302 nm and 330 nm (fig 5a) while shifting is clearly observed at the excitation wavelength of 415, 420 & 435 (fig 5b). The central peaks identified from figure 5(a) are near about 451 nm and from figure 5(b) is near about 457 nm, 461 nm and 476 nm at the excitation wavelength 415 nm, 420 nm and 435 nm respectively.

The shifting of the photoluminescence spectra with increasing of excitation wavelength reflects the change in the distribution of energy levels due to different local environments (structure, strain, etc.) and hence, the exact photoluminescence mechanism of TiO₂ nanocrystals needs further detail investigations^{21, 22}.

5. Conclusion

In the sample, the gel formation takes place after 20-21 hr. The crystalline size of sample is also in the range of 15 nm -17 nm. An XRD pattern has been shows intense peak at near 25° (2 θ). The crystalline size and the anatase phase to rutile phase conversion possibility increases with calcinations temperature. For anatase phase crystalline size is observed between 15 nm and 17 nm at 100°C and 67 nm at 800°C whereas for rutile phase the size increases to 84 nm at 800°C. The crystalline size does depends on the water contains. Both, the rutile and the anatase phases are observed at 800°C as XRD pattern indicates peaks at 27° (rutile) and 25° (anatase). Agglomeration has taken place in powder form²⁰ Photoluminescence shows shifting in the emission spectra, at high excitation wavelength.

The conclusion based on all these facts and available data of the related work that, it is possible to control the size of the titanium nanoparticles by developing a proper mechanism. This study may be useful in the development of value added products biomedical and nanotechnology based industries.

References

1. S. Mahshid, M. Sasani Ghamsari, M. Askari, N. Afshar and S. Lahuti, Semiconductor Physics, *Quantum Electronics & Optoelectronics*, **V.9, N 2.** (2006) 65-68.
2. Weijia Zhou, Hong Liu, Robert I. Boughton, Guojun Du, Jianjian Lin, Jiyang Wanga and Duo Liua, *J. of Mater. Chem.*, **20** (2010) 5993-6008.
3. Banerjee, Soumen Karmakar, Naveen V. Kulkarni, Ashok B. Nawale, V. L. Mathe, A. K. Das and S. V. Bhoraskar, *J. Nanopart Res.*, **12** (2010) 581-590.
4. A. V. Agafonov and A. V. Vinogradov, *High Energy Chemistry*, **42** (7) (2008) 578-580.
5. M. Ferroni, V. Guidi, G. Martinelli and P. Nelli, *Nanostructured Mater*, **7** (1996) 709.
6. J. E. Rekoske and M. A. Barteau, *J. Phys. Chem., B*, **101** (1997) 1113.
7. Y. C. Yeh, T. Y. Tseng and D. A. Chang, *J. Amer. Ceram. Soc.*, **73** (1990) 1992.
8. A. K. Atta, P. K. Biswas and D. Ganguli, *J. Mater. Lett.*, **15** (1992) 99-103.
9. S. R. Dhage, S. P. Gaikwad and V. Ravi, *Bull. Mater. Sci.*, **27** (6) (2004) 487-489.
10. Y. F. Chen, C. Y. Lee, M. Y. Yen, H. T. Chiu, *J. Crystal Growth*, **247** (2003) 363-370.
11. J. Yang, S. Mei and J. M. F. Ferreira, *Mater. Sci. & Eng. C*, **15** (2001) 183-185.
12. E.J. Kim and S. H. Hahn, *J. Mater. Lett.*, **49** (2001) 244-249.
13. X. Z. Ding and X. H. Liu, *J. Alloys & Compounds*, **248** (1997) 143-145.
14. B. Yao and L. Zhang, *J. of Material Science*, **34** (1999) 5983- 5987.
15. S. Karuppuchamy and J. M. Jeong, *J. Oleo Sci.*, **55** (5) (2006) 263-266.
16. Chien-I Wu, Jiann-Wen Huang, Ya-Lan Wen, Shaw-Bing Wen, Yun-Hwei Shen and Mou- Yung Yeh, *Materials Letters*, **62** (2008) 1923-1926.
17. Guo-Bin Shan and George P. Demopoulos, *J. nanotechnology*, **21** (2010) 025604.
18. M. A. Barakat, G. Hayes and S. Ismat Shah, *J. Nanoscience and Nanotechnology*, **5** (2005) 1-7.
19. Greenwood, N. Norman and A. Earnshaw, Chemistry of the Elements, Oxford: Pergamon, (1984) 1117-19.
20. R. Vijayalakshmi and K. V. Rajendran, *The Azo J. of Materials online*, DOI: 10.2240/azojomo0298, (ISSN 1833-122X) **6** (2010).
21. J. Zhou, Y. Zhang, X. S. Zhao and A. K. Ray, *J. of Ind. Eng. Chem. Res.*, **45** (2006) 3503-3511.
22. A. Podhorodecki, G. Zatory, P. Sitarek, J. Misiewicz, D. Kaczmarek, J. Domaradzki, A. Borkowska and E. L. Prociow, *J. Thin solid film*, **517** (2009) 6331-6333.