# THE EFFECT OF ANNEALING TEMPERATURES ON PHASE AND OPTICAL PROPERTIES OF $TIO_2$ NANOPARTICLES FOR SOLAR CELL APPLICATIONS

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**Abstract**

In this research work, effect of annealing temperatures on different properties of $TiO_2$ nanoparticles is being reported for Solar Cell applications. The nanoparticles were synthesized using Sol Gel Method. The solution of ethanol and distilled water was poured drop-wise into the solution of Titanium Butoxide ($Ti(OC_4H_9)_4$) and Hydrochloric Acid (HCl). The precursor of nanoparticles was annealed at 200$^o$C, 450$^o$C and 650$^o$C. The structure and phase determination was obtained using XRD analysis which confirmed very small crystallite size in the range of 6nm to 18nm and amorphous to anatase to rutile transformation with increased in annealing temperatures. UV-Vis spectroscopy helped in studying the influence of temperature on absorption, transmission and reflection with a remarkable red shift. The study revealed that the band gap decreases with increasing temperature.

**Keywords:** XRD, UV-Vis, $TiO_2$.

## Introduction

$TiO_2$ is a semiconductor having wide band gap [1] and high refractive index [2]. It is widely being studied due to its numerous applications especially in the field of optics [3]. It is found in three phases; brookite, anatase and rutile [4]. Among these three phases, rutile is the most stable phase. With the increase in annealing temperatures, $TiO_2$ transformed from amorphous to anatase to rutile phase [5].

$TiO_2$ can be used in nearly all types of solar cells. In organic solar cells, $TiO_2$ thin film can be used as hole blocking layer, due to which increase in efficiency of hybrid solar cells has been reported [6]. Increase in efficiency is also reported for ordered $TiO_2$ nano-layers, as charge transportation problem occurs in random networks [7]. Stability of solar cells can be affected by thickness of $TiO_2$ thin films. These films also act as UV blocker [8] due to high absorption % in UV region. Layer thickness less than 500 nm is unable to stop UV rays from going inside the inverted organic solar cell which can degrade it, but thicker thin film [9] decreases charge transportation. Porous layer of $TiO_2$ nanoparticles is used in dye sensitized solar cells. Dye is used in these type of solar cells to generate photoelectrons [10].

In this research work, $TiO_2$ nanoparticles are prepared using sol gel method. Then effect of annealing temperature is investigated by various characterization techniques such as XRD and UV-Vis Spectroscopy which can be utilized for fabrication of different types of organic solar cells.

## Experimental

Nanoparticles of $TiO_2$ were synthesized using sol gel method. The starting materials were Titanium Butoxide ($Ti(OC_4H_9)_4$) and Hydrochloric Acid (HCL) acted as a catalyst, both were mixed in the ratio of 13:0.8 to form a solution. Another mixture of ethanol ($C_2H_5OH$) and distilled water was prepared in the ratio of 55: 2.5 respectively [11]. Mixture of ethanol and water was added drop wise in Titanium Butoxide and Hydrochloric Acid solution with the help of pipette. Then stirring for 2 hour was done at $50^0$C in nitrogen atmosphere for 2 hour. Then aging of sol was carried out for 24 hours at room temperature giving very fine gel network. After that gel was filtered and washed in ethanol and deionized water. Then 1 hour heat treatment, at $100^0$C, was given to gel for drying it. In last step, precursor was annealed at $200^o$C, $450^o$C and $650^o$C for 1 hour to obtain $TiO_2$ nanoparticles.

Structural and phase analysis was performed using "X'Pert PRO MPD X- ray Diffraction System, PANalytical Company Ltd, Holland". Optical data was acquired using Genesys 10S UV-Vis Spectrophotometer.

**Results and Discussion**

Structural Properties

Combine XRD patterns of $TiO_2$ Nanoparticles are shown in Fig. 1.The broad peaks for $200^o$C signifying very small crystallite size and presences of amorphous factor. Moreover, all peaks are of anatase phase except one peak (121) of brookite phase[12].There is no rutile phase peak present at $450^o$C but almost pure anatase phase with tetragonal structure has been observed matching with JCPDS (Anatase, 01-0562).With increasing temperature, brookite peak has been significantly reduced [13]. Where rutile phase starts emerging near $650^o$C with the diminishing of brookite phase totally [14], matching with JCPDS (Rutile, 78-1510). Crystallite size is increasing with increase in temperature; also sharpness of peaks is improving presenting that material is becoming more crystalline. Crystallite size of $TiO_2$ is calculated using Scherer formula: $D = \frac{K\lambda}{\beta \cos\theta}$, where K is machine constant, λ is the X-Ray wavelength, β is the full width half maximum, D is the crystallite size and $\theta$ is the Bragg diffraction angle. Crystallite size goes from 6nm to 18nm as temperature increases from $200^o$C to $650^o$C.

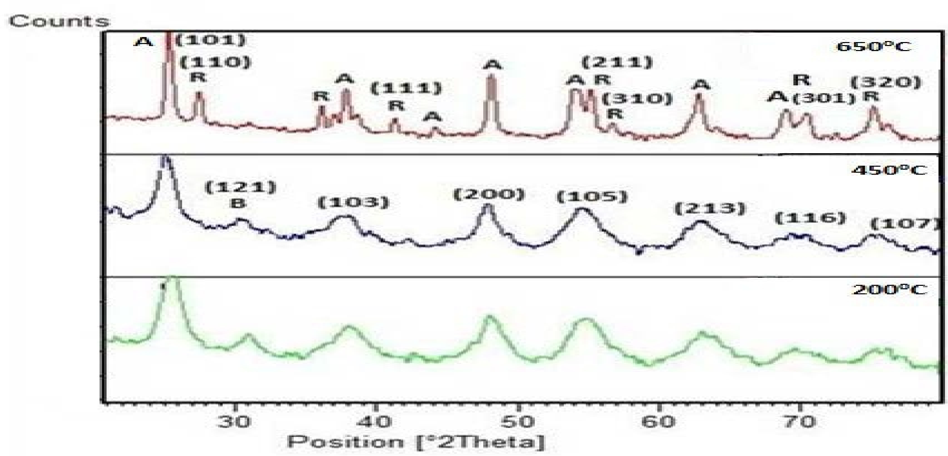


*Fig.1: Combined XRD pattern of $TiO_2$ Nanoparticles showing effect of annealing temperatures*

**Optical properties**

Optical properties are studied by UV- Vis spectroscopy by using UV-Vis spectrophotometer.

Fig. 2(a) showing that with the increase in temperature absorption increases. Moreover, in the UV region, absorption percentage is very high in comparison with visible region, due to which $TiO_2$ can be used as UV blocker in inverted organic solar cells which avoid solar cells from degradation as UV rays are so energetic cells [15].It improves stability of solar cells. The red shift appearing at absorption margin is due to the appearance of rutile phase at 650°C [16].

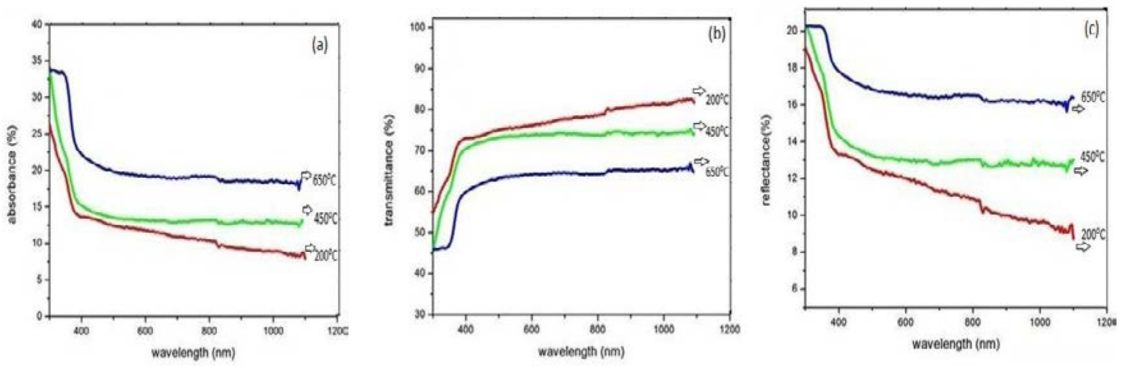


Fig. 2: (a) Graph between absorbance % and wavelength (nm). (b) Graph between transmittance % and wavelength (nm). (c) Graph between reflectance% and wavelength (nm), at various calcinations temperatures 200°C, 450°C and 650°C

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Fig. 2(b) showing that transmission is decreasing with the increase in annealing temperature. At 650°C, near absorption margin red shift appears.

Fig. 2(c) showing that reflection % increases with the increase in temperature but its values are smaller than absorption and reflection percentage values, that's why $TiO_2$ coatings can be used as antireflection coatings particularly in inorganic solar cells.

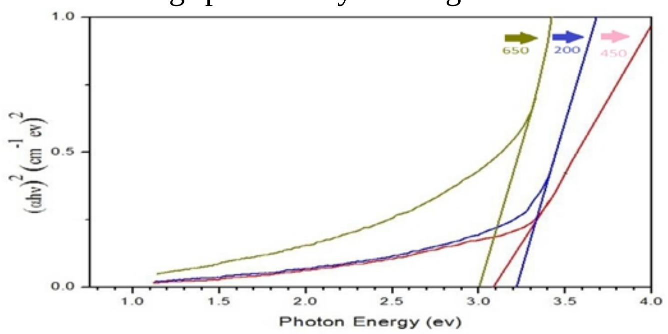


Fig.3 shows the decrease in band gap with increase in temperature

Direct band gap $E_g$ is calculated by using tauc equation which is given below

$$\alpha = k (h \upsilon - E_g)^{1/2} / h \upsilon$$

α is the absorption co-efficient, h υ is the photon energy and , k is the constant,

Extrapolation of straight line of $(\alpha h \upsilon)^2$ vs. h υ curve helped in band gap calculation. It can be seen in Fig.3 that band gap is decreasing from 3.2 ev to 3.0 ev while going from 200°C to 650°C due to effect of quantum confinement.

**Conclusion**

Very small crystallite size is achieved like 6 nm. Confirmation of phase conversion from amorphous to anatase to rutile and increase in crystallite size with increase in temperature was observed by XRD. UV absorption in UV region confirmed $TiO_2$ use as UV blocker. Its thin films can be used for antireflection coatings in solar cells as well as other applications due to less reflectance values than absorption and transmission. Moreover, absorbance increases with increase in temperature. Also band gap decreases from 3.2 ev to 3.0 ev while going from 200$^o$C to 650$^o$C.

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