

Synthesis of TiO₂ nanocrystalline powder prepared by sol-gel technique using TiO₂ powder reagent

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ABSTRACT

TiO₂ is the potential candidate as semiconductor because of its high photochemical stability and low cost. properties are size dependent and when the particle size is reduced to the nano-meter scales it shows some novel properties. in this paper we have prepared nanocrystalline TiO₂ powder using sol-gel technique. In this experiment we have used TiO₂ powder and acetic acid to prepare sol of TiO₂ with DI water and gel was prepared using nitric acid. There are many reports on nanocrystalline TiO₂ using solutions of titanium isopropoxide, but here we are reporting the formation of nanocrystalline TiO₂ from the TiO₂ micro size powder reagent. The uniqueness of this report is the synthesis of nanocrystalline TiO₂ powder by sol gel technique using micro size TiO₂ powder reagent as starting material.

Key words: nanocrystalline TiO₂; X-ray Diffraction, Microstructure; Lattice strain.

INTRODUCTION

Titanium dioxide (TiO₂) or known as titania has been reported widely for its numerous applications from optoelectronics to cosmetics [1-3]. TiO₂ has excellent photocatalytic oxidative properties that depend on the crystallinity and crystal form [4]. Due to the photocatalytic activity, TiO₂ has been used in water and air pollution treatments [5]. It also exhibits unique electrical and chemical properties that can be utilized in various technological and engineering applications such as humidity sensor, gas sensor and membrane [6,7]. In addition, TiO₂ is also proposed for solar cells and laser diodes for its high refractive index and stability [8].

In view of the synthetic methods developed for the preparation of nanostructure TiO₂, a wide variety of approaches including flame synthesis, ultrasonic irradiation, chemical vapor deposition, sol-gel method has been adopted. Among them, Compared to other methods, sol-gel route is regarded as a good method to synthesis ultrafine metallic oxide and has been widely employed for preparing titanium dioxide (TiO₂) particles [9, 10]. Sol-gel process is a convenient and versatile method for preparing transparent thin film at low temperature [11]. The sol-gel process involved many complex processes for both chemical and structural nature. Before gel formation (polymerization), two stages are indentified: i) hydrolysis of the organo-metallic group precursor, and ii) poly- condensation. The physical, chemical and mechanical properties are much dependant on the properties of the precursor solution [12].

In the recent years, scaling optical and electronic properties of nanomaterials, which become strongly size dependant focused attention on the preparation of nanoparticle semi-conductors [13]. TiO₂ is the promising material as semiconductor having high photochemical stability and low cost. Well-dispersed titania nanoparticles with very fine sizes are promising in many applications such as pigments, adsorbents and catalytic supports [14-15]. In almost all of these cases, when the particle size is reduced greatly, especially to several nanometer scales, due to the large surface-to-volume ratio, some novel optical properties can be expected [16].

MATERIALS AND METHODS

TiO₂ Powder 99.9% pure (Merck), Acetic acid, and HNO₃ were used as the starting materials. First proportionate amount of TiO₂ was added with Acetic acid under continuous stirring for 45 minutes and then DI water was added slowly drop wise with continuous stirring in a magnetic stirrer for almost 1 hour for the formation of sol., after that 0.1M HNO₃ was added to the sol and was subjected to continuous stirring for 6 hours at 200 °C and finally the gel was prepared. The prepared gel was dried in a hot plate at a temperature of 300 °C for 30 minutes. Then the powder was grounded in an agate mortar for 2 hours for fine powder. Fine powder was calcined at a temperature of 900 °C for 3 hours in a programmable furnace. The calcined powder was once again grounded using mortar and pestle and was structurally characterized by an x-ray diffractometer (Shimadzu-6100). The x-ray powder diffraction profiles of the samples were recorded using graphite filtered Cu K α radiation from a highly stabilized and automated x-ray generator operated at 30kV and 20 mA. For this experiment, 0.3° divergence slit, 1mm receiving slit were used. The step scan data of step size 0.01° and step scan 0.6s were recorded for the angular range 20-70°.

Theory:

The powder diffraction profile shape was fitted to Pseudo-Voigt using *ProFit* software [17]. The software *ProFit* was developed to study crystallite size, microstrains and other structural imperfections. The profile-fitting program, *ProFit*, has been used to decompose a powder diffraction pattern into its constituent Bragg reflections by fitting analytical profile functions to obtain various parameters, which define the intensity, positions, breadth and shape of each reflection [18].

The *ProFit* mainly based on Pseudo-Voigt profile function $PV(x)$, which is defined as

$$PV(x) = I(x) = I_0 [L(x) + G(x)] \quad (1)$$

where function x is the peak position, $L(x)$ and $G(x)$ are Lorentzian and Gaussian components respectively. From above Eq. (1), the Lorentzian (Cauchy) component is defined as

$$L(x) = \eta \frac{1}{1 + C_L (x - x_0)^2} \quad (2)$$

$$\text{with } C_L = \eta \frac{1}{(w_L)^2}$$

and the Gaussian component is defined as

$$G(x) = (1 - \eta) \cdot \exp[-C_G (x - x_0)^2] \quad (3)$$

$$\text{with } C_G = \eta \frac{\ln 2}{(w_G)^2}$$

where x_0 is the peak position, η is the mixing parameter, $2 w_L$ and $2 w_G$ are the FWHM's of $L(x)$ and $G(x)$, respectively. In the Pseudo-Voigt function, η is the "mixing parameter", which lies in the range $0 \leq \eta \leq 1$, and determines the shape of the profile, with pure Lorentzian (Cauchy) and pure Gaussian as the limiting cases. The intensity I_k of the k_{th} peak of the X-ray powder diffraction pattern is given by,

$$I_k = S M_k L_{p_k} P_k |F_k|^2 \quad (4)$$

S is the scale factor (used to adjust the intensity of the calculated pattern to fit the observed data), M_k multiplicity of the k_{th} reflection, L_{p_k} Lorentz-polarisation factor, P_k effect of preferred orientation, F_k structure factor of k_{th} reflection, The Lorentz-polarisation factor of k_{th} reflection and can be calculated as

$$L_p = \frac{1}{2 \cos \theta \sin^2 \theta} \frac{1 + \cos^2 2\theta_c \cos^2 2\theta}{1 + \cos^2 2\theta_c} \quad (5)$$

where θ is the Bragg angles for diffraction and θ_c is the monochromator angle. Again, the preferred orientation (PO) correction factor can be calculated using March distribution function [19, 20], and is defined as

$$P_k(\phi) = [r^2 \cos^2 \phi + (\sin^2 \phi) / r]^{-3/2} \quad (6)$$

where ϕ is the acute angle between the scattering vector and the normal to the nominated PO plane and r is a refinable parameter.

The calculated intensity (Y_{ic}) at each point (i) in the pattern for a single phase

$$Y_{ic} = Y_{ib} + \sum_{k=k_1}^{k_2} G_{ik} I_k \quad (7)$$

Y_{ib} is the intensity of the background at the i_{th} point in the pattern, G_{ik} is the normalized peak profile function, I_k is the intensity of the k_{th} Bragg reflection k_1 - k_2 are reflections contributing to point i . The peak profile (width and shape) function, G_{ik} , is modeled using Voigt-function as

$$G_{ik} = \frac{C_1^{1/2}}{H_{Gk} \pi^{1/2}} \operatorname{Re} \left[\omega (C_1^{1/2} X_{ik} + i C_3 H_{Lk}) \right] \quad (8)$$

Where $C_1 = 4 \ln 2$, $C_3 = 2^{-3/2}$, H_{Gk} is the FWHM of Gaussian components, H_{Lk} is the FWHM of Lorentzian component, ω is the complex error function and Re is the real part, $X_{ik} = (2\theta_i - 2\theta_k) / \beta$ and $\beta (= H_{Gk} + H_{Lk})$ is the FWHM of k_{th} Bragg reflection.

RESULTS AND DISCUSSION

The diffracted intensity is generally expressed relative to the strongest peak in the diffraction pattern. The intensity I of a diffracted beam can be expressed in terms of structure factor, multiplicity, Lorentz-Polarisation factor, absorption factor and temperature factor as,

$$I = |F|^2 m L - P A(\theta) e^{-2M} \quad (10)$$

where F is the structure factor, m is multiplicity, L - P is Lorentz polarization factor, $A(\theta)$ is absorption factor and e^{-2M} is the temperature factor.

Addition of impure atoms to the parent materials causes the peak shifting due to stacking fault. The expression for change in d_{hkl} due to stacking fault can be measured by noting the change in θ_{hkl} and the wavelength λ by the following equation,

$$d_{hkl} = \frac{\lambda}{2 \sin \theta_{hkl}} \quad (11)$$

Differentiating d_{hkl} w.r.t. θ_{hkl} we can have,

$$\Delta(2\theta)_{hkl} = -2 \frac{\Delta d}{d_{hkl}} \tan \theta_{hkl} \quad (12)$$

where the symbols have their usual meanings. Δd is the change in plane spacing with respect to the virgin sample. The term $\frac{\Delta d}{d_{hkl}}$ is the strain due to the substitution of dopant (Ca, Mg and Sr) ions.

The term crystallite in crystallography usually refers to a coherently diffracting crystallite domain, i.e. the volume from which all waves that are diffracted are in phase. The dimensions of this domain may be smaller than those of grains or particles. Crystallite will be one factor which affects the repeatability and hence the reliability of results. The crystallite size of the identified crystalline phase is calculated using the corrected form of well known Scherrer formula as [21]

$$D_{hkl} = \frac{K\lambda}{\beta' \cos\theta} \quad (13)$$

where $\beta' = (B - b)$ is the FWHM (full width at half maximum); B is the line width; b is the instrumental broadening; K is the shape factor (=0.9); θ is the Bragg angle and λ is the wave length of Cu K_{α_1} (=1.5406 Å).

The XRD pattern of single phase anatase nano crystalline TiO_2 is shown in Fig.1. The structure of the single phase anatase nanocrystalline TiO_2 is identified to be in tetragonal structure with space group no. 141 and space group 141/a m d. The lattice parameters are found to be $a=b=3.786$ Å and $c=9.495$ Å with $\alpha=\beta=\gamma=90^\circ$. Calculated density of the material is estimated to be 3.90 gm/cc with unit cell volume $136.10 \times 10^6/\text{m}^3$. All the planes are labelled and identified. The crystallite size of the planes are calculated and presented in Table-1. Crystallite size varies between 17.3 nm for (0 1 1) at 25. 21° (2 θ) to 27.8 nm at 70. 24° (2 θ). The lattice strain is calculated to be 0.936 at 25. 21° (2 θ) and 0.223 at 70. 24° (2 θ). For all other planes the data are presented in table-1. Using the wyckoff. positions of Ti and O as 4b and 8e and introducing some initial information the structure of the material is obtained as mentioned graphically in fig.2. One can clearly see the tetragonal structure of the material. The generated positions of different atoms are obtained in the crystal co-ordinate for 4 Ti and 8 O atoms and the Bond lengths between them are represented in table-2. In the twelve quant the bond length is between two Ti atoms and is maximum in the material, where as in the eighteen and twenty four quant the bond length between O and Ti atom is almost same, however, a small difference of the order of 0.0343 nm exist.

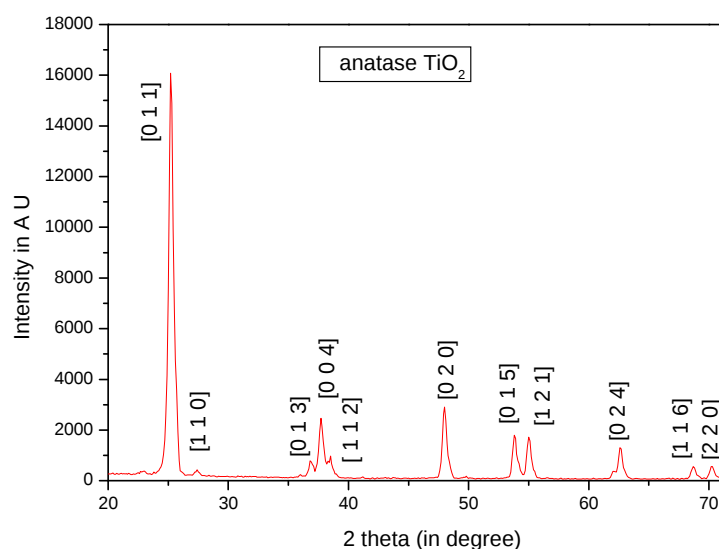


Fig: 1 XRD spectrum of sol-gel derived nanocrystalline TiO_2 powder

Table-1: Microstructure of nanocrystalline TiO_2 powder

S. No	Angle(2 θ) in Degree	FWHM	D in Å	Int. Breadth	RI	Crystallite Size in nm	Strain
1	25.2097	0.48	3.5298	0.64	100	17.3	0.936
2	27.3852	0.48	3.2541	0.64	1.44	17.4	0.859
3	36.8766	0.36	2.4355	0.48	3.89	23.9	0.471
4	37.7160	0.48	2.3832	0.64	14.72	17.9	0.613
5	38.5185	0.36	2.2355	0.48	5.29	24.0	0.449
6	47.9738	0.48	1.8948	0.64	17.66	18.5	0.471
7	53.7937	0.48	1.7027	0.64	10.65	19.0	0.413
8	55.0016	0.48	1.6682	0.64	10.22	19.1	0.402
9	62.6233	0.36	1.4822	0.48	7.79	26.6	0.258
10	68.6950	0.48	1.3653	0.64	3.05	20.5	0.306
11	70.2434	0.36	1.3389	0.48	3.19	27.8	0.223

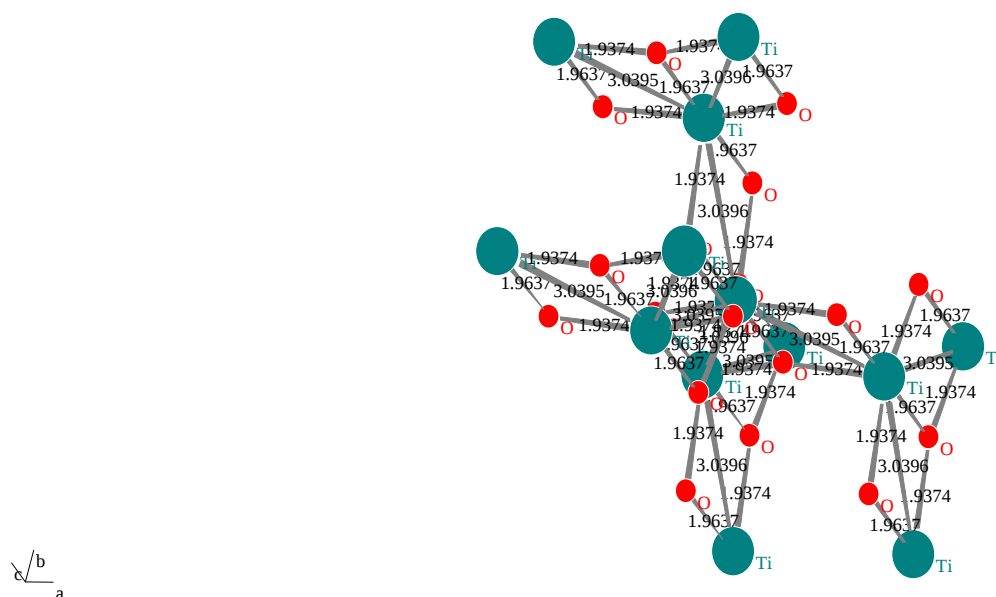
Fig. 2 Simulated Structure of Nano TiO₂ Powder

Table-2 : Bond lengths between different atoms

S. No	Atom 1	Atom 2	Distance in nm	Quant
1	O	Ti	1.9374	24
2	O	Ti	1.9637	18
3	Ti	Ti	3.0396	12

Fig. 3 shows the variation of crystallite size in nm with respect to different planes, where as fig. 4 says about the lattice strain of different planes. From fig.3 it is seen that crystallite size of 100% RI(relative intense) peak is smallest and is equal to 17.3 nm. It can also be seen that, the average crystallite size of the material lies between 20 nm for lower reflection angle i.e. up to $2\theta = 55^\circ$, except at the overlapping reflections at $2\theta = 36.87^\circ$ and 38.51° . However, at the higher reflections the crystallite size increases relatively. As a matter of fact, the higher reflections are less informative and hence not much of importance.

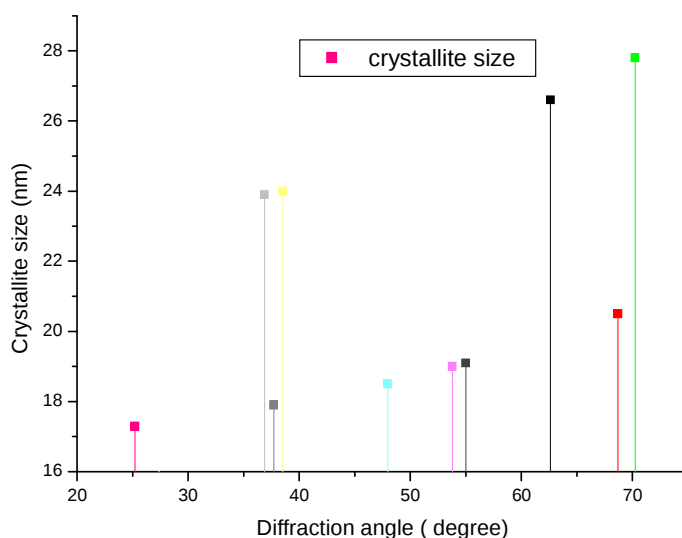


Fig. 3 Variation of crystallite size as function of diffraction angle

From Fig. 4 it is seen that, the lattice strain decreases gradually with increasing reflection angle. It is seen that the lattice strain is always less than 1 irrespective of the planes. This development of strain may be due to the lattice imperfection during the synthesis process and might have been introduced at the grinding process or at the time of nuclear division during sol-gel process.

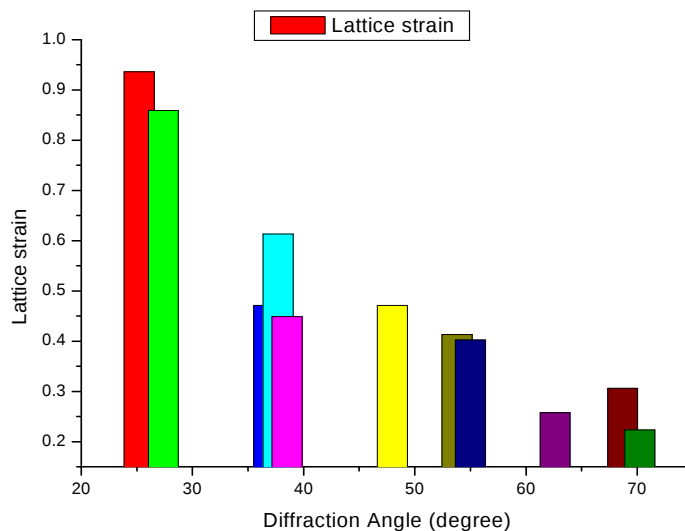


Fig. 4 Variation of lattice strain as a function of diffraction angle

CONCLUSION

Starting with micro size TiO_2 powder reagent nanocrystalline single phase anatase TiO_2 powder is synthesized, and is different from the conventional sol-gel technique. The crystallite size of the material is estimated for different planes along with their lattice strain. Lastly using the microstructural parameters and some basic information of the nanocrystalline anatase TiO_2 structure, one graphical visual structure is generated which clearly shows the tetragonal nature of the nanocrystalline anatase TiO_2 powder with different bond lengths and generated positions of different atoms and their bond angles (not mentioned here).

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