

Preparation and characterization of TiO₂ nano particles via Microwave assisted Solvothermal method

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ABSTRACT

Nanoparticles of titanium dioxide have been synthesized via Microwave assisted Solvothermal method using Titanium tetra isopropoxide (TTIP) and Acetic acid as a precursors. The obtained nanopowders were characterized by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR) and Ultraviolet Visible (UV-Vis). XRD pattern indicates the cubic TiO₂ structure with average crystallite size of 12 nm. FTIR spectra showed the vibrational bands of Ti-O. The morphology of the as prepared samples and chemical constituents of the nanoparticles studied using SEM and EDAX analysis. AC and DC electrical measurements are done on samples at various temperatures ranging from 303 K- 383 K. From the UV-Vis spectra the optical properties of TiO₂ were studied and discussed.

Keywords: *TiO₂, Nanoparticles, microwave*

I. INTRODUCTION

TiO₂ is a multi-functional material whose physical and chemical properties have allowed to be suitable for a wide range of applications; it exhibits non-toxic properties and it is chemically inert and thermally stable. Particularly titanium dioxide, TiO₂, has been studied extensively as photo catalyst to deal with environment pollution, water purification, wastewater treatment, hazardous waste control and air purification [1-5]. Titanium dioxide (TiO₂) is of great interest in technological applications due to its morphology and crystalline phase. TiO₂ exists three different phases, i.e., anatase, rutile, and Brookite. The active crystallite phases of TiO₂ are anatase and rutile [6,7]. TiO₂ has been widely studied regarding various applications, utilizing the photo catalytic and transparent conductivity, which strongly depend on the crystalline structure, morphology and crystallite size [8]. TiO₂ nanoparticles have been prepared by different methods such as, chemical precipitation method [9], chemical vapour deposition (CVD) [10], the sol-gel technique [11], sputtering [12], hydrolysis, micro emulsion method [13], spray deposition [14], aerosol-assisted chemical vapour deposition [15], thermal plasma [16], hydrothermal method [17], microwave assisted hydrothermal synthesis [18], solvothermal method [19] and flame combustion method [20]. Among these methods microwave assisted solvothermal method is a simple method to synthesis TiO₂ nanoparticles.

It is reported that nano particles can be prepared in an easy manner using a domestic microwave oven [17]. This method has been successfully applied for the preparation of nanosized inorganic materials [18-20]. Compared with conventional heating, microwave heating has an advantage of high efficiency and rapid formation

of nanoparticles with a nano size distribution. In this work, we have prepared TiO₂ nanoparticles using micro wave assisted solution method.

II. EXPERIMENTAL

2.1 Materials : Titanium tetraisopropoxide (TTIP, 97%, (AR grade MERCK), Acetic acid [CH₃COOH] (Analytical reagent, RANBAXY fine chemicals Limited, india) Deionised water

2.2 Synthesis of TiO₂ Nanoparticles

The entire chemicals were purchased from Merck and used as received without further purification. In a typical reaction process, Titanim Tetra Isoprpxide (TTIP) was dissolved in Acetic acid [CH₃COOH] with a constant stirring at room temperature and then pH value was adjusted to 10 by drop wise addition of Sodium Hydroxide. During the synthesis, medium power was maintained and the temperature was maintained approximately at 70 ° C. After the reaction was over to form the nanoparticles, they were centrifuged and filtered out. Then the nanoparticles were washed with de-ionized water for five or six times to remove the unwanted residues. The synthesized nanoparticles of TiO₂ were dried in an oven at 50 ° C. The synthesized nanoparticles were observed to be white in colour and very fine powder of TiO₂.

2.3 Material Characterization

The structure and phase purity of the powders were examined by powder X-ray diffraction (XRD) technique using an X-ray diffractometer (Model Bruker D-8). The phase purity and the presence of functional groups of the as-prepared ceria nanoparticles are analyzed using FT-IR spectroscopy (Shimadzu 8400S FT-IR spectrometer). To study the size-dependent quantum size effect and the optical quality of the TiO₂ nanoparticles, optical absorption studies are carried out by UV-1800 series spectrophotometer. The morphologies of as-prepared samples were investigated through SEM (Hitachi).

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD) studies

The powder XRD pattern for the as-prepared pure TiO₂ nanoparticles is presented in the figure 1. It is observed that the XRD reflection peaks for pure TiO₂ sample are in a perfect match with the diffraction pattern of TiO₂ published in the (JCPDS File No.21-1272). All the reflections of powder XRD patterns of this work were indexed using the TREOR and INDEXING software packages. The lattice parameters from powder XRD data were found using the UNITCELL software package and the obtained values were found to be $a = b = 3.7852 \text{ \AA}$, $c = 9.5139 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ Thus phase of TiO₂ was observed to be cubic. The Powder X-Ray Diffraction patterns of the as prepared TiO₂ showed the presence of broad peaks. The broad peaks indicate either particles of very small crystalline size, or particles are semi crystalline in nature.

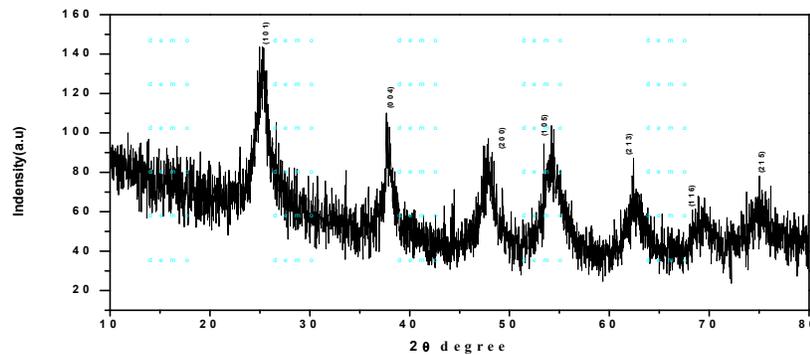


Fig 1 X-ray diffraction pattern of TiO₂nanopartilces

The particle size of nanoparticles was determined using the Scherrer's relation

$$d = (0.9\lambda) / (\beta \cos\theta)$$

where β is the full width at half maximum in radians, λ is the wavelength of X-rays used, θ is the Bragg's angle. The sample are typical anatase titania crystal structure (21-1272) with peaks at corresponding to (1 0 1), (004), (2 0 0), (1 0 5), (2 1 3), (1 1 6) and (2 1 5)]. From the Powder XRD spectrum the average crystallite size is found to be 12 nm.

3.2 FTIR Analysis

The Infrared spectroscopy is effectively used to identify the functional groups of the synthesized compounds. The figure 2 shows the absorption peaks/bands in the FTIR spectrum of TiO₂ nanoparticles.

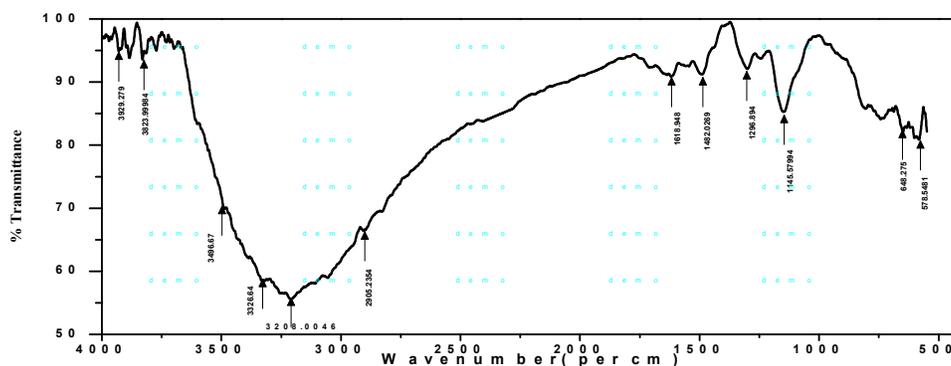


Fig 2 FTIR spectrum of TiO₂ nanoparticles

From this spectrum, it can be observed apparently that strong band in the range of 580 to 660 cm^{-1} is associated with the characteristic modes of TiO₂. The absorption range around 3200 cm^{-1} indicates that the presence of hydroxyl (stretching), which is probably due to the fact that the spectra were recorded in situ and some readsorption of water from the ambient atmosphere has occurred [25]. The absorption range around 1618 cm^{-1} may be related to hydroxyl (bending) groups of molecular water [20].

3.3 UV-visible absorption studies

UV-visible absorption spectral study may be assisted in understanding electronic structure of the optical band gap of the material.

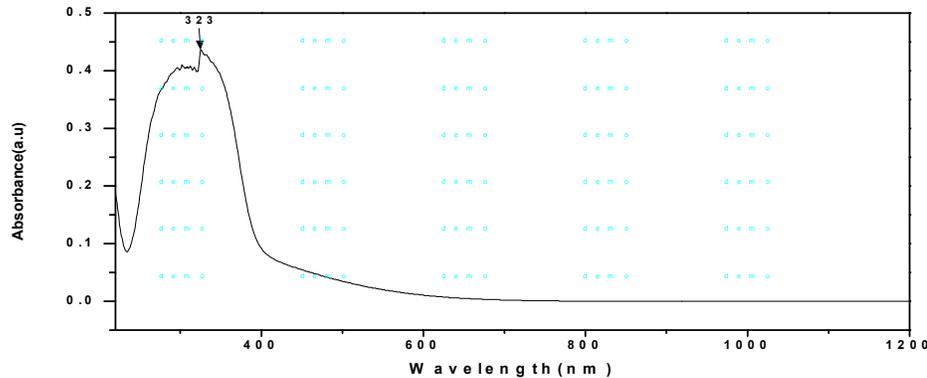


Fig3. UV-visible absorption spectra of TiO₂

Absorption in the near ultraviolet region arises from electronic transitions associated within the sample. UV-visible absorption spectra of pure Titanium dioxide nanoparticles were recorded and they are presented in the figure3. The spectrum in the figure 3 shows a strong absorption band in the UV region due to the charge transfer transitions between the energy states. In the figure 3, the absorption peak around 323 nm. It is found that the band gap of the TiO₂ nanoparticles in the present study is 3.15 eV and this value is found to be smaller than that of bulk TiO₂ nanoparticles. The bulk band gap of TiO₂ is 3.2 eV .

3.4 SEM and HRTEM Studies:

The surface morphology of TiO₂ has been studied using Scanning Electron Microscope. The SEM investigations of all the nano TiO₂ samples reveal that the crystallites are nanometre size. Therefore the growth of Nano phase crystalline TiO₂ particles is accelerated at higher calcinating temperature. Samples shows uniform morphology in the form of TiO₂ nano clusters.

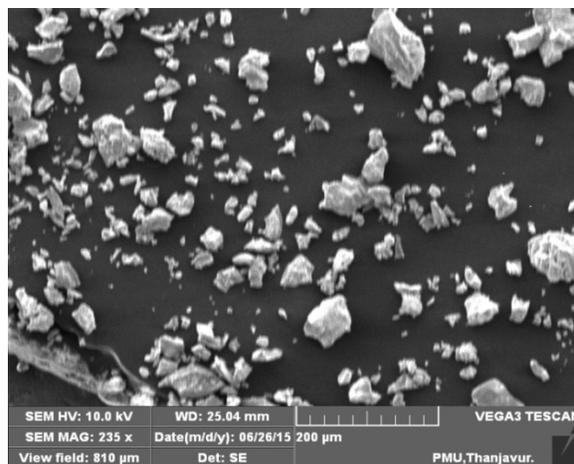


Fig 4. SEM image of TiO₂

HRTEM analysis provides information on particle size and shape, as shown in TEM images in Fig 5. of TiO₂. These images shows that the range of particles from 10 to 20 nm. It will give proof for the confirmation of supraaggregates as found in the image of HRTEM.

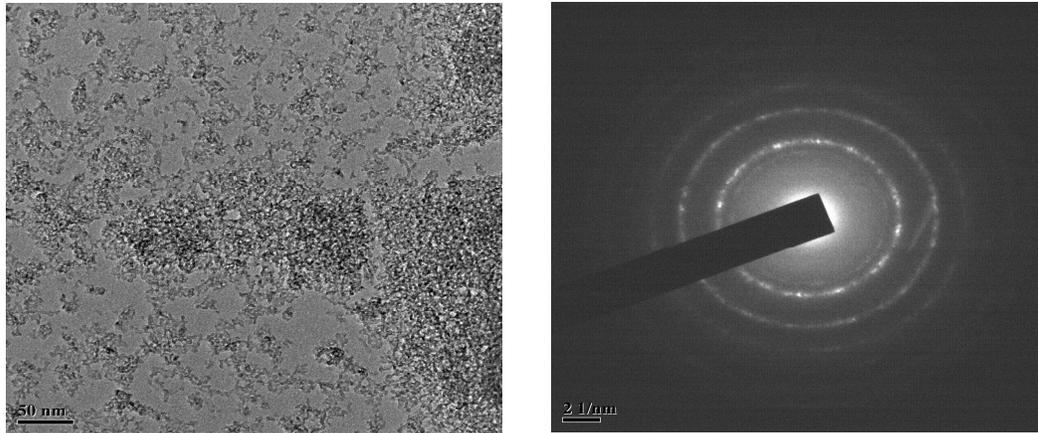


Fig 5. TEM image of TiO₂

3.5 Dielectric properties

The frequency variation studies are carried out to understand the electrical homogeneity of the material by identifying the relaxation mechanism as well as the nature of electrical conduction. These studies also help to find out the dielectric parameters of the material. Dielectric properties are associated with electro-optic property of the materials. Microelectronics industry needs low dielectric constant (ϵ_r) materials as an interlayer dielectric [26-27].

The complex permittivity (ϵ^*) or dielectric constant of a system was defined by the equation,

$$\epsilon^* = \epsilon' - j\epsilon'' - j(\sigma/\omega\epsilon_0)$$

where ϵ' , ϵ'' , σ , ω , ϵ_0 represented real part of dielectric constant of the material, imaginary part of dielectric constant of the material, conductivity, angular frequency and permittivity of free space, respectively

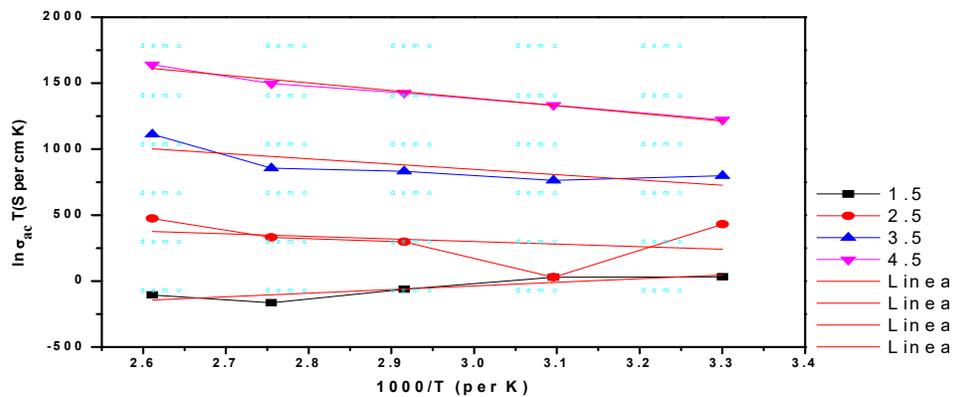


Fig 6. Plot of $\ln(\sigma_{ac})$ versus $1000/T$ for TiO₂ nano particles

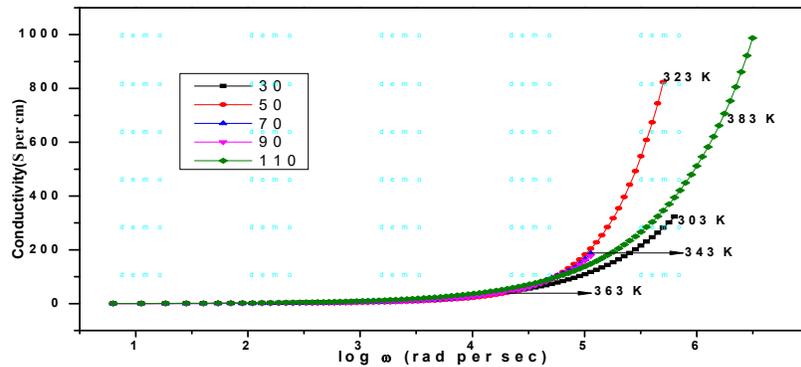


Fig 7. The log ω vs. conductivity graph for TiO₂

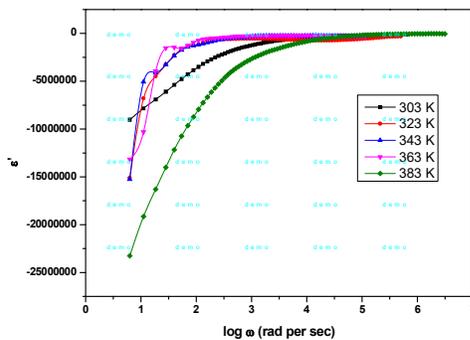


Fig 8. log ω vs ε' graph for TiO₂

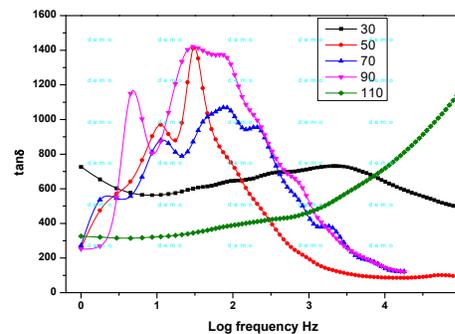


Fig.9 . Loss tangent spectra of TiO₂ nano particles

The electrical resistivity of nanocrystalline material is higher than that of both conventional coarse grained polycrystalline material and alloys. The magnitude of electrical resistivity and hence the conductivity in composites can be changed by altering the size of the electrically conducting component. The hopping (exchange) of the charge carriers in the lattice sites (which is responsible for electrical conduction) is thermally activated by increasing temperature. As a result, dielectric polarization increases causing an increase in dielectric constant and dielectric loss. Electrical conductivity depends on thermal treatment of materials. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies predominantly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift.

The dielectric relaxation parameter of the TiO₂ was obtained from the plot of Tan δ as a function of frequency. The dielectric loss tangent (Tan δ) was defined by the equation, $Tan \delta = \epsilon''/\epsilon'$. The variation of Tan δ with frequency has been presented in figure 9. Tan δ increased with increasing frequency thereby reaching a maximum, and then, decreased with further increase of frequency.

IV. CONCLUSIONS

TiO₂ Nano powders were successfully synthesized by Microwave assisted method using Titanium tetra isopropoxide and Acetic acid. The prepared TiO₂ nanopowders were characterized by Powder XRD, FTIR, UV and SEM, analysis. The XRD spectra reveal that, the main phase of TiO₂ nanopowders are anatase phase. FTIR spectra displayed the peaks attributed to the presence of O-H groups at 3220 cm⁻¹ and 1618 cm⁻¹. Also FTIR spectra show the vibrational mode of TiO₂ around 600 cm⁻¹. SEM image displayed the uniform morphology in the form of nano clusters. From UV-Vis spectra the band gap of TiO₂ 3.15 eV. The frequency dependence Ac conductivity was calculated by with help of different temperature region.

REFERENCES

- [1]. U. Diebold, Surf. Sci. Rep. 48(2003) 53.
- [2]. A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1
- [3]. Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, Environ. Sci. Technol. 35 (2001) 2635.
- [4]. J. Rodriguez, T. Jirsak, G. Liu, J. Herbek, J. Dvorak, A. Maiti. J. Am. Chem. Soc. 123 (2001) 9597
- [5]. J. Aguado, R. Van Grieken, M.J. Lopez-Munoz, J. Murugan, Catal. Today 75 (2002) 95
- [6]. K. Joseph Antony Raj, B. Vishwanathan, Indian J. Chem. 48 A(2009) 1378-1382.
- [7]. L. Gang, W. Xuewen, C. Zhigang, C. Hui-Ming, L. Gao Qing (Max), Colloid Interface Sci 329 (2009) 331-338.
- [8]. H. Nakano, H. Hasuike, K. Kisoda, K. Nishio, H. Harima, J. Phys.: Condens. Matter 21 (2009) m064214.
- [9]. S. Mashid, M. Sasani Ghamsari, M. Afshar, S. Lahuti, Semiconductor physics, Quant. Electron. Optoelectron. 9 (2006) 65-68.
- [10]. S. Jian, W. Xudong, Cryst. Growth Des. 11 (2011) 949-954
- [11]. N. Bahadur, K. Jian, R. Pasricha, Govind, S. Chand, Sensors and Actuators B 159 (2011) 112-120.
- [12]. S. Song, T. Li, Z.Y. Pang, L. Lin, M. Lu, S. Han, Vacuum 83 (2009) 1091-1094.
- [13]. X. Shen, J. Zhang, B. Tian, J. Hazard. Mater. 192 (2011) 651- 657.
- [14]. M. Uzunova-Bujnova, R. Kralchevska, M. Milnova, R. Todorovska, D. Hristov, D. Todorovsky, Catal. Today 151 (2010) 14-20
- [15]. T.A. Asif Ali Tahir, K.G. Nirmal Peiris, W. Upul Chem. Vap. Dep. 18 (2012) 107-111.
- [16]. Y. Tanaka, H. Sakai, T. Tsuke, Y. Uesugi, Y. Sakai, K. Nakamura. Thin Solid Films 519 (2011) 7100-7105.
- [17]. J.-K. Oh, J.-K. Lee, S.J. Kim, K.-W. Park, J. Indust. Engg. and Chem. 15 (2009) 270-274.
- [18]. A. Melis, L. Petra, S.C. Hopkins, P. Glenn, E. Johan vander, R. Susugna, G. Xavier, B.A. Glowacki, V.D Isabel, Nanotechnology 23 (2012) 165603.
- [19]. Y. Zhang, H. Zheng, G. Liu, Y. Battaglia, Acta 54(2009) 4079-4083.
- [20]. Y. Zhao, C. Li, X. Liu, F. Gu, H. Jiang, W. Shao, L. Zhang, Y. He. Mater. Letter. 61 (2007) 79-83.
- [21]. M. Brightson, S. Meenakshi sundar, T.H. Freeda, P. Selvarajan, (EAST 2007), Noorul Islam College of engineering, 25-27 October, 2007.
- [22]. X.H. Liao, J.J. Zhu, H.Y. Chen, Mater. Sci. Eng B85(2001)85

[23] W.X. Tu, H.F. Liu, J. Mater. Chem. 10(2000)2207.

[24] H. Wang, J.Z. Xu, J.J. Zhu, H.Y. Chen, J. Cryst. Growth 224(2002)88.

[25]. A.N Jose A, J.T. Juan, D. Pablo, R.P. Javier, R. Diana, I.L. Marta, Appl. Catal., A Gen. 178 (1999) 91.

[26] Z. Y. Zhang, X. Y. Yong, M. Xiao, Appl. Phys. Lett., 2002, 81, 2076.

[27] S. Datta, B. Das, Appl Phys Lett., 1990, 56, 665.