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Phase Change on TiO_2 Nanoparticles by Annealing

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ABSTRACT

TiO_2 nanoparticles have been prepared by a step process of hydrothermal redox route and annealed at different temperatures. The as-prepared TiO_2 are amorphous, and then it transformed into anatase phase on annealing at 550°C, and rutile phase on annealing at 950°C. The X-ray diffraction results showed that TiO_2 wafer-like structure with grain size in the range of 30 to 45 nm for anatase phase and 65 to 80 nm for rutile phase have been obtained. SEM images show the formation of TiO_2 nanoparticles. Optical absorption studies reveal that the absorption edge shifts towards longer wavelength (red shift) with increase of annealing temperature.

Keywords: TiO_2 nanoparticles, Anatase phase, Rutile phase, Structural property and Optical property.

INTRODUCTION

Titanium dioxide or Titania, (TiO_2) is of great interest in various electronic applications, utilizing the photocatalytic nature and transparent conductivity, which strongly depend on the crystalline structure, morphology, and crystallite size. 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] although brookite TiO_2 was occasionally reported[2]. Due to the photosemiconductor properties of TiO_2, it may find applications as antibacterial agents for the decomposition of organisms[3]. Titania is able to kill microorganisms; therefore it is used as a biocide[4]. TiO_2 nanoparticles have been prepared by different methods such as, chemical precipitation method[5], chemical vapor deposition (CVD)[6], the sol–gel technique[7], sputtering[8], and hydrothermal method[9]. Among these methods, chemical precipitation and hydrothermal method is a simple process to synthesis TiO_2 nanoparticles. The chemical method of preparation uses an environmentally friendly reaction medium. In the present work, the phase change by annealing on TiO_2 nanoparticles has been studied.

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. Titania has been formed by mixing 0.5 M titanium butoxide and 0.3 M acetyl acetone with ethanol in alkaline medium at room temperature. Acetyl acetone was added to slow down the hydrolysis and poly condensation reaction. The final mixture solution was stirred for about 4 hour. After 4 hours, the solution was transferred into a stainless steel autoclave with a Teflon liner, which was then filled with distilled water to 70% of its capacity. The autoclave was sealed and maintained at 180°C for 36 hours, then allowed cool to room temperature. Then the supernatants were removed and the deposited precipitate was centrifuged and washed with water and ethanol several times. After this, the samples were dried at 60°C for 1 hour. The obtained TiO_2 samples were then annealed in muffle furnace at 550°C and 950°C for 1 hour to obtain pure crystalline TiO_2 nanoparticles.

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. Optical absorption spectrum has been recorded using JASCO-UV–Vis-NIR Spectrophotometer (JASCO V570).

RESULT AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of as prepared and annealed (550°C and 950°C) TiO_2 samples. Figure 1(a) the diffraction peaks corresponding to the (101), (004), (200), (105), (211), (204) and (107) crystal planes of tetragonal BCC of the anatase phase of TiO_2. The lattice constants have been found to be a = 3.745Å and c = 9.510Å, and are in good agreement with those on the standard card (JCPDS card No. 89-4921). Figure 1(b) shows the diffraction peaks corresponding to the (101), (004) and (200) planes of anatase phase and (110), (101), (200), (111), (210), (211), (220), (002), (310), (301) and (112) crystal planes of tetragonal primitive of the rutile phase of TiO_2 with lattice constants a = 4.572Å and c = 2.945Å, 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 of the TiO_2 nanoparticles annealed at 550°C is mainly of nano-crystalline anatase type tetragonal symmetry and these annealed at 950°C is of nano-crystalline rutile phase with anatase type tetragonal symmetry also present. As the temperature increases from 550 to 950°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:

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

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the x-ray radiation, β is the full width at half maximum and θ is the angle of diffraction The grain size of TiO_2 nanoparticles annealed at 550°C and 950°C have been calculated and the average values are found to lie in the range of 30 to 45 nm for anatase phase and 65 to 80 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.

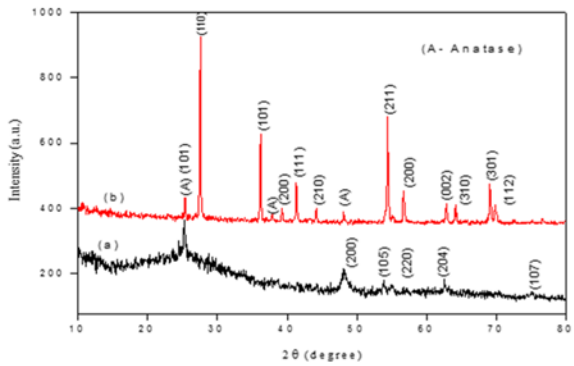

Figure 1 X-ray diffraction pattern of TiO_2 nanoparticles (a) 550°C annealed and (b) 950°C annealed

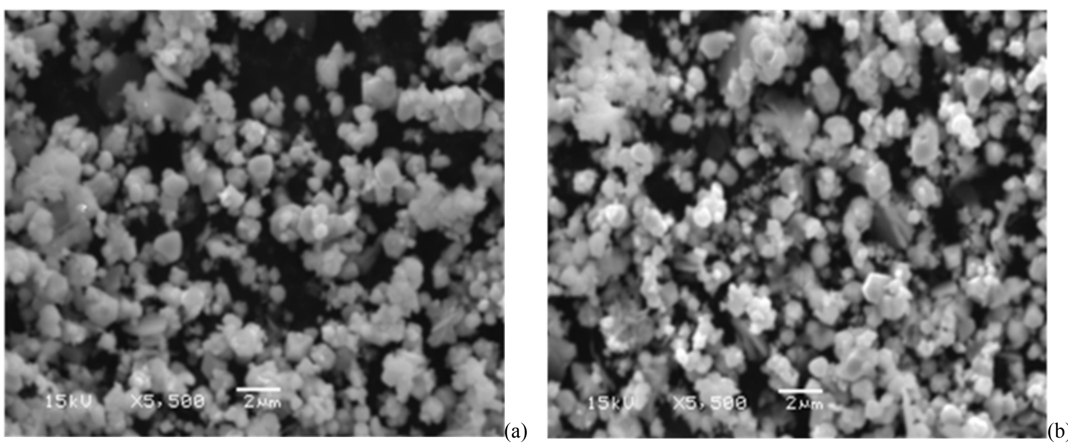

Figure 2 Scanning Electron Microscopy of TiO_2 nanoparticles (a) 550°C annealed and (b) 950°C annealed

The surface morphology of TiO_2 nanoparticles has been studied using scanning electron microscope. Figure 2 shows the SEM image of TiO_2 nanoparticles annealed at 550°C and 950°. SEM image of TiO_2 nanoparticles at 550°C is shown in Figure 2(a) shows that the nanoparticles are very small in size. As the annealing temperature is increased to 950°C, the nanoparticles agglomerate resulting in increase of wafer size (Figure 2(b)). The SEM investigations of both samples reveal that the crystallites are of nanometer size. Therefore, the growth of nanophase crystalline TiO_2 nanoparticles 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. Figures 3(a & 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.

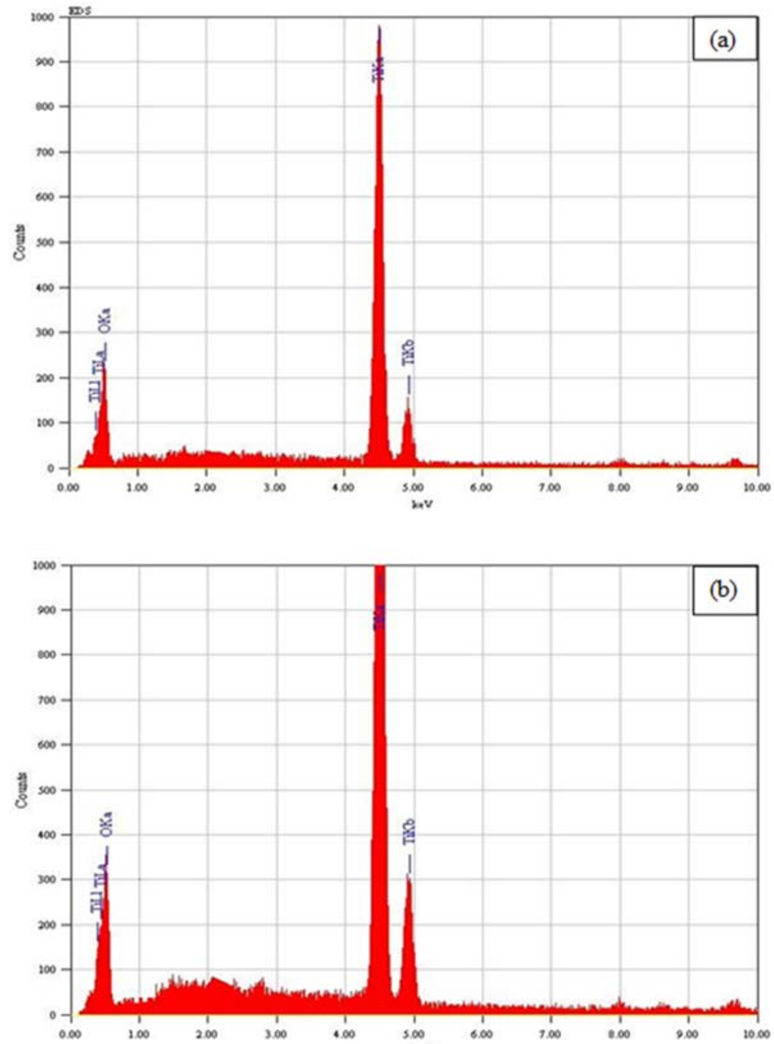

Figure 3 EDS pattern of annealed TiO_2 nanoparticles (a) 550°C and (b) 950°C

Figure 4 (a&b) shows the UV – VIS absorption spectra of TiO_2 wafer-like structure annealed at two different temperatures. The shift of the absorption edge to the longer wavelength range with the phase transformation from anatase to rutile phase and also indicates that the grain size increases with increasing of annealing temperature. This shift is proved the results of XRD. The absorption edges of the rutile TiO_2 nanoparticle annealed at 950°C is red shifted; this shift is ascribed to the difference in band gap energy of the anatase and rutile TiO_2 wafer-like structure. The redshift of absorption edge can be related to the generation of more rutile phase. It is remarkable to note that the absorption of 950°C annealed TiO_2 wafer-like structure is considerably increased. This is due to the absorption resulting from the phase transformation from anatase-to-rutile phase, and the light scattering increases with crystallite size of nanoparticles and agglomerates of the primary particles.

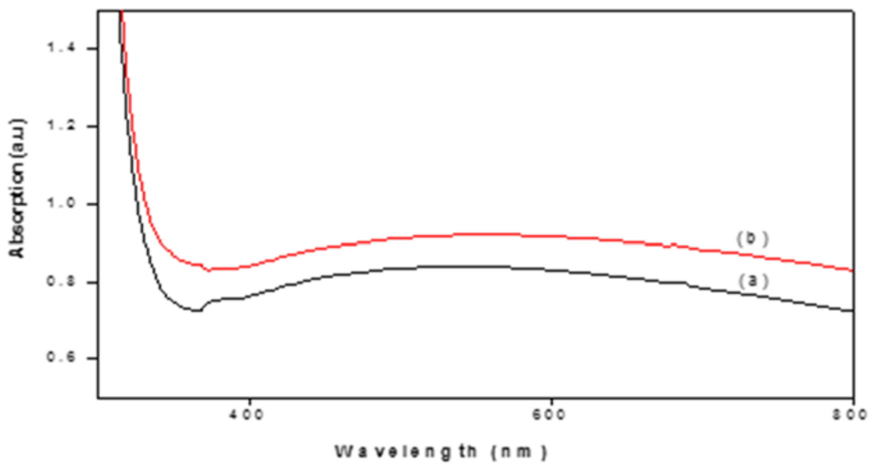

Figure 4 UV-VIS spectra of annealed TiO_2 nanoparticles (a) 550°C and (b) 950°C

CONCLUSION

TiO_2 wafer-like structure has been prepared by hydrothermal method. XRD analysis of TiO_2 shows that 550°C annealed TiO_2 exhibits anatase phases and 950°C annealed samples exhibits a mixture of anatase and rutile phase. The average grain size of TiO_2 nanoparticles is found to lie in the range of 30–45 nm and 65–80 nm, which is proved by X-ray diffraction. The optical absorption is found to increase and the red shift in the absorption edge is observed with increase of annealing temperature. In this study, we have successfully fabricated TiO_2 nanoparticles with desired size with phase transformation by using the titanium butoxide as a starting material.

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