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SYNTHESIS AND CHARACTERIZATION OF NANOSIZED TIO$_2$ POWDER DERIVED FROM A SOL–GEL PROCESS IN ACIDIC CONDITIONS

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ABSTRACT

In this paper, we report the comparison between nanosized TiO_2 powders prepared via two different acidic conditions (i) pH2 (ii) pH4. The study presents the synthesis of nanosized TiO_2 powder with anatase structure was derived from sol-gel process. Data concerning the effect of pH towards the development of TiO_2 nanoparticles is reported. The samples were examined by SEM- EDAX, XRD, and FT-IR analysis. Surface morphological studies obtained from SEM micrograph. The Crystalline size of TiO_2 powder has obtained for (i) pH 2 is ~3nm (ii) pH 4 is ~ 6nm at 400 ºC by controlling the acidity. In FT-IR, all the peaks observed were around 460-560 cm^{-1} due to stretching and bending vibrations of -OH groups. It was also found the pH of the solution affect the agglomeration of the particles.

KEYWORDS: *Nano Tio_2, Synthesis, Acidic conditions, Anatase, Sol-gel, X-ray diffraction (XRD)*

I. INTRODUCTION

Titanium dioxide (Tio_2) has attracted great attention in the fields of environmental purification [1] and can be used as a kind of solar energy cell [2, 3]. When irradiated with UV light, Tio_2 nanosized powder shows strong oxidizability and reducibility [4, 5]. It is well known fact that Tio_2 has three crystalline forms of anatase, rutile and brookite. Among these three crystalline forms, rutile phase is the most thermodynamically stable, whereas brookite and anatase are metastable and transformed to rutile on heating [6]. Different synthesis methods such as sol-gel [7, 8], microemulsion or reverse micelles [9], and hydrothermal synthesis [10] have been used to derive the nanoparticles of titanium dioxide. Compared to other methods, sol-gel process is regarded as a good method to synthesis ultra-fine metallic oxide [11] and has been widely employed for preparing titanium dioxide nano particles [12]. In this paper, we report that novel sol-gel process to derived nano sized titanium dioxide powder at two different acidic conditions and the procured powder was analyzed for Grain size by XRD, Surface morphology by SEM, Chemical composition by EDAX and Metal oxide bonds by FTIR.

II. EXPERIMENTAL

2.1. Materials

All reagents used were of analytical grade purity and were procured from Sigma Aldrich 97% Co. Ltd. India

2.2 Sample Preparation

All of the chemicals were analytical grade. Titanium dioxide nano powders were derived from sol–gel process using titanium tetraisopropoxide (TTIP, sigma Aldrich), deionised water, and ethyl alcohol (EtOH, Merck) as the starting materials. The sol-gel synthesized TiO_2 was obtained from Titanium tetraisopropoxide (Ti(O*i*Pr)4) was dissolved in absolute ethanol and deionised water was added to the solution in terms of a molar ratio of TTIP: H_2O=1:4. Nitric acid (HNO_3) was used to adjust the pH range. The pH was measured using a pH meter (Elico: L1610) and values are in the range of (i) pH2, (ii) pH4 and for restrain the hydrolysis process of the solution. The obtained solutions were kept under slow-speed constant stirring on a magnetic stirrer (Remi: 1MLH) for 40 min at room temperature. In order to obtain nanoparticles, the gels were dried under 50ºC for 1.5 hr to evaporate water and organic material to the maximum extent [13, 14]. After ball milling (at 900 rpm) [15] the dried powders obtained were calcinated at 400ºC (Genuine hot air oven) for 2 h to carry out to obtain desired TiO_2 nanocrystalline. The photographic view of portable ball miller (FRITSCH, Germany) as shown in the fig.2.1 and Steps involved in the synthesis of nanostructured TiO_2 through a Sol-Gel process is shown in fig.2.2.

Figure 2.1 The photographic view of Portable ball milling

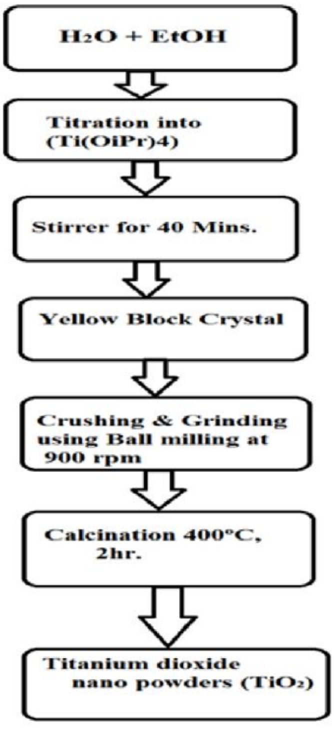

Figure2.2 Steps involved in the synthesis of nanostructured TiO_2 through a Sol-Gel process

2.3 Sample Characterization

The prepared samples were characterized for the crystalline structure using D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using

Cu$K\alpha$ radiation (λ = 0.15406 nm). The crystal size was calculated by Debye-Scherrer's formula. Surface morphology was studied by using SEM-EDAX (Model JSM 6390LV, JOEL, USA) and FTIR spectra were measured on an AVATAR 370-IR spectrometer (Thermo Nicolet, USA) with a wave number range of 4000 to 400 cm−1.

III. RESULTS AND DISCUSSIONS

3.1. Calcination temperature

The figure shows that the X-ray diffraction (XRD) patterns of the powder samples were prepared in initial solution with different pH. XRD patterns of dried sample at 50 ºC were largely amorphous. XRD patterns of TiO_2 powders calcinated at 400ºC is shown in Fig.3.1. (a) And Fig. 3.1 (b). Then distinct peaks were noted in the XRD patterns at 25.4°. It is also noticed that pH affects particles size and degree of crystallinity. The peaks located at 25.4, 37.8, 48.0, 54.5 respond to the (101), (004), (200), (105 and 211) planes of the anatase phase (JCPDS 21-1272), and the peaks located at 27.5, 36.1, 54.4^0 respond to the (110), (101), (211) planes of the rutile phase (JCPDS 21-1276), respectively. A trace of rutile was found in sample prepared at pH 2 at 27.3 ° corresponding to anatase phase (110). The peak locations and relative intensities for TiO_2 are cited from the Joint Committee on Powder Diffraction Standards (JCPDS) database. In this case, it is found that high acidity in medium solution will favor the formation of rutile phase while lower acidity will favor anatase formation. The results show high acidity favor formation of rutile.

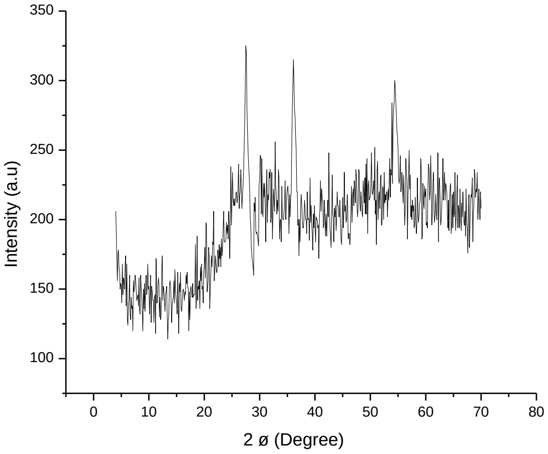

Figure3.1 (a) XRD patterns of titania particles calcined at 400°C for pH2

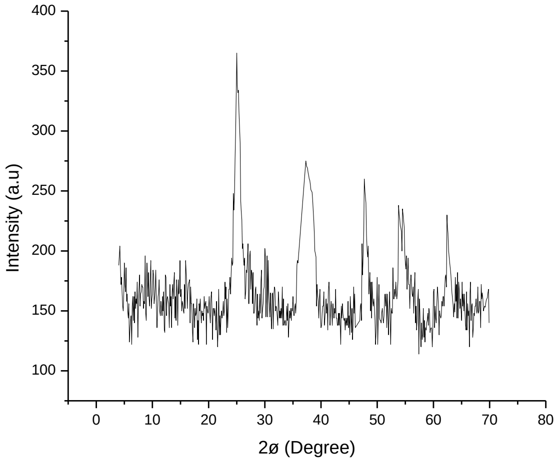

Figure 3.1 (b) XRD patterns of titania particles calcined at 400°C for pH4

Calcination is a common treatment used to improve the crystallinity of TiO_2 powders. It can be obviously seen from fig.3.1 the phase transformation from amorphous to anatase occurred at about 400ºC. Crystallite size was obtained by Debye-Scherrer's formula given by equation

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

Where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the line width at half-maximum height [16]. The Crystalline size of TiO_2 nano powder has obtained for (i) pH 2 is ~3nm (ii) pH 4 is ~ 6nm for anatase at 400 ºC by using the formula.

3.2. SEM Morphology

The morphology of calcinated titania powders at 400 ºC observed by SEM is shown in fig.3.2 (a) & (b). The pure TiO_2 particles exhibited irregular morphology due to the agglomeration of primary particles and with an average diameter for (i) pH 2 is ~3nm (ii) pH 4 is ~6nm

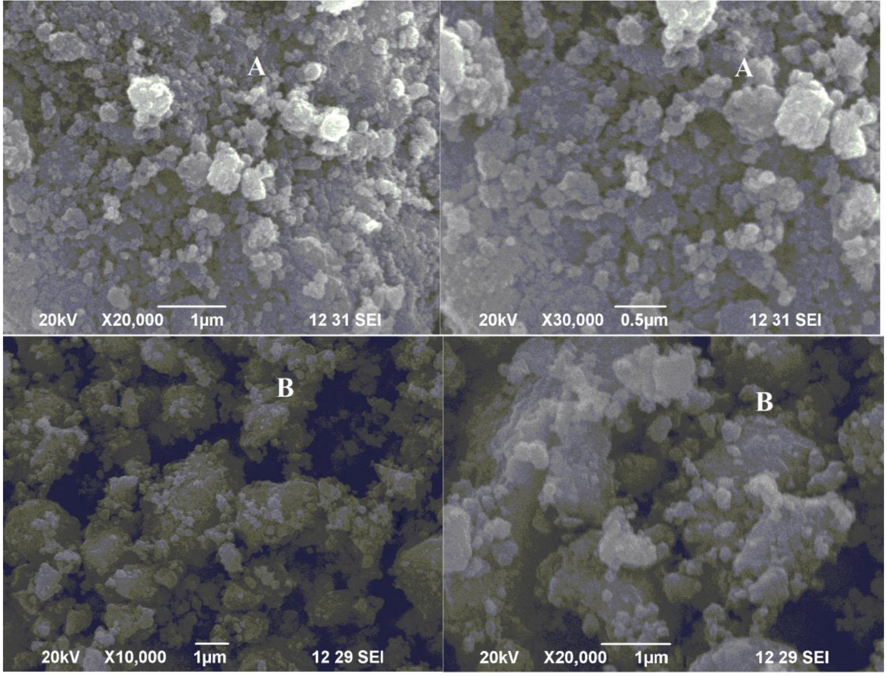

Figure 3.2: (a) SEM Morphology of calcinated titania powder at 400^0c for pH2 (b) SEM Morphology of calcinated titania powder at 400^0c for pH4

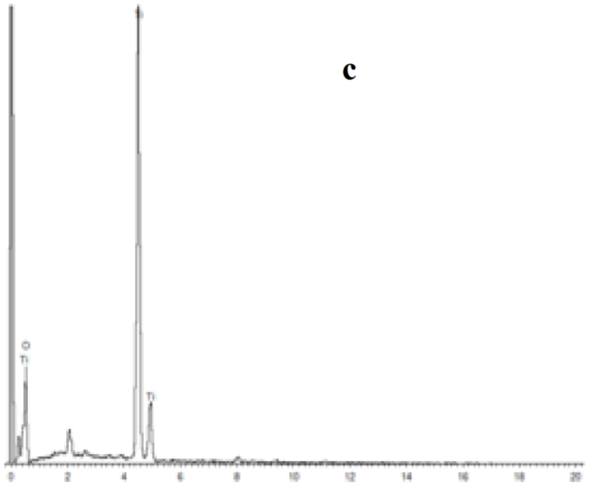

Figure3.2 (c) EDAX images of TiO_2

Figure 3.2 (a) & (b) shows the surface morphology of TiO_2 powders pH2, and pH4 respectively. The picture showed that TiO_2 powders prepared at pH 2 consists of anatase and rutile. While figure 3.2 b prepared at pH 4 is spherical in shape. The size of the particles at higher pH values is smaller and agglomerate. According to several studies, the variety of TiO_2 surface charge is pH dependent. TiO_2 in sols possess electrical charge due to the absorption of H+ or OH- in aqueous suspension.

3.3 FT-IR Spectroscopy

Figure 3.3 represents the FT-IR spectra of sol-gel derived TiO_2. The peaks at 3400 and 1650 cm^{-1} in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO_2, the peaks at 550 cm^{-1} show stretching vibration of Ti-O and peaks at 1450 cm^{-1} shows stretching vibrations of Ti-O-Ti. Further EDAX confirms presence the Ti-O-Ti as shown in the figure 3.2 (c) K.Balachandran et al. [17].

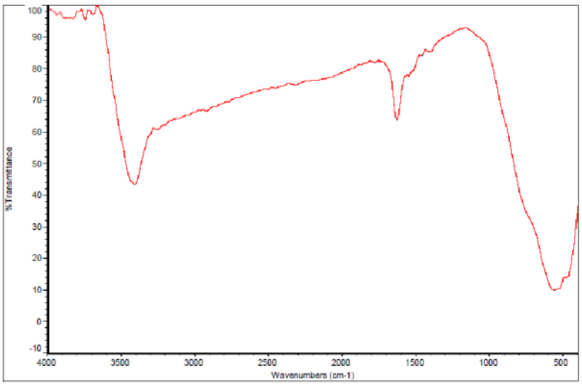

Figure 3.3 FT-IR spectrum of the synthesized nano TiO_2

IV. CONCLUSION

Nanosized Titanium dioxide (Tio_2) powders were prepared via two different acidic conditions (i) pH2 (ii) pH4 successfully. It was observed that pH plays an important role towards the formation of TiO_2 structure. Lower acidity promotes anatase structure while higher acidity results in rutile phase. Degree of crystallinity of anatase is pH dependent and lower acidity enhanced the crystallinity also promotes formation of big crystallite size. By controlling the conditions properly, nano-TiO_2 powders with the average grain size for (i) pH 2 is ~3nm (ii) pH 4 is ~6nm could be obtained. Data concerning the effect of pH towards the development of TiO_2 nanoparticles is reported. In the FT-IR spectra, all the peaks observed were around 460-560 cm^{-1} due to stretching and bending vibrations of -OH groups.

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REFERENCES

[1] D. F. Ollis and H. AL-Ekabi (eds.), “Photocatalytic Purification of Water and Air” (Elsevier, Amsterdam, 1993).
[2] U. Bach, D. Lupo, P. Comte, J . E. Moser, F. Weissortel, J . Salbeck, H. Spreitzer and M. Gratzel, Nature **395** (1998) 583.
[3] B. O’Regan and M. Gratzel, ibid. **353** (1991) 737.
[4] W. A. Zeltner, C. G. Hill and M. A. Anderson, Chemtech **5** (1993) 21.
[5] X. FU, W. Zeltner and M. A. Anderson, Appl. Catal. B : Environmental (1995) 209.
[6] S.J. Moon, w.w. So, S.B. Park, K.J. Kim, C.H. Shin, J. Mat. Sci. 36 (2001) 4299.
[7] M. Lal, V. Chhabra, P. Ayyub, A. Maitra , J. Mater. Res. 13 (1988) 1249.
[8] U. Selvaraj, A.V. Prasadrao, S. Komerneni, R. Roy, J. Am. Ceram. Soc. 75 (1992) 1167.
[9] R.R. Bacsa, M. Grätzel, J. Am. Ceram. Soc. 79 (1996) 2185.
[10] T.R.N. Kutty, R. Vivekanandan, P. Murugaraj, Mater. Chem. Phys. 19 (1988) 533.
[11] B. Li, X. Wang, M. Yan, L. Li, Mater. Chem. Phys. 78 (2002) 184.
[12] M.J. Hague, D.C. Mayo, J. Am. Ceram. Soc. 77 (1994) 1957.

[13] P. Chenga, C. Denga, M. Gub and A. X. Dai, “Effect of Urea on the Photoactivity of Titania Powder Prepared by Sol-Gel Method,” Materials Chemistry and Physics, Vol. 107, No. 1, January 2008, pp. 77-81.
[14] Z. Wang, U. Helmersson and P. Kall, “Optical Properties of Anatase TiO2 Thin Films Prepared by Aqueous Sol- Gel Process at Low Temperature.” Thin Solid Films, Vol. 405, No. 1-2, February 2002, pp. 50-54.
[15] N. Babaei et al, 2006 Preparation of TiO2/Al Nanocomposite Powders via the Ball milling, First International Congress on Nanoscience and Nanotechnology, Tehran (Iran), 18-20 December.
[16] B.D. Cullity, Elements of X-Ray Diffraction, Adison-Wesley, 1978.
[17] K.Balachandran, R.Venckatesh, Rajeshwari Sivaraj, 2010 Synthesis of NanoTiO2-SiO2 composite using sol-gel method: Effect of size, surface morphology and thermal stability, IJEST, 2 (8), pp.3695-3700

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