Equilibrium state of anatase to rutile transformation for nano-structured Titanium Dioxide powder using polymer template method.

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Abstract.   In this work we report the novel synthesis procedure of phase-pure nano-structured titania in anatase phase using polyacrylamide gel based polymer template method. The evolution of rutile phased titania with increasing temperature has also been investigated. The synthesized nano-materials are characterized using X-ray diffraction, Brunauer - Emmett - Teller surface analysis technique and Scanning electron microscopy. We have used dual phase Rietveld refinement method to analyse the X-Ray diffraction data to get clear picture of crystallographic information of the prepared samples.

1. Introduction

Titanium dioxide also known as Titania (TiO_2) in different polymorphs is an important electronic ceramic material for its potential use in various device applications such as photocatalysis and photovoltics, electrolysis of water to generate hydrogen, dye-sensitised solar cells, gas sensors, purifier of environmental pollutants, ceramic membranes, self cleaning materials etc [1, 2]. Titania show three different polymorphs namely, (i) anatase, (ii) rutile and (iii) brookite. Among these three phases rutile is stable whereas anatase and brookite are metastable phase. Therefore anatase and brookite titania are difficult to synthesize. From crystallographic point of view anatase ($I4_1/amd$) and rutile ($P4_2/mnm$) are of tetragonal crystal structure, whereas brookite ($Pbca$) is of orthorhombic crystal structure [3, 4].

The physical and chemical properties of different polymorphs of TiO_2 are affected by size and related surface effects. The reduction of size down to nano scale induces a marked differences in band gaps, refractive index and the charge transfer characteristics across the granular interface. As a result remarkable improvement of properties, for example photo-catalytic properties in anatase phase can be observed [5]. Literature suggests that enhancement of photo-catalytic activity is even larger for nano-meter sized systems containing mixed polymorphs of TiO_2 [3]. The reason behind this may be the effective separation of charge carriers in the different phases, which suppresses the electron-hole recombination. In brief pure phased polymorphs as well as mixed phased polymorphs of TiO_2 are equally important form the application point of view.

The present work aims to clarify the transformation in between the two main polymorphs of TiO_2 i.e. anatase and rutile. It also clarifies the principle of controlling the compositional phase percentage in a particular TiO_2 sample with different synthesis temperature in gel

template synthesis technique. Keeping these in mind in the present study we have successfully prepared phase pure anatase polymorph of TiO_2 using poly-acrylamide gel based polymer template synthesis technique and thereafter with increasing temperature we have studied the transformation of anatase to rutile phase of titania.

2. Experimenal Details

2.1. Synthesis Technique

Titanium isopropoxide $(Ti(OCH\ (CH_3))_4)$ is taken as the source of titanium. Two and half ml of titanium isopropoxide is added drop wise in a beaker filled with 50 ml of deionized water kept at 4°C under vigorous stirring. Instantaneously yellowish white precipitate of titanic acid $(Ti(OH)_4\ )$ is observed. This precipitates are collected and dissolved in dilute nitric acid keeping temperature of the solution below 4°C. With this clear solution of titanyl nitrate $(TiO(NO_3\ )_2)$ is obtained. Optimized amount of acrylamide, N,N-methylenebisacrylamide are dissolved to this solution and mixed thoroughly. To initiate the gelation 0.5 ml ammonium persulfate (10 wt.%) solution is added and mixed again. The mixture is kept at 40°C in a water bath for 5 h to get acrylamide hydrogel. Acrylamide hydrogel is then heat treated at 300°C for 2 h to get the black network like structure. This network like structure is then ground to get fine powder using mortal pestle and calcined at different temperatures ranging from 450°C to 650°C to obtain TiO_2 samples. Figure.1 is representing the synthesis procedure of nano-crystalline TiO_2 in form of flow chart.
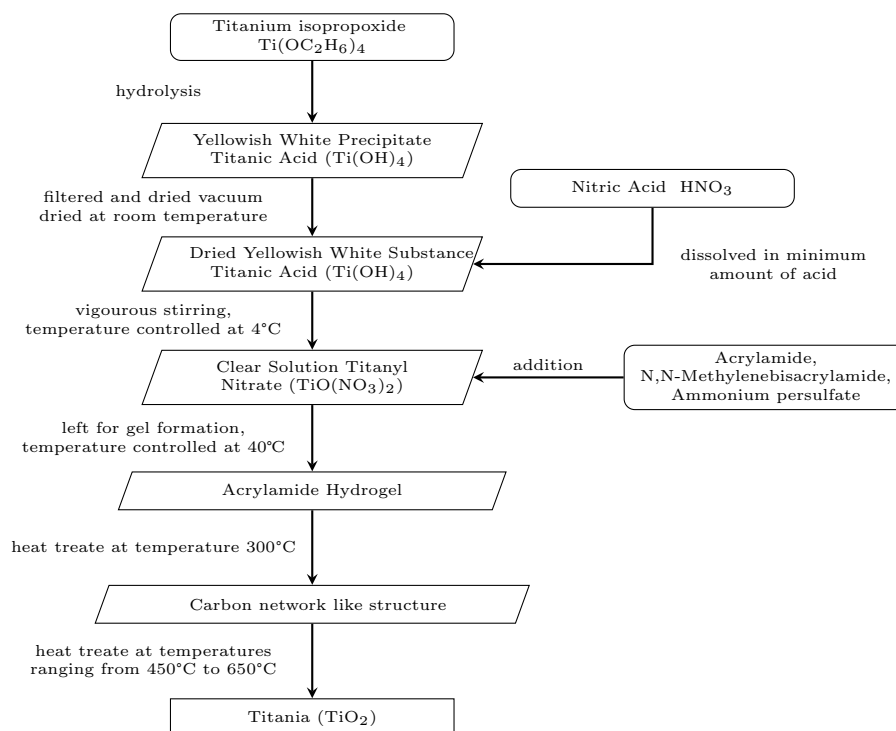

Figure 1. Flow chart for the synthesis of nano-crystalline TiO_2 using polyacrylamide gel template method.

2.2. Characterization Techniques
Crystallographic properties of the synthesized titania samples are investigated using X-ray diffraction (XRD) technique. XRD patterns of TiO_2 samples are recorded using Rigaku Ultima-IV X-Ray diffractometer operated at 40 kV and 40 mA current with Cu $K_{\alpha 1}$ radiation (1.5405Å). XRD patterns are recorded with a scanning step of 0.002° and rate 3° per minute with Bragg angle ranging from 15° to 75°. Surface morphology of the prepared samples are studied with Field Emission - Scanning Electron Microscopy (FE-SEM) micrographs recorded using Nova-Nano FE-SEM. Surface analysis are carried out with Autosorb iQ Quantachrome system. For surface analysis samples are degassed at 200°C for 1 h before commencing the measurement.

3. Results & Discussion
3.1. Crystallographic study
In Figure.2 we have shown the XRD patterns of synthesized TiO_2 samples for different calcination temperatures. The XRD patterns suggests that upto 500°C, only anatase phase of TiO_2 is synthesized, whereas with further increase in temperature the presence of secondary rutile phase of TiO_2 is observed. Again it can be noticed that with increasing calcination temperature the XRD peaks are becoming sharper and stronger, indicating increase in crystallinity for both anatase and rutile polymorphs. The relative intensity of strongest peak of rutile phase (110) is found to increase as compared to the strongest peak of anatase (101) phase of TiO_2. Anatase being a metastable phase compared to stable phase of rutile, any transition from anatase to rutile will be irreversible in nature[3, 6]. From XRD patterns we can conclude that the irreversible transition between anatase to rutile polymorphs of of TiO_2 starts after 500°C.

Rietveld refinement analysis of XRD pattern of titania synthesized at 650°C using FULLPROF package is shown in Figure.3. Similar refinements are carried out for other samples of TiO_2 synthesized at different temperatures. The refined parameters, obtained from Rietveld analysis are presented in Table.1. From Rietveld analysis percentage of rutile phase in the prepared samples are evaluated and found to increase with increase in temperature. At 550°C
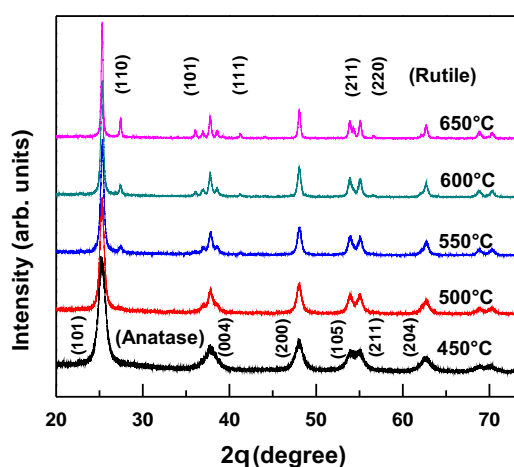

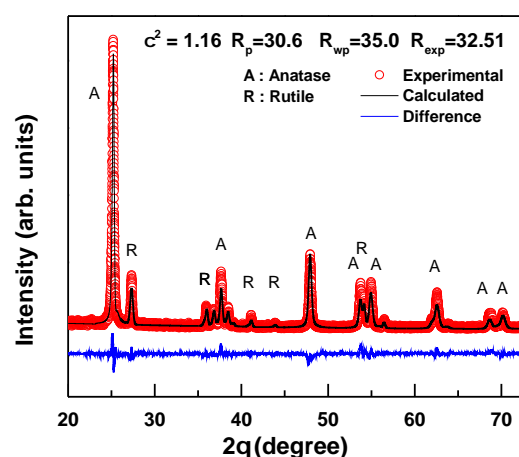**Figure 2.** X-Ray diffracttion pattern for titania synthesized at different temperatures.

Figure 3. The Rietveld refined XRD pattern of titania synthesized at 650°C.

the percentage of rutile phase is 3.29 and it increases to 16.37 percent for sample synthesized at 650°C.

The diffraction profile from polycrystalline materials of all size and shape in different orientation is represented by the Fourier series coefficients which are considered to be the natural characteristic of the profile[7]. According to convolution theorem, the Fourier transform of the nth order pure diffraction profile will be the product of nth order Fourier transform of particle size $A_L^P(n)$, strain $A_L^S(n)$ and faulting $A_L^D(n)$ respectively i.e. $A_L(n) = A_L^P(n) \times A_L^S(n) \times A_L^D(n)$. Consequently,

$$\left[\frac{dA_L}{dL}\right]_{L=0} = \left[\frac{dA_L^P}{dL}\right]_{L=0} = -\frac{1}{p}$$

Here, $L = na$ with a representing the real distance in the crystallite and can be obtained using the following equation

$$\frac{2a(sin\theta_1 - sin\theta)}{\lambda} = \frac{2a(sin\theta - sin\theta_2)}{\lambda} = \frac{1}{2}$$

Here, θ refers to Bragg angle corresponding to peak position of intensity distribution for wavelength λ. θ_1 and θ_2 are Bragg angles corresponding to peak position in the intensity distribution where tail merges in to the background and p is the crystallite size in the crystallographic direction considered [8]. The line broadening parameters of (101) and (200) diffraction lines of anatase are obtained from fitting experimental data with Pseudo-Voigt function. The parameters of Pseudo-Voigt function are then used to calculate crystallite size and crystallite size distribution using BREADTH Programme. Figure.4 show Fourier size coefficients (A_s) of the X-ray line profile versus coherent length for (101) and (200) reflections of anatase TiO$_2$. In the inset of Figure.4 we have shown crystallite size distributions (P_v) for different TiO$_2$ samples. It can be observed that the average crystallite size of the prepared samples increases and the sample become poly-disperse in nature with increasing synthesis temperature.
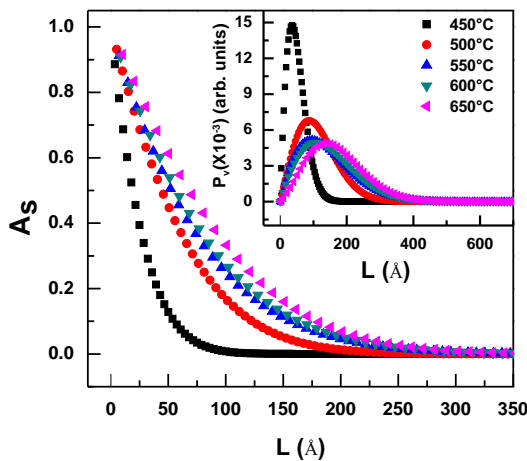

Figure 4. Fourier size coefficients (A_s) of the X-ray line profile versus coherent length for (101) & (200) reflection of anatase TiO$_2$. Inset show volume-weighted domain-size-distribution (P_v) as a function of coherent length.
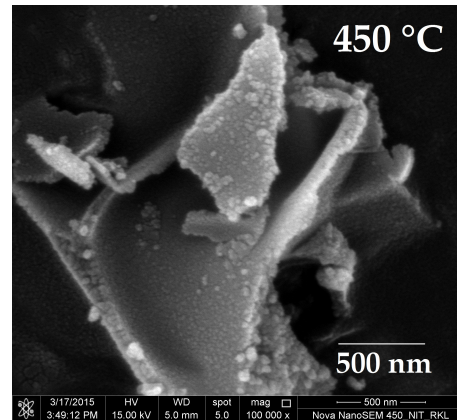

Figure 5. FE-SEM micrographs of titania sample synthesized at 450°C.

Table 1. Rietveld refined structural parameters of TiO_2 samples synthesized at different temperatures obtained using FULLPROF software.

Parameters		450°C	500°C	550°C	600°C	650°C
			$Anatase(I4_1/amd)$			
Lattice Constant (Å)	a	3.7834(6)	3.8026(4)	3.7945(4)	3.7933(3)	3.7916(3)
	c	9.5043(7)	9.5527(3)	9.5341(2)	9.5371(2)	9.5395(2)
Atomic Position	Ti(4a)	0, 0.75, 0.125	0, 0.75, 0.125	0, 0.75, 0.125	0, 0.75, 0.125	0, 0.75, 0.125
	O(8e)	0, 0.75, 0.331	0, 0.75, 0.336	0, 0.75, 0.332	0, 0.75, 0.331	0, 0.75, 0.338
Phase Percent		100	100	96.71	92.16	83.63
			$Rutile(P4_2/mnm)$			
Lattice Constant (Å)	a	–	–	3.7945(4)	3.7933(3)	3.7916(3)
	c	–	–	9.5341(2)	9.5371(2)	9.5395(2)
Atomic Position	Ti(2a)	–	–	0, 0, 0	0, 0, 0	0, 0, 0
	O(4f)	–	–	0.311, 0.311, 0	0.311, 0.311, 0	0.303, 0.303, 0
Phase Percent		0	0	3.29	7.84	16.37
χ^2		1.85	1.77	1.30	1.13	1.16

3.2. Surface morphology

Surface morphology and surface properties are studied using microscopy and BET analysis respectively. Figure.5 show the TiO_2 sample prepared at 450°C. FE-SEM micrographs of the synthesized samples reveal the flake like structure of prepared TiO_2 samples. Adsorption and desorption isotherm of TiO_2 samples prepared at 500°C are shown in Figure.6. On analysing with multipoint Brunauer - Emmett - Teller (BET) technique the effective surface area of the TiO_2 sample prepared at 500°C is found 39.876 m^2/g. With density functional theory [9] method applied to the adsorption and desorption isotherm confirms the highly porous nature of the samples with half pore width 21.714 Å. This is in close agreement with different literature producing nano-crystalline TiO_2 without any stabilizer in various other synthesis techniques[10, 11].
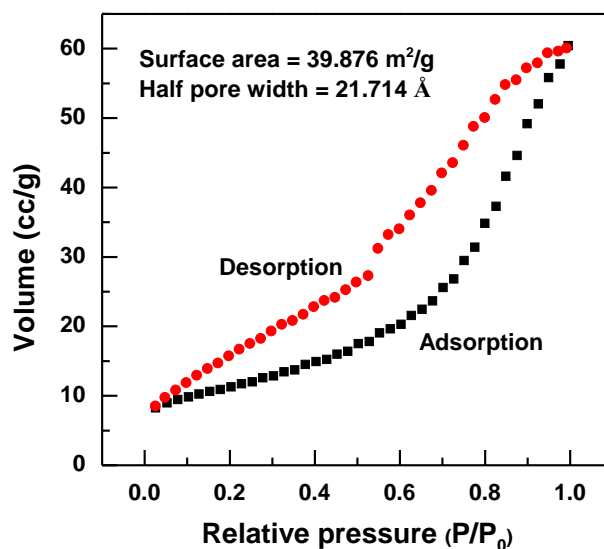
Figure 6. Adsorption and desorption isotherm of TiO_2 samples prepared at 500°C.

4. Conclusion

A series of titania samples are prepared using poly-acrylamide gel template method with different calcination temperatures ranging from 450°C to 650°C. X-Ray diffraction reveal upto 500°C temperature pure anatase polymorph of titania is synthesized whereas at temperatures beyond 500°C synthesis temperature a mixed phased titania of anatase and rutile is obtained. It is found that metastable anatase phase starts transforming to stable rutile phase at elevated temperatures. Size distribution of the synthesized nano-crystalline samples are analysed with Fourier technique and a good agreement is found between XRD and Microscopic analysis. Poly-acrylamide gel template synthesis technique provides ease in processing technique. In addition to this it also helps in controlling the percentage of different polymorphs of titania in a particular sample which is essential for large scale industrial and commercial applications of TiO_2 based systems.

Acknowledgments

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