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# Effect of annealing on $TiO_2$ nanoparticles

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ABSTRACT

$TiO_2$ nanoparticles have been prepared by simple chemical precipitation method and annealed at different temperatures. The as-prepared $TiO_2$ are amorphous, and they transform into anatase phase on annealing at 450 °C, and rutile phase on annealing at 900 °C. The X-ray diffraction results showed that $TiO_2$ nanoparticles with grain size in the range of 21–24 nm for anatase phase and 69–74 nm for rutile phase have been obtained. FESEM images show the formation of $TiO_2$ nanoparticles with small size in structure. The FTIR and Raman spectra exhibited peaks corresponding to the anatase and rutile structure phases of $TiO_2$. Optical absorption studies reveal that the absorption edge shifts towards longer wavelength (red shift) with increase of annealing temperature.



## 1. Introduction

Titanium dioxide or Titania, ($TiO_2$) is of great interest in technological applications due to its morphology and crystalline phase. $TiO_2$ exists in three different phases' i.e., anatase, rutile and brookite. The active crystallite phases of $TiO_2$ are anatase and rutile [1,2] although brookite $TiO_2$ was occasionally reported [3–5]. $TiO_2$ has been widely studied regarding various electronic applications, utilizing the photocatalytic nature and transparent conductivity, which strongly depend on the crystalline structure, morphology, and crystallite size [6]. Due to the photosemiconductor properties of $TiO_2$, it may find applications as antibacterial agents for the decomposition of organisms [7,8]. Titania is able to kill microorganisms; therefore it is used as a biocide [9–11]. The photocatalytic activity of $TiO_2$ nanoparticles is mainly determined by its crystalline phase (anatase and rutile), crystallite size, specific surface area, pore structure, and crystallinity [12–18]. The chemical precipitation method is one of the attractive powder synthesis methods, because it is possible to produce nanoparticles with high specific surface area and improved crystallinity. $TiO_2$ nanoparticles have been prepared by different methods such as, chemical precipitation method [19], chemical vapor deposition (CVD) [20], the sol–gel technique [21,22], sputtering [23], hydrolysis, microemulsion method [24], spray deposition [25], aerosol-assisted chemical vapour deposition method [26], thermal plasma [27], hydrothermal method [28] and microwave-assisted hydrothermal synthesis [29]. Among these methods, chemical precipitation method is a simple process to synthesis $TiO_2$ nanoparticles. The chemical method of preparation uses an environmentally friendly reaction medium. The annealing process also carried out for structural phase transformation of anatase to rutile phase with high temperature, reproducible results, promising for scaling up and low cost $TiO_2$ nanocrystallites are usually synthesized by chemical reaction using titanium alkoxides as source materials [30], since properties like the particle size, structural phase and morphology of the nanocrystallites could be easily controlled by this method. Particularly, there are three kinds of alkoxides of titanium that are often used, tetraethyl titanate (TTET), tetrabutyl titanate (TTBT) and titanium isopropoxide (TIP), among which TIP has been used in the present study because of its moderate hydrolysis rate compared to the other two alkoxides. In the present work, the effect of annealing on $TiO_2$ nanoparticles has been studied.

## 2. Experiment

Chemical method is one of the simplest and economical techniques available for the synthesis of nanoparticles. Titanium dioxide is synthesized by the reaction of hydrolysis using the required precursors. In brief, 0.4 M of titanium isopropoxide (TIP) is added to 0.1 M of ethyl alcohol in alkaline medium at room temperature. Here absolute ethyl alcohol was used as a solvent and alkaline acts as a catalyst controlling the pH (8.5) of the hydrolysis reactions in the solution. The final mixture solution was stirred for about 1 hour. The suspension was centrifuged and washed with water and ethanol several times. After this, the samples were dried at 60 °C for 1 h. The obtained $TiO_2$ samples were then annealed in muffle furnace at 450 °C and 900 °C for 1 h to obtain pure crystalline $TiO_2$ nanoparticles.

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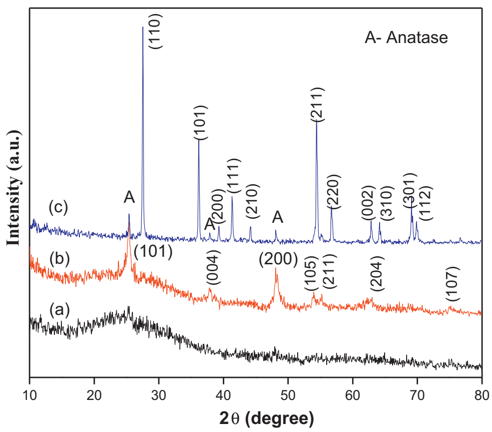


**Fig. 1.** X-ray diffraction pattern of $TiO_2$ nanoparticles (a) as prepared, (b) 450 °C annealed and (c) 900 °C annealed.

The structure and particle size of the prepared $TiO_2$ nanoparticles have been studied using X-ray diffraction pattern recorded using PANalytical X-ray diffractometer. Surface morphology of the samples has been studied using JEM JEOL-6500 Field emission scanning electron microscope (FESEM). Compositional analysis of the samples has been carried out using energy dispersive analysis of X-rays using JEOL Model JSM-6360. Raman spectra of the samples have been recorded using HORIBA JOBIN YUON HR (800) spectrometer. Fourier Transform Infrared spectrum has been recorded using SHIMKDZU IRAffinity – 1 instrument. Optical absorption spectrum has been recorded using JASCO-UV–Vis-NIR Spectrophotometer (JASCO V570).

## 3. Result and discussion

Fig. 1 shows the X-ray diffraction patterns of as prepared and annealed (450 °C and 900 °C) $TiO_2$ samples. Fig. 1(a) shows the pattern of as prepared $TiO_2$ samples which has no peak indicating the amorphous nature. Fig. 1(b) the diffraction peaks corresponding to the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4) and (1 0 7) crystal planes of tetragonal BCC of the anatase phase of $TiO_2$. The lattice constants have been found to be $a$ = 3.745 Å and $c$ = 9.510 Å, and are in good agreement with those on the standard card (JCPDS card No. 89-4921). Fig. 1(c) shows the diffraction peaks corresponding to the (1 0 1), (0 0 4) and (2 0 0) planes of anatase phase and (1 1 0), (1 0 1), (2 0 0), (1 1 1), (2 1 0), (2 1 1), (2 2 0), (0 0 2), (3 1 0), (3 0 1) and (1 1 2) crystal planes of tetragonal primitive of the rutile phase of $TiO_2$ with lattice constants $a$ = 4.572 Å and $c$ = 2.945 Å, and are in good agreement with those on the standard card (JCPDS card No. 89-4920). It can be obviously seen from the XRD patterns that the phase structure of the $TiO_2$ nanoparticles annealed at 450 °C is mainly of nano-crystalline anatase type tetragonal symmetry and these annealed at 900 °C is of nano-crystalline rutile phase with anatase type tetragonal symmetry also present. As the temperature increases from 450 to 900 °C, we observe that the intensities corresponding to the peaks characteristic of rutile phase increases.

The average grain size has been determined using Scherrer's equation [31]:

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

where, $D$ is the grain size, $K$ is a constant taken to be 0.94, $\lambda$ is the wavelength of the X-ray radiation, $\beta$ is the full width at half maximum and $\theta$ is the angle of diffraction The grain size of $TiO_2$ nanoparticles annealed at 450 °C and 900 °C have been calculated and the average values are found to lie in the range of 21–24 nm for anatase phase and 69–74 nm for rutile phase, respectively. These observations indicate that the particle size of $TiO_2$ nanoparticles increase with increasing annealing temperature and the crystallite size improvement is responsible for the sharpness in the diffraction peak.

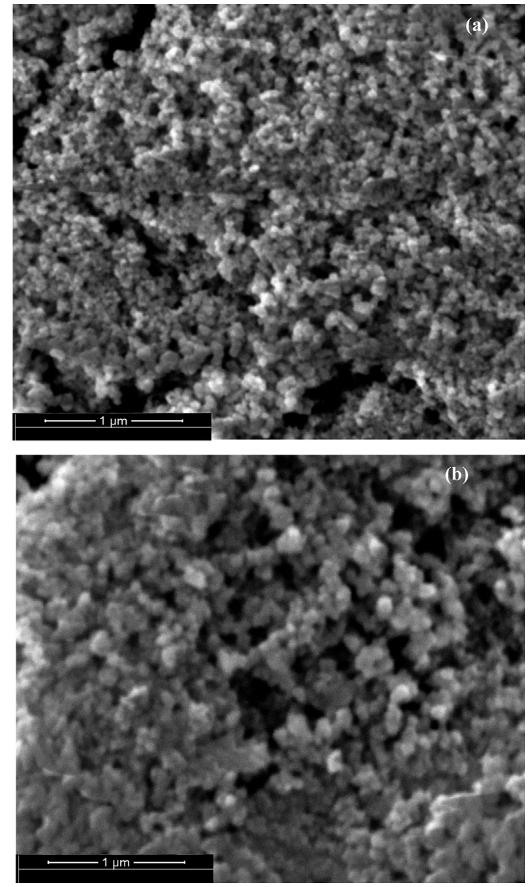


**Fig. 2.** Scanning Electron Microscopy of $TiO_2$ nanoparticles annealed at 450 °C (a) and 900 °C (b).

The surface morphology of $TiO_2$ nanoparticles has been studied using field emission scanning electron microscope. Fig. 2 shows the FESEM image of $TiO_2$ nanoparticles annealed at 450 °C and 900°. FESEM image of $TiO_2$ nanoparticles annealed at 450 °C is shown in Fig. 2a, shows that the grains are very small in size. As the annealing temperature is increased to 900 °C, the particles agglomerate resulting in increase of particle size (Fig. 2b). It is observed from the FESEM image that there is uniform grain distribution with well connected grains. The FESEM investigations of both samples reveal that the crystallites are of nanometer size. Therefore, the growth of nanophase crystalline $TiO_2$ particles is accelerated at higher annealed temperatures. This may be related to a change in the particles structure of $TiO_2$ due to crystal phase transformation, as shown in XRD results [32]. Fig. 3(a and b) shows chemical constituents Ti and O present in the samples according to the energy dispersive spectrum (EDS) analysis of the annealed $TiO_2$ samples.

Fourier transform infrared spectra in the wavenumber region 4000–400 $cm^{-1}$ were recorded using a SHIMKDZU IRAffinity – 1 spectrometer. The $TiO_2$ powders were combined with KBr were pressed until transparent clear pellets were obtained for measurements. Fig. 4 shows FTIR spectra of the annealed samples. Fig. 4(a) shows the spectrum of a $TiO_2$ annealed at 450 °C. A broad peak can be seen at 3413 $cm^{-1}$, assigned to stretching vibration mode of OH groups and the symmetric and antisymmetric OH modes of molecular water with in $TiO_2$ nanoparticles [33]. The