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Fabrication and Characterization of Rutile TiO_2 Nanocrystals by Water Soluble Precursor

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In this research, TiO_2 nanoparticles were synthesized by a simple wet chemical method. $TiCl_4$ was used as precursor in hydrogen peroxide and ethanol. The TiO_2 nanoparticles were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), electron dispersive spectroscopy (EDS) and UV-Vis spectrophotometer. The particle size of the as-synthesized TiO_2 was estimated by XRD and TEM analyses in the range of 5-10 nm. The SEM images showed that the size of sphere-like shaped nanoparticles decrease with increasing annealing temperature. The prepared TiO_2 nanoparticles were characterized for phase composition, using X-ray diffractometry. The crystal structure of the nanoparticles after annealing was measured by XRD analysis. It was realized that phase transition from anatase to rutile occurs after heat treatment at 600 °C. The particle size of the annealed sample was also calculated about 20 nm by XRD analysis. The EDS spectrum showed peaks of titanium and oxygen with fewer impurities. The UV-Vis spectrum showed anatase and rutile phase at wavelength about 375 nm (E_g = 3.30 eV) and 470 nm (E_g = 2.63 eV) for as-prepared TiO_2 and annealed TiO_2 nanoparticles respectively.

Keywords: TiO_2 nanocrystals, Wet chemical, Anatase, Phase transition, Rutile

INTRODUCTION

There are many routes to fabricate titanium dioxide (TiO_2) nanoparticles reported by researchers. These nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts [1]. TiO_2 nanoparticles have many applications in optical devices, sensors, and photocatalysis [2,3]. To determine important properties such as the particle size, crystallinity and morphology, there are several factors affecting the performance of TiO_2 in applications [4,5,6]. TiO_2 has been studied in wide applications, such as gas sensing [7], photocatalytic [8] and photoelectric devices [9]. There are three forms of TiO_2 crystal structure: brookite, anatase and rutile. The photocatalytic activity of TiO_2 is dependent on its crystal structure, crystal size distribution, surface roughness, surface hydroxyl group density, *etc*. [10]. The studies show that anatase form structure has better photocatalytic properties [11,12,13,14,15]. The anatase form shows better application such as antibacterial self-cleaning building materials like bathroom tile [16,17]. Anatase-to-rutile transformation usually occurs at temperature more than 600 °C [18]. Phase transition to rutile is nonreversible because of the greater thermodynamic stability of rutile phase [19]. A number of studies have focused on the synthesis of titanium dioxide nanoparticles [20]. Anatase phase is commonly obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$) [21] or titanium alkoxides ($Ti(OR)_4$), in solution [22]. In this article, TiO_2 nanoparticles are synthesized *via* wet chemical route. Synthesis of anatase TiO_2 by wet synthesis technique is reported by $TiCl_4$ solution precursor and calcined at 600 °C. Characterization of the TiO_2 nanoparticles has been studied by XRD, EDS, TEM, UV-Vis and SEM analyses.

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EXPERIMENTAL

TiO_2 nanoparticles were prepared using H_2O_2 solution added to ethanol solution of titanium tetrachloride ($TiCl_4$). 5 ml ethanol solution was added drop wise into 5 ml $TiCl_4$ precursor and stirred for 5 min at room temperature. At first, a large amount of HCl gas was exhausted during the mixing process. The light yellow solution was obtained at this step. After that 10 ml hydrogen peroxide, H_2O_2, was added to the solution. The light yellow colored solution changed to red. The total volume of the solution was adjusted to 100 ml by adding ethanol solution. The solution was then heated at 80 °C for 1 h in a closed vessel. Then, the product was aged at 220 °C for 2.5 h without any washing and purification. Finally, the powder was calcined at 600 °C for 3 h to obtain white titanium oxide nanopowder. The morphology of the as-synthesis and annealed TiO_2 nanoparticles were done. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern was recorded with 2θ in the range of 4-85° with type X-Pert Pro MPD, Cu-K$_\alpha$: λ = 1.54 Å. The morphology was characterized by field emission scanning electron microscopy (SEM) with type KYKY-EM3200, 25 kV and transmission electron microscopy (TEM) with type Zeiss EM-900, 80 kV. The Ti and O elemental analysis of the samples was performed by energy dispersive spectroscopy (EDS) type VEGA, 15 kV. The optical properties of absorption were acquired by ultraviolet-visible spectrophotometer (UV-Vis) with optima SP-300 plus. All measurements were carried out at room temperature.

RESULT AND DISCUSSIONS

Figure 1 shows the XRD morphology of TiO_2 nanoparticles annealed at 1000 °C and indicates the structure of rutile phase. The mean size of the ordered TiO_2 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer formula according to equation the following:

$$D = \frac{0.89\lambda}{B\cos\theta} \quad (1)$$

where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half of the maximum intensity

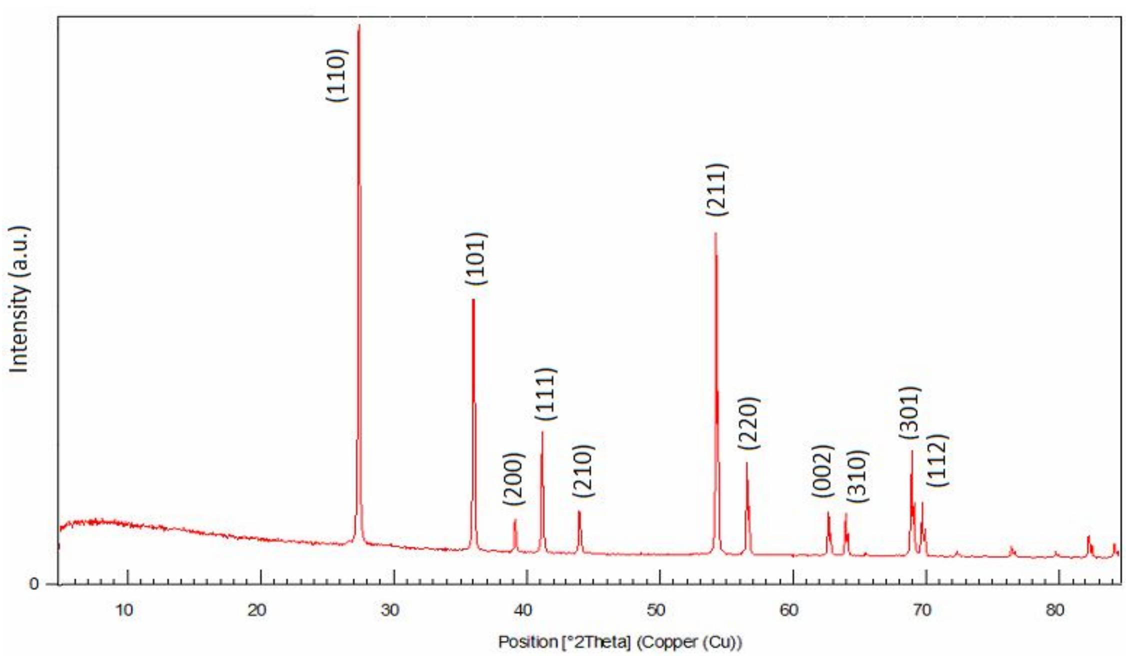

Fig. 1. XRD pattern of annealed TiO_2 nanoparticles.

(FWHM) in radians, and θ is the Bragg angle. The mean size of annealed TiO_2 nanoparticles was measured 20 nm from this Debye-Sherrer equation.

SEM images show that with increasing temperature the morphology of the particles changes to the spherical shape and nanopowders were less agglomerate. Figure 2a shows the SEM images of the as-prepared TiO_2 nanoparticles prepared by wet chemical method. In this figure the number of small particles is decreased. Figure 2b shows the SEM images of the annealed TiO_2 nanoparticles at 600 °C for 3 h. As seen from SEM images, the spherical-shaped TiO_2 were not agglomerated. The average crystallite size of annealed nanocrystals is about 20 nm through the SEM images.

Figure 3 shows the as-synthesized TEM image of titanium dioxide prepared by wet synthesis. It is observed that the anatase TiO_2 nanoparticles are built in the size range of 10-30 nm. Agglomeration of the nanoparticles, because of absence of surfactants, is clearly seen in this figure.

Energy dispersive spectroscopy (EDS) of TiO_2 prepared by wet synthesis is shown in Fig. 4 which confirms the existence of Ti and O with weight percent. EDS was used to analyze the chemical composition of a material under FE-SEM. EDS shows peaks of titanium and oxygen and indicates fewer impurities such as chlorine in prepared TiO_2.

UV-Vis absorption spectra of as-prepared and annealed TiO_2 nanoparticles are shown in Fig. 5. For as-synthesized TiO_2 nanoparticles, the strong absorption band at low wavelength near 375 nm for anatase related to band gap about 3.30 eV (Fig. 5a) and for annealed TiO_2 nanoparticles the strong absorption band at low wavelength near 470 nm for rutile phase related to band gap about 2.63 eV (Fig. 5b) indicate the presence of phase transition of anatase to rutile for TiO_2 nanoparticles under heat treatment at 600 °C.

CONCLUSIONS

TiO_2 nanoparticles were successfully synthesized by wet synthesis method. The results showed that anatase to rutile phase transition of TiO_2 occurs at 600 °C. TEM studies showed spherical structure of TiO_2 nanoparticles in the range size of 5-10 nm. SEM images showed that with increasing temperature the size of particles decrease with less agglomeration. The average size of annealed TiO_2 was

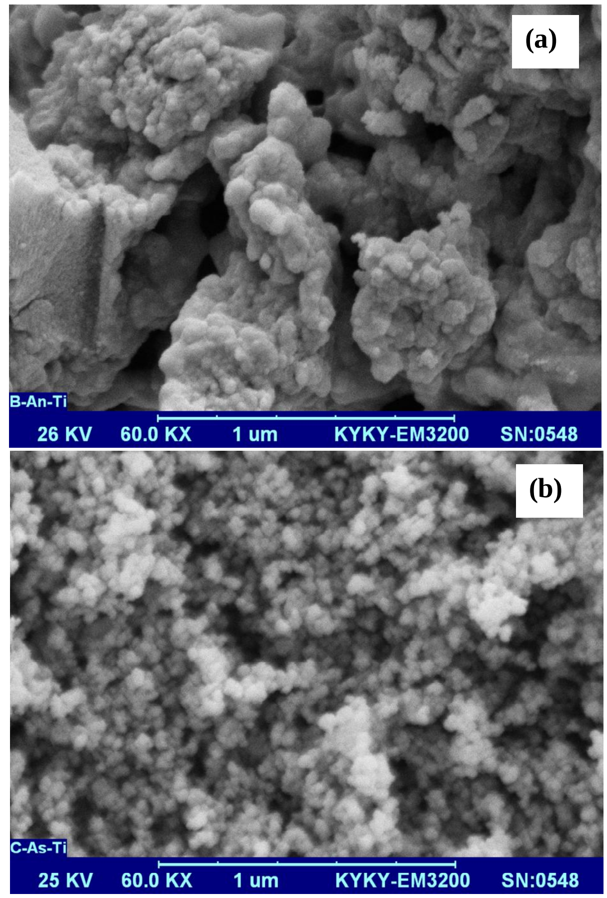

Fig. 2. SEM images of the TiO_2 samples (a) as-prepared (b) annealed at 600 °C.

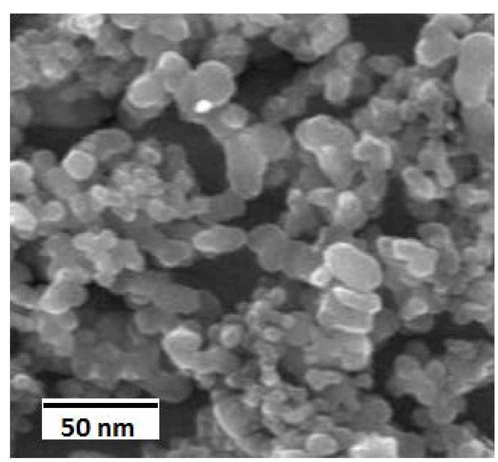

Fig. 3. TEM images of the as-prepared TiO_2 nanoparticles.

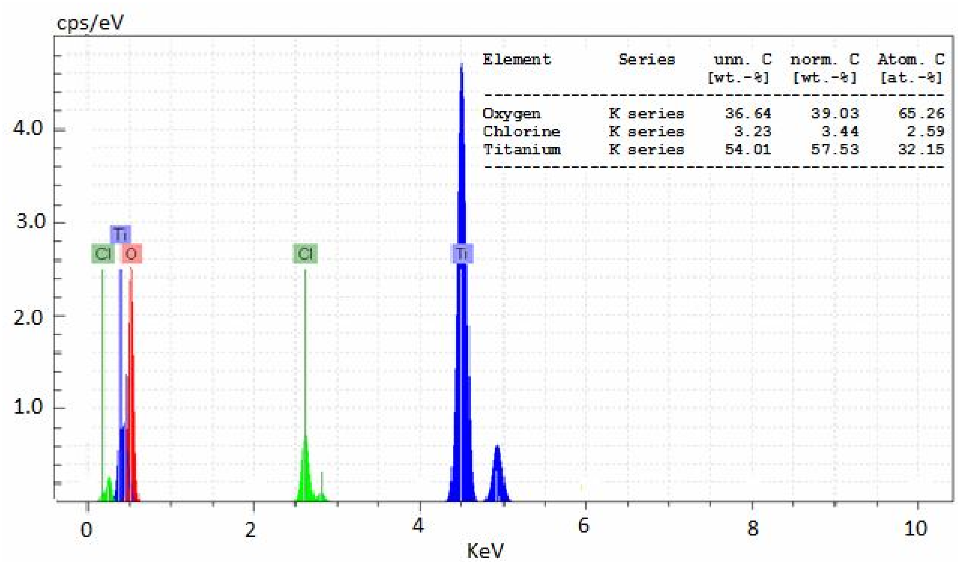

Fig. 4. EDS spectra of the as-synthesized TiO_2 prepared by wet synthesis.

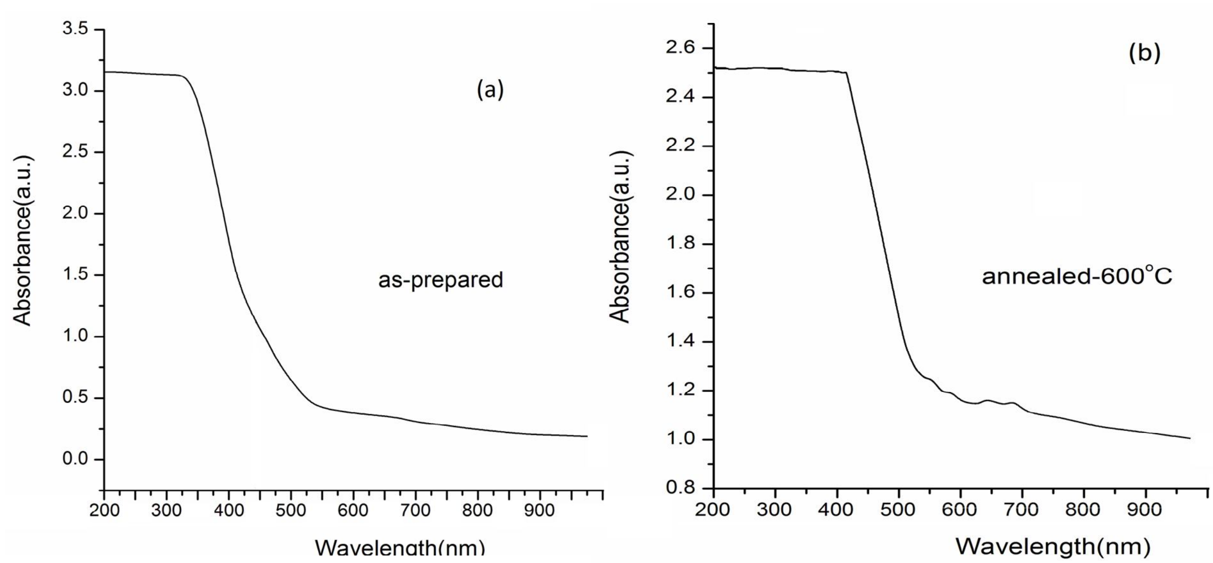

Fig. 5. UV-Vis absorption spectra of (a) as-prepared and (b) annealed TiO_2 nanoparticles.

about 20 nm. XRD pattern of annealed TiO_2 nanoparticles indicated tetragonal rutile phase at 600 °C. EDS showed the absence of impurities in prepared TiO_2. The UV-Vis spectrum showed anatase and rutile phase at wavelength about 375 nm corresponding to the band gap about 3.30 eV and 470 nm corresponding to the band gap about 2.63 eV for as-prepared TiO_2 and annealed TiO_2 nanoparticles, respectively.

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