

Structural Analysis of Cu Doped TiO₂ Nanoparticles using Williamson-Hall Method

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ABSTRACT

Pure and doped Ti_{1-x}Cu_xO₂ nanoparticle is synthesized by co-precipitation technique successfully with nominal composite of x=0.0,0.01,0.02 and 0.03 at room temperature. The precursors were further calcined at 500 to 600°C for 6hrs in furnace which results in the formation of different TiO₂ phase compositions. The structural analysis carried out by XRD (Bruker D8 Cu-Kα1). X-ray peak broadening analysis was used to evaluate the crystalline sizes, the lattice parameters, number of unit cell per particle, c/a ratio and Volume of unit cell. The Williamson Hall analysis is used to find grain size and Strain of prepared TiO₂ nano particles. Crystalline TiO₂ with a Tetragonal Anatase phase is confirmed by XRD results. The grain size of pure and Cu doped samples were found in the range of 10nm to 18nm. All the physical parameters of anatase tetragonal TiO₂ nanoparticles were calculated more precisely using modified W-H plot a uniform deformation model (UDM). The results calculated were approximately similar with standard values.

Keyword: TiO₂; Co-precipitation; Particle Size; W-H analysis

I. INTRODUCTION

In the recent day's research activities, semiconductor plays an important roll across the world. As the properties of semiconductors are very much dependent of particle size, hence it is considered as important part of material science and technology [1]. Titanium dioxide is the very popular semiconductor due to its wide band gap (3.3 eV), excellent chemical stability, large exciton binding energy. Titanium dioxide is immensely useful in various applications like gas sensors, solar cell, photocatalytic degradation and photo luminescence etc. The crystal morphology and particle size plays vital role in these applications which have attracted most researchers to synthesis nano-crystalline TiO₂ in recent years. There are various techniques adopted by the researchers to synthesis TiO₂ nanoparticles such as sol-gel, co-precipitation and hydrothermal etc. The co-precipitation is an alternative, cheap and simple method for preparation of nanostructure TiO₂[2]. Ulrich

Gesenhues et al. represented that the properties of TiO₂ depends on various internal and external parameters like: dopants, concentrations of surface hydroxyls, electric surface charges accumulated from different rates of consumption of e⁻ and h⁺ outside the particle or from acid base reactions of the surface, adsorption of the molecules, etc.[3] Investigations of the influence of dopants on the properties of TiO₂ provide huge space for the researchers.

The crystalline size and lattice strain are mainly extracted from the peak width technique. The light scattering technique, scanning electron microscopy and transmission electron microscopy analysis are the most commonly used techniques for the measurement of particle size. The technique to measure lattice strain is X-ray peak broadening [4-5].

In the present work the lattice parameters, number of unit cell per particle, c/a ratio and Volume of unit cell

are reported. Further we reported a comparative study of particle size of pure and Cu doped TiO₂ nanoparticles and the strain due to lattice deformation obtained by Uniform Deformation Model (UDM) and Scherer model.

II. METHODS AND MATERIAL

2.1 Material preparation

Titanium tetra isopropoxide (TTIP) and Copper Acetate reagents of analytical grade without further purification were used to prepare pure and Cu doped TiO₂ nanoparticles. To prepare pure and Cu doped TiO₂, TTIP was dissolved into distilled water for 1M solution with continuous stirring for half an hour. Another solution of copper acetate in distilled water was prepared separately for appropriate doping concentration. The solution of copper acetate further added drop wise into TTIP solution for half an hour and the solution was kept for rigorous stirring for 2 hours. The obtained precipitate was filtered and washed with water for several times and found white precipitate. The 30ml H₂O₂ was further mixed with white precipitate and got transparent orange solution. This solution was further diluted with distilled water and color changed from orange to yellow. The solution was kept for 2 days for aging and followed by filtering and washing for several times. Then precipitate was dried in air at 100°C and calcined at 500 to 600°C for 6 hours to obtain Cu doped TiO₂ nanoparticles (x = 0.01, 0.02 and 0.03).

2.2 Characterization

The X-ray diffraction data of synthesized pure and Cu doped TiO₂ samples were recorded on Bruker D8 Advance Diffractometer with Cu-Kα1 radiation (λ=1.5418 Å) and collected over the range 20° < 2θ < 80° at room temperature.

III. RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD graphs of Ti_{1-x}Cu_xO nanoparticles with concentration x = 0.0, 0.01, 0.02 and 0.03 are shown in figure 1. The XRD analysis were determined by X-ray diffractometer (Bruker D8 Advance Diffractometer) with CuKα radiations (λ = 1.5418 Å) in the 2θ range of 20° to 80° at room temperature. The dominant peak is

obtained at 2θ = 25.387 corresponding to (101) plane of TiO₂. Rest of the peaks are at 2θ = 37.889, 48.143, 54.131, 55.081, 68.947, 70.365 corresponds to (004), (200), (105), (211), (116) and (220) respectively. These peaks confirm that the prepared TiO₂ is an anatase tetragonal crystal structure and agree with JCPDS data (73-1764). Further it is observed that in pure TiO₂ samples some peaks of rutile structure are present (2θ = 27.479 and 36.166 corresponds to (110) and (101) respectively is matching with JCPDS data (84-1284)). It may be due to the annealing temperature was at 500°C to 600°C. Yan Hua Peng et al reported that at 600°C temperature mixture of anatase and rutile phase are present [6]. As the Cu concentration increases rutile peaks reduce. It may be due to the active surface area increases by increasing copper concentration and by increasing active surface area rutile converts into anatase phase [7].

The anatase tetragonal lattice parameters such as the distance between adjacent planes in the miller indices 'd' (calculated from Bragg's equation nλ=2d sinθ) and lattice constant 'a' and 'c' calculated from Lattice Geometry equation as shown in equation 1 and 2 [8]. The lattice parameters of pure and Cu doped TiO₂ nanoparticles are summarized in table 1.

$$d^2 = \frac{\lambda^2}{4\sin^2\theta} \Rightarrow \frac{1}{d^2} = \frac{4\sin^2\theta}{\lambda^2} \text{----- (1)}$$

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \text{----- (2)}$$

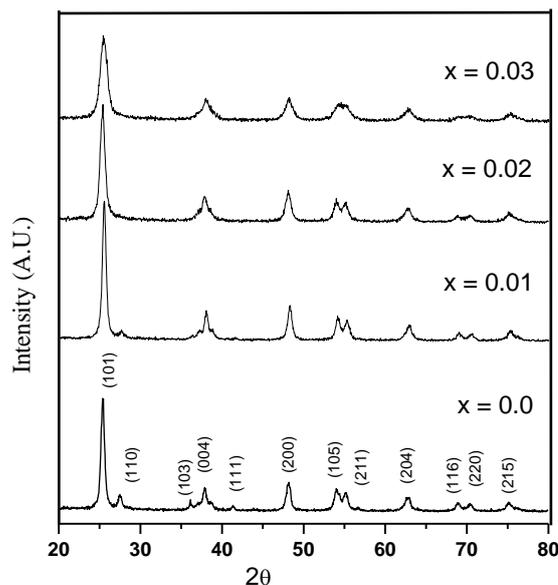


Figure 1: XRD pattern of Ti_{1-x}Cu_xO₂ samples with concentration x = 0.0, 0.01, 0.02 and 0.03.

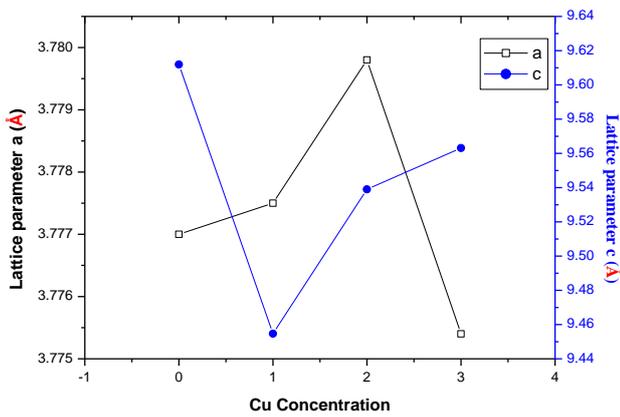


Figure 2: Lattice parameters ‘a’ and ‘c’ versus Cu concentration.

The figure 2 shows the plot between lattice parameters ‘a’ and ‘c’ versus Cu concentration. From the plot it is observed that the lattice parameter ‘c’ decreases rapidly upto 1%, then increase upto 2% and then slowly increases. At the same time the lattice parameter ‘a’ slowly increases upto 1%, then rapidly increases upto 2% and then decreases rapidly. The region behind this we have discussed in our previous article [11]. This may be due to the Cu can exist in Cu^{1+} , Cu^{2+} and Cu^{3+} ions having ionic radii 0.77\AA , 0.73\AA & 0.54\AA respectively and Ti can exist in Ti^{2+} , Ti^{3+} and Ti^{4+} ions having ionic radii 0.86\AA , 0.67\AA , & 0.69\AA respectively. There are random difference between ionic radii of Cu and Ti. The volume of unit cell can be determined by using well known formula

$$V = a^2 c \text{-----} (3)$$

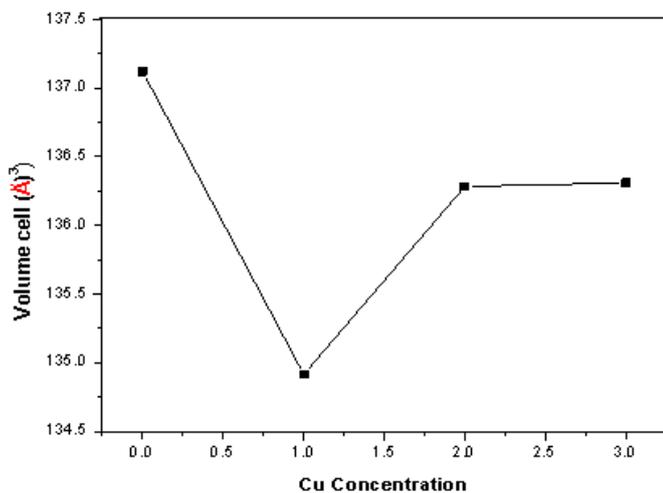


Figure 3: Volume of unit cell versus Cu concentration.

The Volume of unit cell versus Cu concentration is shown in figure 3. It is observed that the volume of unit cell decreases rapidly upto 1% of dopant concentration and then suddenly increases upto 2% and then slightly increase. This random variation of volume of unit cell may lead due to the anisotropic nature of TiO_2 .

The number of unit cell in particle is calculated by using formula given below [9]:

$$N = \frac{4}{3\pi^2} \frac{D}{2V} \text{-----} (4)$$

Where D is particle size and V is volume of the unit cell.

The number of unit cell in particle for pure and Cu doped TiO_2 are listed in table 1.

Table 1: Lattice Parameters of $\text{Ti}_{1-x}\text{Cu}_x\text{O}_2$ samples with concentration $x = 0.0, 0.01, 0.02$ and 0.03 .

Cu Conc. (x)	$d_{(hkl)}$ at $2\theta = 25.4$	Lattice parameter in (Å)		c/a ratio	No. of unit cell per particle	Volume in (Å) ³
		a	c			
0.00	3.505 569	3.77 70	9.61 19	2.54 49	6.524 2	137.1 208
0.01	3.495 683	3.77 75	9.45 47	2.50 29	6.600 5	134.9 139
0.02	3.513 055	3.77 98	9.53 90	2.52 37	8.837 3	136.2 826
0.03	3.503 126	3.77 54	9.56 31	2.53 30	12.25 66	136.3 090

3.2 Particle size and strain

3.2.1 Debye Scherer method

The particle size and lattice strain of the pure and Cu doped TiO_2 sample were calculated by the x-ray line broadening technique using Debye Scherer equation below:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{----- (5)}$$

Where D is the particle size in nanometer, λ is the wavelength of the radiation ($\lambda = 1.5418\text{\AA}$), k is a constant (0.94), β is the peak width at half maximum (FWHM) in radian and θ is the peak position. The particle size (D) and strain were calculated for the major XRD peak (101) using the Scherer's formula (5). The particle size and strain were calculated for pure and Cu doped TiO₂ samples are listed in Table 2.

3.2.2 Williamson Hall method

In order to understand the peak broadening with lattice strains, various peaks appeared in the XRD pattern were used. The Stokes and Wilson [12] formula given in equation (6) were used to calculate the strain induced broadening of the Bragg's diffraction peak.

$$\varepsilon = \frac{\beta_{hkl}}{4 \tan \theta} \quad \text{----- (6)}$$

In addition of Scherer equation and equation (6) results in following equations [8]:

$$\beta_{hkl} = \beta_s + \beta_D \quad \text{----- (7)}$$

$$\beta_{hkl} = \frac{k\lambda}{D \cos \theta} + 4\varepsilon \tan \theta \quad \text{----- (8)}$$

Rearranging the equation (8) gives:

$$\beta_{hkl} \cos \theta = \left(\frac{k\lambda}{D}\right) + 4\varepsilon \sin \theta \quad \text{----- (9)}$$

The W-H plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for Ti_{1-x}Cu_xO samples with concentration x = 0.0, 0.01, 0.02 and 0.03 are shown in figure 4 (a, b, c and d). It is well known that, in the absence of strain in broadening of peak, the $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ plot is expected to be a horizontal line parallel to the $4 \sin \theta$ axis and in the presence of strain in broadening of peak, it should have a non – zero slope. The obtained values of grain size and strain induced in the broadening of the peak are tabulated in table 2. It is observed that the strain values are varying randomly. This may be due to the increment in number of unit cell per particle as a result of substitution of Cu¹⁺, Cu²⁺ and Cu³⁺ ions in Ti site.

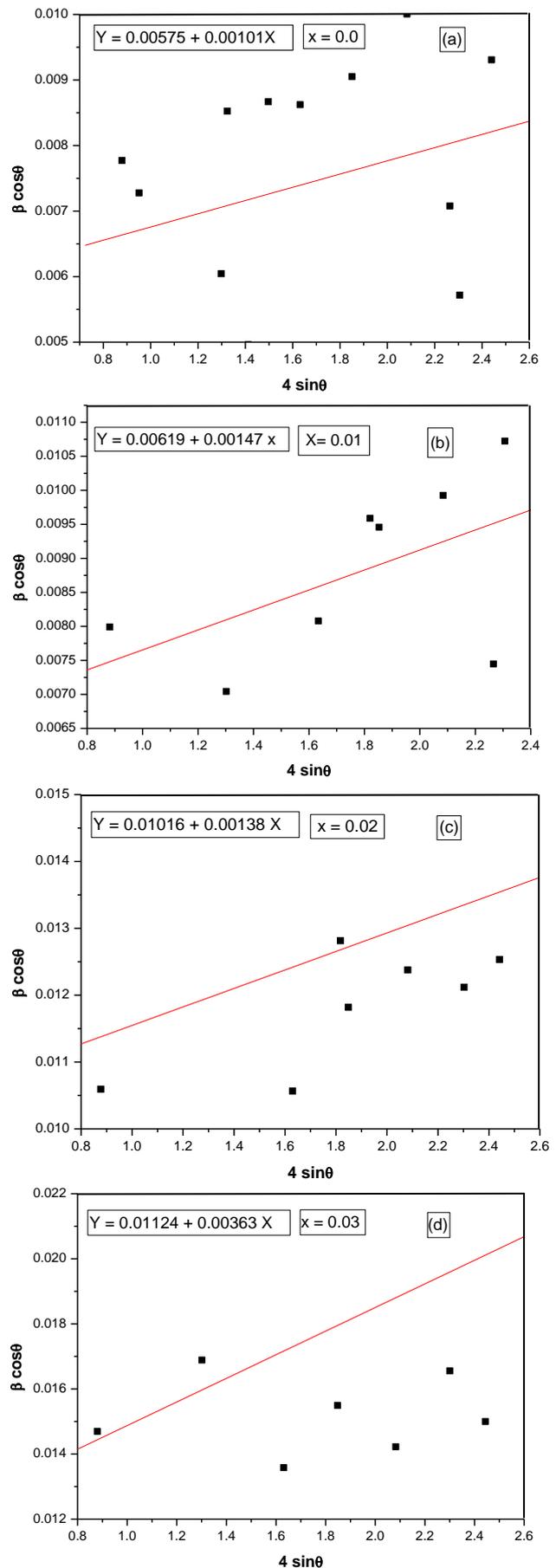


Figure 4: The W-H plot of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$ for Ti_{1-x}Cu_xO₂ samples.

Table 2: Geometric parameters of $Ti_{1-x}Cu_xO_2$ samples with concentration $x = 0.0, 0.01, 0.02$ and 0.03 .

Cu Concentration (x)	Scherer Method D (nm)	Williamson Hall Method	
		D (nm)	$\epsilon \times 10^{-3}$
0.00	17.84	25.20	0.00101
0.01	17.35	23.41	0.00147
0.02	13.09	14.26	0.00138
0.03	9.44	12.34	0.00363

IV. CONCLUSION

It is summarizing that using the co-precipitation method we have successfully synthesized pure and Cu doped ($x = 0.0, 0.01, 0.02$ and 0.03) TiO_2 nanoparticles at room temperature. This method is simple, economic, catalyst free and nontoxic which makes it suitable for various applications. From the XRD analysis it is confirmed that all the samples are good crystalline in nature tetragonal anatase TiO_2 . The lattice parameters calculated are matching with standard values which agree with JCPDS data (73-1764). The grain size and lattice strain calculated by both the techniques are nearly same.

V. ACKNOWLEDGMENT

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