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Micro Strain and Morphological Studies of Anatase and Rutile Phase TiO_2 Nanocrystals Prepared via Sol-Gel and Solvothermal Method - A Comparative Study

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ABSTRACT

Nanocrystals of Titanium dioxide were prepared via sol-gel and solvothermal method. They were characterized by X-ray diffraction and Scanning Electron Microscopy studies. The anatase and rutile phase reflections of the Titanium dioxide nanocrystals were identified by X-ray diffraction data. The micro strain value of the nanocrystals were analysed by W-H plot method. Very small value of micro strain was observed in all the samples. The sample ST-600 shows zero micro strain. The morphology shows increase of size due to agglomeration at higher calcination temperatures.

Key Words: Titanium Dioxide, Anatase, Rutile, W-H Plot, Micro Strain

I. INTRODUCTION

Three crystalline polymorphs occur in Titanium dioxide (TiO_2). They are anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). Rutile is known to be the most stable phase [1]. Among these three phases anatase phase Titanium dioxide (TiO_2) is the most widely applicable material in photocatalysis. The rutile phase TiO_2 is highly applicable in white pigments [2]. Different forms of TiO_2 nanocrystals were produced to change its structures, crystal size, phase, morphology, and surface area using different synthesis techniques. Sol-gel synthesis is the most widely used technique based on the hydrolysis and polycondensation of a metal alkoxide precursor [3]. In solvothermal synthesis, chemical reactions can occur under self-produced pressure at temperature about 250˚C in aqueous or organic media [4]. In this study TiO_2 nanocrystals were prepared via sol-gel and solvothermal method. They were annealed to various temperatures to change the crystalline phase. The prepared and annealed TiO_2 nanocrystals were characterized by X-ray diffraction to identify the crystalline phase. The micro strain values were found out using Williamson-Hall method from X-ray diffraction data. The morphology of the samples was observed by Scanning electron microscope.

II. METHODS AND MATERIAL

2.1 Materials

TTIP ($Ti(OCH(CH_3)_2)_4$, 97%, Aldrich), Isopropyl alcohol (99.9%, RANKEM) ,Toluene (99.8%, HPLC), Deionised water.

2.2 Synthesis of TiO_2 - Sol-gel method

0.5 M of TTIP was added to 100 ml Isopropyl alcohol in a 200 ml beaker. The solution was stirred well for 15 min. Now the p^H value of the mixed solution adjusted to desired value. Then 10 ml of deionised water was taken in a burette and added drop wise to the mixed solution. Now the hydrolysis reaction took place. The TiO_2 nanocrystals were produced in the form of precipitate at the bottom of the beaker. After ageing for 24 hours the precipitate was filtered and dried. The dried TiO_2

nanocrystals were annealed to 600˚C, 800˚C and 1000˚C. The annealed samples were named SG-600, SG-800 and SG-1000. The prepared TiO_2 was named SGP.

2.2 Synthesis of TiO_2 - Solvothermal method

0.5 M of TTIP was mixed with 100 ml toluene in Teflon lined stainless steel autoclave without stirring (200 ml capacity, 80% filling). Then it was heated to 250˚C with a rate of 5˚C/min and maintained up to five hours in an oven. After cooling gradually to room temperature, the obtained precipitate was separated with centrifugal separator, washed and then dried. The collected products were annealed to three various temperatures about 600˚C, 800˚C and 1000˚C. They are named ST-600, ST-800 and ST-1000. The prepared TiO_2 was named STP.

III. CHARACTERIZATION

The crystallographic structures of the TiO2 nanocrystals were determined by using XPERTPRO Powder X-ray diffraction diffractometer. SEM images were taken with JEOL Model JSM-6390LV scanning electron microscope.

IV. RESULTS AND DISCUSSION

3.1 Powder X-ray diffraction analysis

Figure (1) shows the X-ray diffraction pattern of TiO_2 nanocrystals prepared via sol-gel method. Figure (2) shows the X-ray diffraction pattern of TiO_2 nanocrystals prepared via solvothermal method. In general, XRD characteristic peaks at 25.3° and 27.4° are identified as the anatase and rutile phase of TiO_2 nanocrystals, respectively. The samples SG-600, STP, ST-600 and ST-800 shows peak at 25.3°. All these samples are in anatase phase. These data are in good agreement with standard JCPDS (JCPDS 21-1272) of an anatase crystalline phase of TiO_2 nanocrystal. The samples SG-800, SG-1000 and ST-1000 show peak at 27.4° and assigned to rutile crystalline phase. The data of these samples are in good agreement with standard JCPDS (JCPDS 21-1276) of rutile phase TiO_2 nanocrystal. With increasing calcination temperature the width of the peak narrowed [5]. This indicates the degree of crystallinity of samples and the increase in crystallite size.

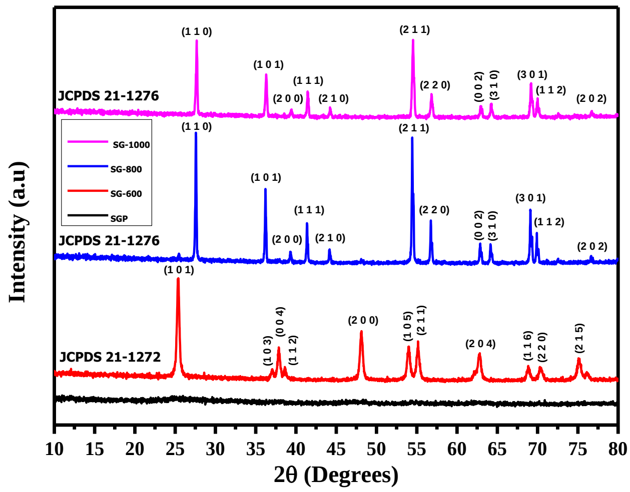

Figure 1. X-ray diffraction data for TiO_2 nanocrystals prepared via sol-gel method

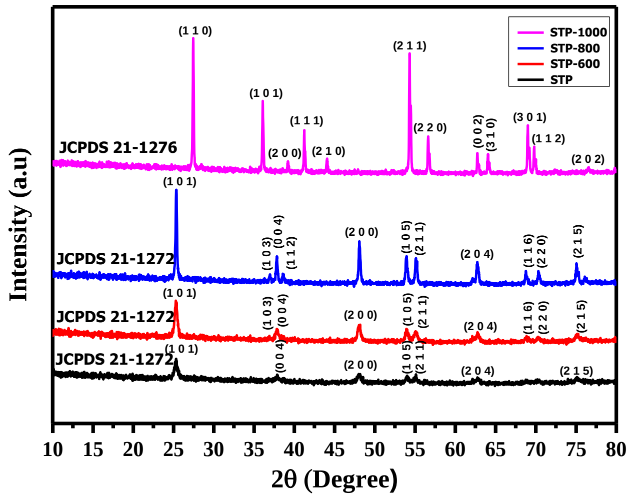

Figure 2. X-ray diffraction data for TiO_2 nanocrystals prepared via solvothermal method

The crystallite size of the TiO2 nanocrystals were calculated by using Scherrer equation,

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the crystallite size, K is the constant and usually taken as 0.89, λ is the wavelength of X-ray radiation, β is the full width at half maximum value of the (1 0 1) peak for anatase phase and (110) peak for rutile phase and θ is the Bragg diffraction angle [5-7]. The calculated crystallite sizes are shown in table 1.

Table 1. Lattice parameter values of TiO_2 nanocrystals

Lattice parameters	Crystalline phase	a(Å)	b(Å)	c(Å)
SGP	Amorphous	-	-	-
SG-600	Anatase	3.7819	3.7819	9.5015
SG-800	Rutile	4.5841	4.5841	2.9507
SG-1000	Rutile	4.5741	4.5741	2.9483
STP	Anatase	3.7838	3.7838	9.5054
ST-600	Anatase	3.7847	3.7847	9.5088
ST-800	Anatase	3.7859	3.7859	9.5136
ST-1000	Rutile	4.5948	4.5948	2.9612

3.2 Micro strain analysis using Williamson-Hall plot (W-H plot)

The strain produced by crystal defects were analyzed by using modified Williamson-Hall equation,

$$\beta \cos\theta = \frac{K\lambda}{D} + 4\,\varepsilon \sin\theta$$

λ is the wavelength of X-ray radiation, β is the full width at half maximum, θ is the Bragg diffraction angle, where D is the effective crystallite size, ε is the effective value of micro strain. A plot is drawn with $4\sin\theta$ along X-axis and $\beta\cos\theta$ along Y-axis. The strain and particle size were calculated using linear fit. The intercept gives the value of D and the slope value gives the value of ε [8].

Table 2. Crystallite size and micro strain values of TiO_2 nanocrystals

Name of the sample	Crystallite size (nm) (Scherrer formula)	Crystallite size (nm) (W–H plot)	Micro strain (ε)
SG-600	30.4	34.8	0.000178
SG-800	69.8	47.5	-0.000536
SG-1000	122	98.3	0.000601
STP	40.5	32.6	0.000547
ST-600	30.4	26.8	0.000022
ST-800	60.8	49.6	-0.000124
ST-1000	69.8	72.6	-0.000092

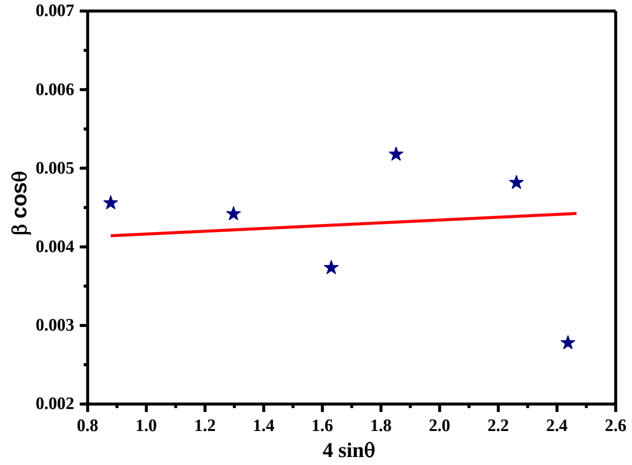

Figure 3. W-H plot for sample SG-600

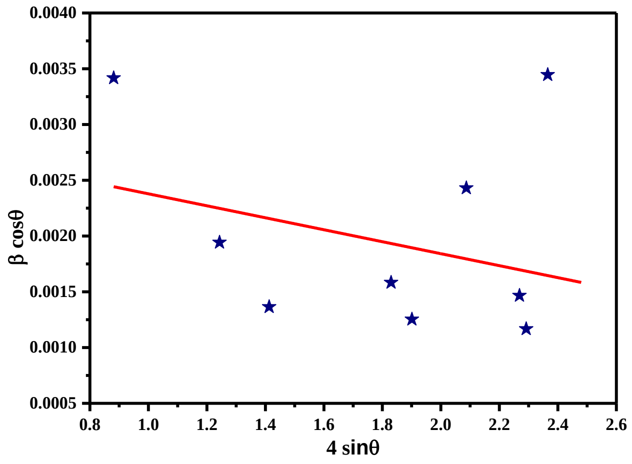

Figure 4. W-H plot for sample SG-800

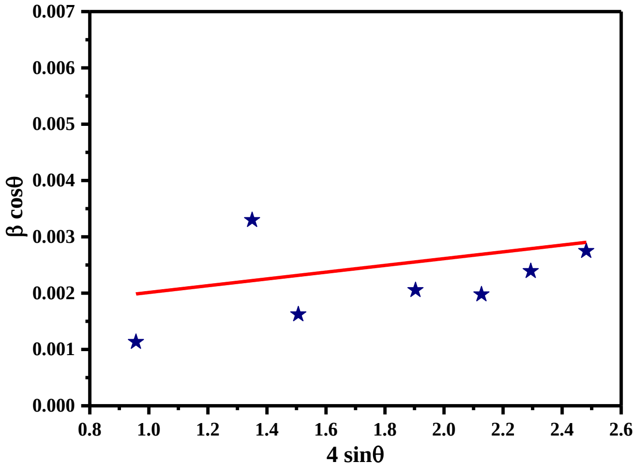

Figure 5. W-H plot for sample SG-1000

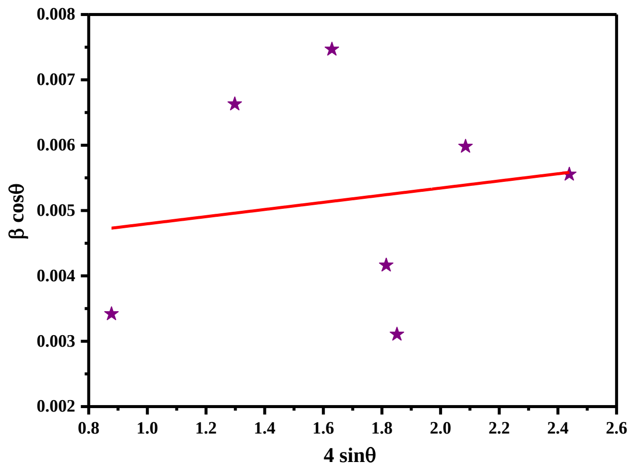

Figure 6. W-H plot for sample STP

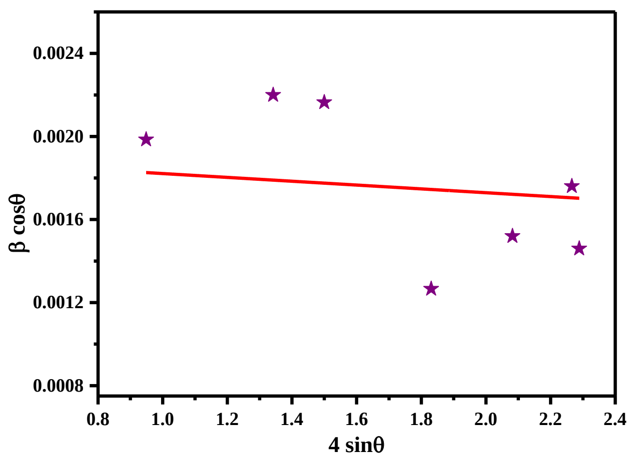

Figure 9. W-H plot for sample ST-1000

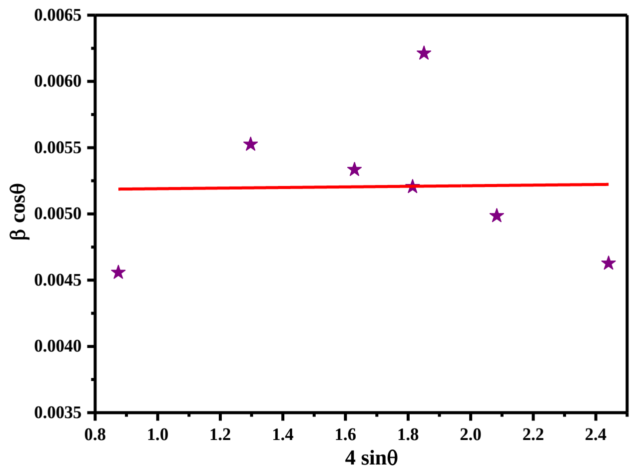

Figure 7. W-H plot for sample ST-600

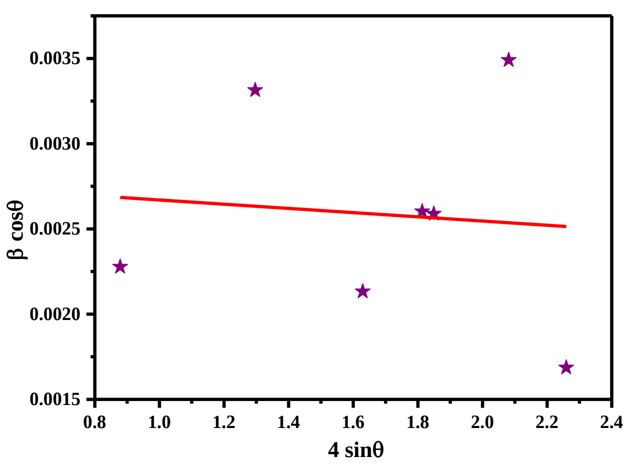

Figure 8. W-H plot for sample ST-800

Figure (3-9) shows the W-H plot for the sol-gel and solvothermally derived TiO_2 nanocrystals. In our samples Sol- gel derived sample SGP is in amorphous form. According to the reports of B. Choudhury and A. Choudhury, the excess number of atoms and defects on the amorphous grain boundary results increases the value of strain. At amorphous grain boundary these defects and excess atoms produce a stress field imposing a strain in the system. At higher calcination temperatures the defects are gradually removed and the size of the crystallite increases. Increase of crystallite size and the removal of grain boundary defects decrease the stress field in that region causing release of lattice strain [9]. Positive slope in the plot indicates that the system is under tensile strain. Negative slope in the plot indicates that the system is under compressive strain [10]. In our samples the W-H plots of samples SG-600, SG-800 and SG-1000 suggest very low strain values due to higher value of calcination temperatures. Also, the lattice constant value of rutile phase SG-1000 is lowered when compared to rutile phase SG-800. A. Maurya and et al. reported that in rutile TiO_2 nanocrystals decrease in lattice constant a(=b) and c indicates the development of tensile strain [10]. This result was confirmed by positive slope of the sample SG-1000. The W-H plots of samples ST-600, ST-800 and ST-1000 show low micro strain value compared to the sample STP. This is due to the release of lattice strain at higher calcination temperatures [9]. The sample ST-600 shows the horizontal slope. This indicates the homogeneity of the nanoparticles. ie, particles free from micro strain [11].

3.3 SEM analysis

The surface morphology of TiO_2 nanocrystals were studied using scanning electron microscope.

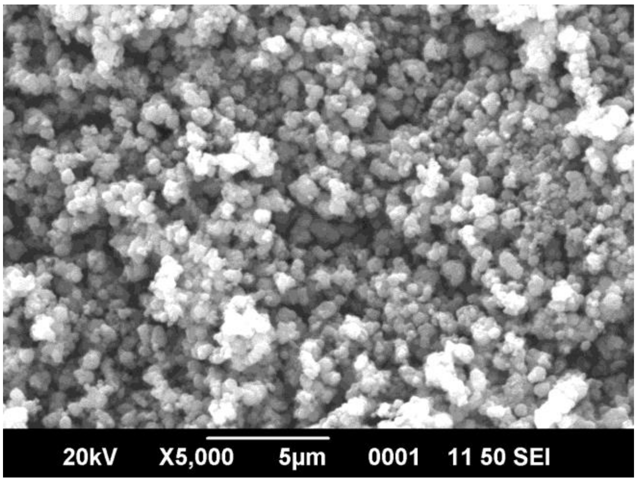

Figure 10. SEM image of anatase phase (SG- 600) TiO_2 nanocrystals

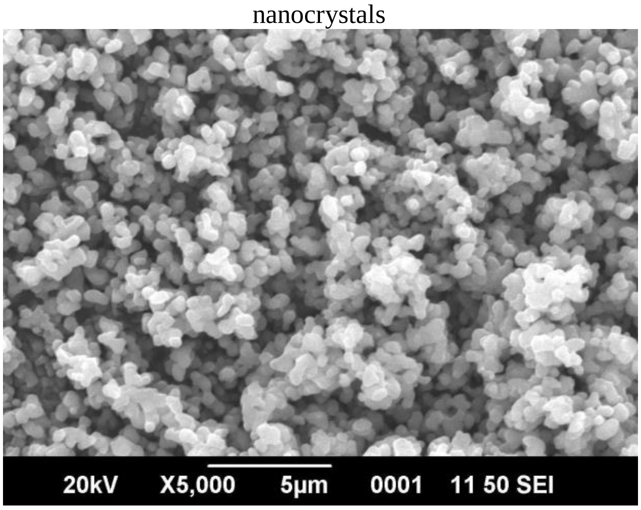

Figure 11. SEM image of rutile phase (SG- 1000) TiO_2 nanocrystals

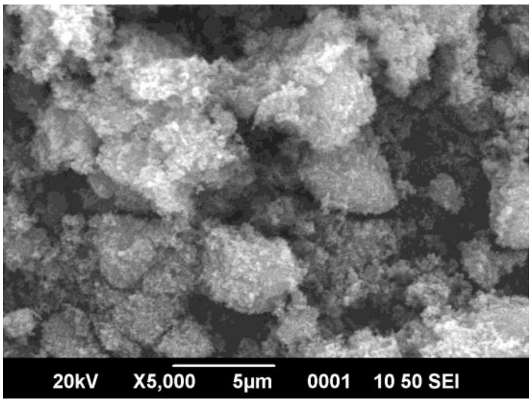

Figure 12. SEM image of anatase phase (STP) TiO_2 nanocrystals

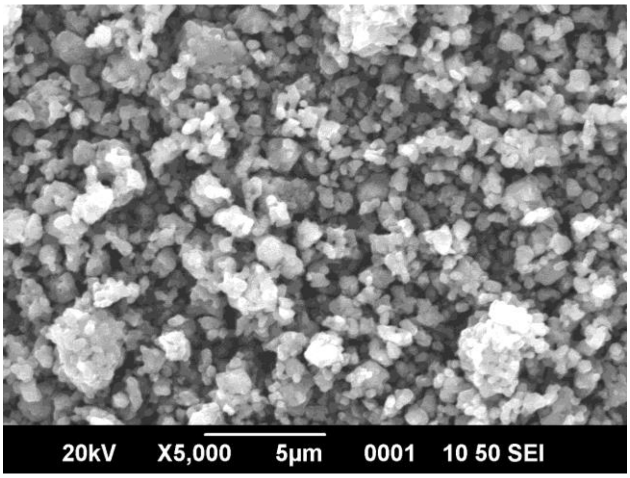

Figure 13. SEM image of rutile phase (ST- 1000) TiO_2 nanocrystals

Figure 10 & 11 show the SEM image of SG-600(anatase) and SG-1000(rutile) TiO_2 nanocrystals. SEM image of anatase phase SG-600 TiO_2 nanocrystals shows that the grains are very smaller in size. SEM image of rutile phase SG-1000 TiO_2 nanocrystals shows that the particles are ordered and agglomerate resulting in increase of particle size. Figure 12 & 13 show the SEM image of STP (anatase) and ST-1000 (rutile) TiO_2 nanocrystals. SEM image of anatase phase STP TiO_2 nanocrystals shows agglomerated particles with bigger size. The SEM image of rutile phase sample ST-1000 shows the morphology of aggregated particles due to higher calcination temperature. From the SEM results it is observed that the grains are uniformly distributed and well-connected together. The SEM investigations of both the preparation methods reveal that the crystallites are in nanometer size [12].

V. CONCLUSION

Nanocrystals of Titanium dioxide were successfully synthesized by sol-gel and solvothermal method using the precursor TTIP. The phases of the synthesized nanocrystals were modified by calcination process. It is very well understand from the observation of the PXRD, the phase transformation of anatase to rutile occurs above 600˚C for sol gel derived TiO2 nanocrystals and above 800˚C for solvothermally derived TiO2 nanocrystals. Also, PXRD analysis reveals that increase in crystallite size with increasing calcination temperatures. The micro strain values of materials were identified from Williamson-Hall plot model and it shows all the samples were very low value of micro strain due to calcination. SEM images suggest the uniform distribution of TiO_2 nanocrystals.

VI. ACKNOWLEDGEMENT

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