XRD and SEM Studies on Annealed Nanocrystalline Titanium Dioxide Powder

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ABSTRACT

Nanocrystalline (nC) Titanium dioxide powder with the average grain size of 30nm was annealed at various temperatures between 150 and 1200^{o}C. Resulting change of phases was analyzed by XRD and SEM techniques. On annealing till 600^{o}C an improvement in crystallinity of anatase phase is observed. Scherrer's formula was used to calculate the particle size from the FWHM of the characteristic peaks which were found to be in agreement with the calculated values from a computer program. The program also calculated the lattice constants and the percentage of anatase and rutile phases. The phase transformation process begins above 600^{o}C and a complete transformation to rutile phase is observed at 900^{o}C. This makes it possible to adjust the relative ratio of anatase and rutile. It is observed that the particle size of both phases increase with annealing temperature. SEM micrographs show that the particles agglomerate into larger clusters with increasing temperatures.

Keywords: Titanium dioxide, XRD, SEM, Anatase-Rutile transformation

1 INTRODUCTION

Titanium dioxide has been studied for nearly a century for its many interesting and useful properties. Being non-toxic it has found wide applications in paints, pigments, cosmetics and medicine. However, more recently with the advent of nanotechnology there has been a renewed interest in the study of titanium dioxide both in the thin film and powder form. Apart from its use in such exciting fields like; photo-catalysis [1], splitting of water to produce hydrogen [2], it is also used as an electrode material in the third generation solar cells like the Dye Sensitized Solar Cells (DSSCs) and Extremely Thin Absorber (ETA) Solar Cells [3,4]. Amongst various techniques, nanocrystalline powder suspended in an organic liquid is used to fabricate these mesoporous electrodes by the doctor's blade method [5]. The deposited film of nanocrystalline powder is then thermally treated to produce the desired phase or a mixture of phases to optimize the electrode performance. For solar cell applications anatase phase titanium dioxide mesoporous photo-anodes are a popular choice. Anatase phase has a wide bandgap of 3.2eV and admits a larger portion of the solar spectrum enhancing the cell performance.

Titanium dioxide has three main polymorphs namely; brookite, anatase and rutile. [6]. Experiments have demonstrated that photo-anodes fabricated with a mixture of anatase and rutile in the ratio 85: 15 yield electrodes with a lower resistance. This has been attributed to better carrier transport properties of rutile which give a lower resistance to the electrodes. It has also been demonstrated that different ratios of anatase and rutile phase titanium dioxide can determine the band structure and the movement of solar generated carriers in the composite electrodes. [7]. Likewise, the photo-catalytic performance of anatase phase is dramatically enhanced by the addition of rutile phase by enhancing the charge carrier transfer in the photo-catalytic process. Photo-splitting efficiency of water has been shown to increase by using a mixture of anatase and rutile phases of titanium dioxide over pure anatase phase [7]. It has also been reported that for improved efficiency the two phases (anatase and rutile) should be in good physical contact to facilitate an efficient charge transfer from anatase to the rutile phase [8]. The conduction band of anatase is 0.1eV higher than the conduction band of rutile which helps in the transfer of electrons. Experimentally it is well established that a mixture of anatase and rutile phases of titanium dioxide results in improved performance in a wide variety of applications of nanocrystalline titanium dioxide.

In the study reported here attempts have been made to produce a mixture of anatase and rutile phases, in a specified ratio, by annealing the nanocrystalline powder of titanium dioxide at appropriate temperatures.

2 EXPERIMENTAL

99.9% pure nanocrystalline titanium dioxide powder with an average grain size of 30nm was obtained from Alpha Aeser Company. The as supplied powder which contained a mixture of 90% anatase phase and 10% rutile phase was used as the starting material. The nC-powder samples were subjected to a wide range of annealing temperatures from 150^{o}C to 1200^{o}C in air in an oven at a heating rate of 5^{o}C/min. The resulting powder was analyzed by XRD technique to determine and verify the existence of anatase and rutile phases, particle size and lattice constants. XRD spectra were taken on a Rigaku Ultima – IV multipurpose diffractometer. The existence of phases was identified from the characteristic peaks. Scherrer's formula, using the Full

Width Half maximum (FWHM) of the characteristic peaks, was used to calculate the particle size for respective phases. SEM images were used to study the surface morphology and how the morphology changes with annealing temperature. A Jeol JSM-7600F micrograph was used for this purpose. A computer program "PDXL Version 2 Software" was used to determine the particle size, reflection planes, lattice parameters and the percentage of both anatase and rutile phases at different annealing temperatures.

3 RESULTS AND DISCUSSION

3.1 Phase transformation

Fig 1 shows the XRD spectra for the nanocrystalline powder annealed between 150 and 600°C. The spectra shows characteristic peaks which occur at 2θ = 25.25°, 36.93°, 37.78°, 38.56°, 48.03°, 53.85°, 55.05°, 62.79°, 68.79°, 70.19° and 75.02° corresponding to the (101), (103), (004), (112), (200), (105), (211), (213), (116), (220) and (215) planes of the anatase phase according to the Joint Committee on Powder Diffraction Standards (JCPDS) file No: 21-1272. Small characteristic peaks at 2θ = 27.44°, 36.09° and 54.30° corresponding to (110), (101) and (211) planes of the rutile phase according JCPDS file No. 21-1276 are also observed [9]. It can be observed from the XRD spectra that for temperatures less than 600°C the major component is the anatase phase with a small fraction of rutile phase.

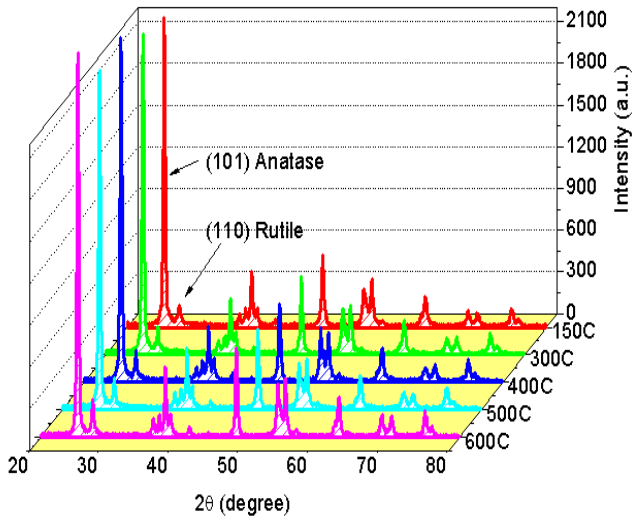

Figure 1: XRD spectra of nC-TiO2 powder annealed at temperature range 150 – 600C

The structural (phase) transformation of the nanocrystalline powder over the temperature range 600 to 900°C is shown in fig 2

It is seen that with increasing annealing temperature the fraction of anatase decreases and that of rutile increases.
The behaviour of two prominent peaks of anatase and rutile phases which occur at 2θ = 25.3° and 2744° corresponding to reflections from (101)A and (110)R planes respectively has been analyzed here in fig 2 in some detail to study the phase transition. These two peaks are plotted on an expanded scale in fig 2 to compare their relative magnitudes as a function of annealing temperature. A closer look at the spectra of the annealed samples indicate that for temperatures lower than 600°C anatase is the major component with a small fraction of the rutile phase indicated by a very small (110) peak at 2θ = 27.44°..

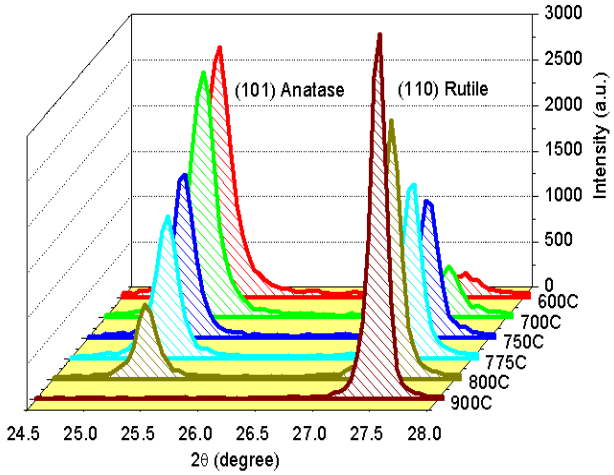

Figure 2: Main characteristic peaks of anatase and rutile phases between the transition temperatures 600 to 900C

Further increasing the annealing temperature causes the rutile phase to grow more rapidly at the expense of anatase phase. The amplitude of the anatase peak (101) rapidly decreases while the (110) rutile peak continues to increase. Above 900°C no anatase peak is visible signaling the complete conversion of anatase to rutile phase. This is confirmed by the XRD peaks at 2θ = 27.44°, 36.09°, 39.27°, 41.28°, 44,08°, 54.37°, 56.67°, 62.81°, 64.10°, 69.06°, 69.83°, 76.59° and 79.89o corresponding to (110), (101), (200), (111), (210), (211), (220), (002), (310), (301), (112), (202) and (210) planes. [JCPDS Card No: 75-1755]. The observed conversion temperature is in agreement with those reported by other workers [10].
The percentage of the rutile phase has been determined from the respective prominent peaks of the two phases using the computer program "PDXL Version 2 Software". The percentage of rutile phase is shown plotted in figure 3 as a function of annealing temperature. It can be seen that the initial ~10% component of the rutile phase increases very slowly initially. However, at 700°C a very rapid transformation takes place reaching a complete transformation at 900°C

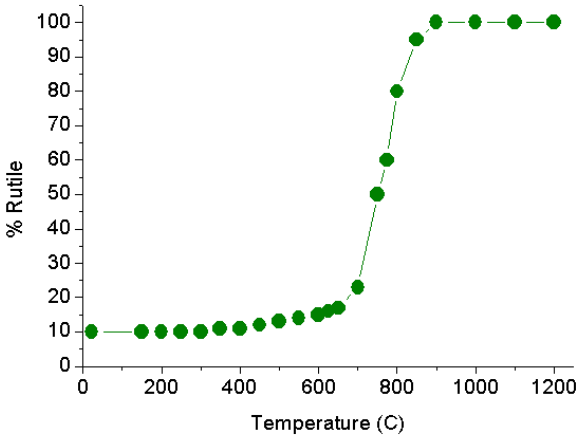

Figure 3: Percentage of rutile phase as a function of annealing temperature.

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3.2 Particle size and lattice parameters

Particle size of the titanium dioxide powder has been calculated over the full range of annealing temperatures using Scherrer's formula and the computer program "PDXL Version 2 Software". The temperature range covers both phases. According to the Scherrer's formula the average particle size d is given by [11];

$$d = K\lambda / \beta \cos\theta$$

Where K is the size factor and usually taken as 0.9, λ is the wavelength of X-rays which in the present case is 0.154nm for Cu-α line, β is the Full-Width-Half-Maximum (FWHM) of the diffraction lines and θ is the angle at which diffraction occurs. FWHM has been derived from the main peaks (101)A and (110)R for the anatase and rutile phases respectively. The calculated values and those determined from the computer program are in close agreement.

The values determined from the computer program are plotted in fig 4. It can be seen that the particle size is around 30nm for both phases up to nearly 600°C. For annealing temperatures beyond 600°C particle size for both phases increase more rapidly. Particle size for anatase phase increase up to 800°C at which point it converts into rutile phase and ceases to exist. Particles size for the rutile phase however, continues to increase rapidly reaching a size of 85nm at 1200°C.

Lattice parameters (a and c) of anatase and rutile phases, both of which have the tetragonal structure, were determined from the XRD data using the computer program "PDXL Version 2 Software". These were found to be in good agreement with reported values in standards data in JCPDS 89-4291.These are shown in table 1 for both anatase and rutile phases.

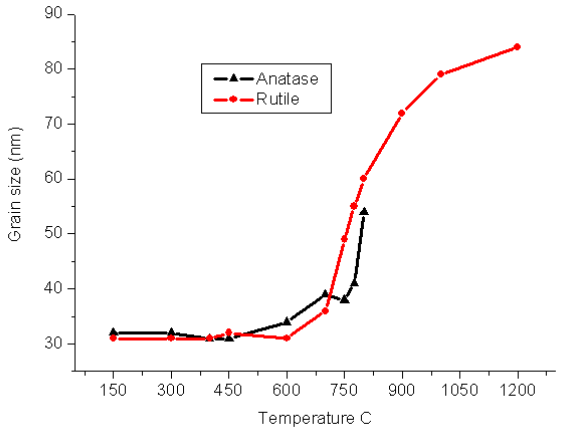

Figure 4: Grain size of anatase and rutile phases as a function of annealing temperature

Temp.	Anatase		Rutile	
T (C)	a (A)	c (A)	a (A)	c (A)
150	3.786	9.51	4.59	2.9532
200	3.774	9.5	4.6107	2.9552
250	3.785	9.509	4.5888	2.9578
300	3.7851	9.512	4.6054	2.9609
350	3.7851	9.501	4.5948	2.9563
400	3.775	9.44	4.6113	2.9588
450	3.7867	9.508	4.596	2.9575
550	3.7824	9.508	4.6	2.9596
600	3.7854	9.506	4.5946	2.9579
650	3.7833	9.508	4.959	2.958
700	3.783	9.491	4.594	2.9578
750	3.7853	9.5079	4.5914	2.9574
775	3.7849	9.507	4.591	2.9575
800	3.7854	9.5099	4.5932	2.9586
900	Does not exist		4.5899	2.9572
1000	Does not exist		4.5902	2.9575
1200	Does not exist		4.5875	2.9574

Table 1: Lattice constants for anatase and rutile phases at different temperatures

3.3 Surface morphology

The changing particle size determined from the XRD studies are supported by the SEM images given in fig 5; a, b, c and d.

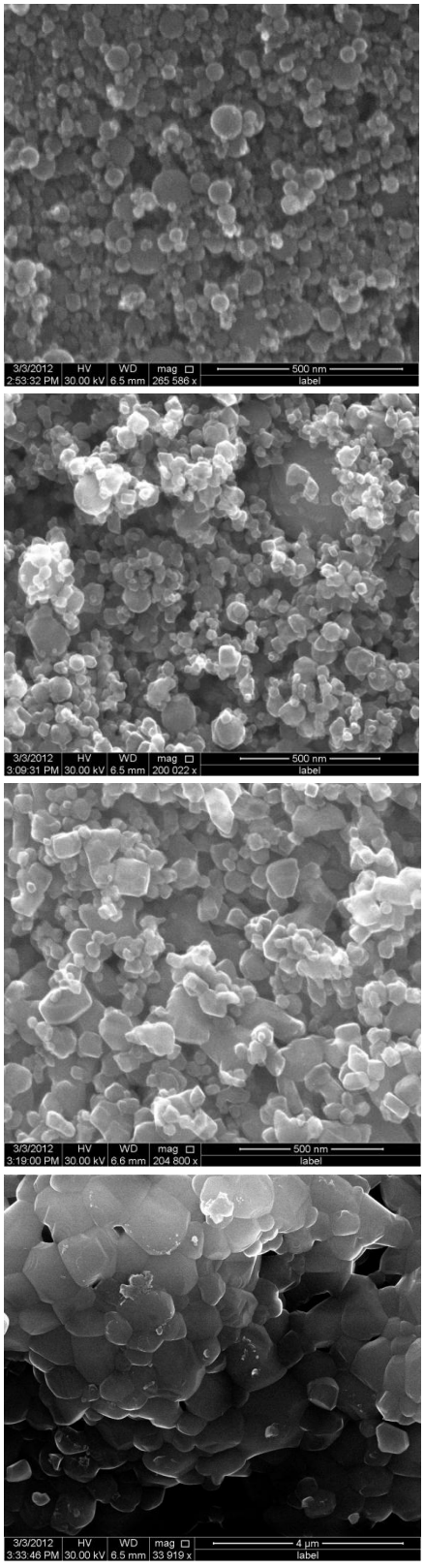

Figure 5: SEM images of nC TiO2 powder annealed at (a) 400°C (b) 700°C (c) 800°C (d) 1000°C

The images show the particle size for powder annealed at 400, 700, 800 and 1000°C. The increase in the size of the particles from 400°C anneal till 700°C anneal is relatively small. However, for 800°C anneal the particle appear to agglomerate into larger clusters. This is accompanied by the decrease of the anatase phase. Atoms constituting this phase reorient themselves around the particles of rutile phase which grows at the expense of anatase phase. On increasing the annealing temperature further to 1000°C rutile particles tend to coalesce into a continuous structure with increased crystallinity. This inference is supported by the successive decrease in FWHM values of rutile peaks with increasing annealing temperatures

4 CONCLUSIONS

XRD analysis of the annealed nC-TiO_2 powder has clearly demonstrated that it is possible to tune the anatase-rutile ratio in nanocrystalline titanium dioxide powder by annealing at precisely controlled temperatures. Anatase-rutile mixture of nC-TiO_2 powder undergoes 100% transformation to rutile phase around 900°C. Also, the particle size of the rutile phase increases and later agglomerates into a continuous matrix

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