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RESEARCH ARTICLE

One-step synthesis of TiO_2 nanoparticles using simple chemical technique

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Abstract: Titanium dioxide nanoparticles (TiO_2) have been extensively investigated because of its high chemical sustainability, optic properties, and adaptation to the environment. These studies include applications in heterogeneous catalysts, solar cells, coating technology, and electrical devices. TiO_2 particles in the nanometer scale can remove limitations, such as the absorbance of organic materials, because of a high surface area to volume ratio. Titanium dioxide nanoparticles, were synthesized using a simple wet chemical method. Their physico-chemical properties were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses. The TEM results showed that the mean size of as-synthesized TiO_2 was 5 nm with high crystalline anatase phase. The SEM observations revealed that the size of nanoparticles increased with annealing temperature and the morphology of the particles changed to the spherical shape. The crystal structure of the nanoparticles before and after annealing was done by XRD analysis. The rutile phase was formed after heat treatment at 600^{o}C for 3 hours.

Keywords: TiO_2 nanoparticles, wet chemical synthesis, rutile phase

1 Introduction

Metal oxides have recently become widely used in the field of medical and industrial applications[1–25] . TiO_2 nanoparticles have attracted attention in the fields of environmental purification, solar energy cells, photocatalysts, gas sensors, photo electrodes and electronic devices. It has been widely used as a pigment in paints, ointments, toothpaste etc[26] . Nanosized TiO_2 particles are of particular interest due to their specifically size-related properties. Generally it is in three forms, anatase (tetragonal, a=b=3.78 $\AA$, c=9.5 $\AA$), rutile (tetragonal, a=b=4.58 $\AA$, c=2.95 $\AA$) and brookite (rhombohedral, a=5.43 $\AA$, b=9.16 $\AA$, c=5.13 $\AA$). Among various phases of titania reported, anatase shows a better photocatalytic activity and antibacterial performance[27] . A stable anatase up to the sintering temperature of the ceramic substrates is most desirable for applications on antibacterial self-cleaning building materials like bathroom tile, sanitary ware and self-cleaning applications[28] . Anatase-to-rutile transformation is usually occurs at 600 to 700°C[29] . Phase transition to rutile is nonreversible because of the greater thermodynamic stability of rutile phase[30] . There are several factors in determining the important properties such as the particle size, crystallinity and morphology that affect in the performance of TiO_2 in applications[31] . A number of studies have focused on the synthesis of titanium dioxide nanoparticles[32] . Anatase and rutile are commonly obtained by hydrolysis of titanium compounds, such as titanium tetrachloride ($TiCl_4$)[33] or titanium alkoxides ($Ti(OR)_4$), in solution[34] . Brookite is sometimes observed as a by-product of the precipitation reaction carried out in acidic medium at low temperature.[34,35] Brookite is also obtained as large crystals by hydrothermal methods at high temperature and pressure in aqueous[36] or in organic media[37] . In the present work, we focused on synthesis of TiO_2 nanoparticles system by wet chemical route. This method has novel features which are of considerable interest due to its low cost, easy preparation and industrial viability. Synthesis of rutile form by wet synthesis technique is reported by $TiCl_4$ solution precursor and calcined at 600^{0}C. The structural and optical properties of TiO_2 have been studied by XRD, SEM and TEM analyses.

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2 Experimental detail

TiO_2 nanoparticles were synthesized by a new approach according to the following manner. 20 mL NaOH solution (64.8 g/l) was added drop wise into 100 mL deionized water with stirring. Then, 5cc $TiCl_4$ solution (200 g/l) was added drop wise to the solution and stirred for 5 min at room temperature. At first a large amount of HCl gas was exhausted during the mixing process and then light yellow solution was obtained. Resulting TiO_2 slurry and an aqueous solution of HNO_3 (2 mL) were dried at 65^0C for 1 h, cooled to room temperature and neutralized with 26% of aqueous ammonia (10 mL) and stirred again for 10 min. The pH was adjusted by adding nitric acid in the range for 2.0 to 2.5. Then, the product was aged at 220^oC for 2.5 hours and finally calcined at 600^0C for 3 hours. The white TiO_2 powder was later obtained.

The specification of the size, structure and optical properties of the as-synthesis and annealed TiO_2 nanoparticles were carried out. X-ray diffractometer (XRD) was used to identify the crystalline phase and to estimate the crystalline size. The XRD pattern were recorded with 2θ in the range of 4-85^o with type X-Pert Pro MPD, Cu-K_α: λ = 1.54 $\mathring{A}$. 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.

3 Results and discussion

X-rar diffraction (XRD) at 40Kv was used to identify crystalline phases and to estimate the crystalline sizes. Figure 1(a) shows the XRD morphology of TiO_2 nanoparticles and indicates the structure of tetragonal anatase phase. The XRD patterns showed this sample have four sharp peaks 2θ angle at the peak position at 25.2^o, 37.7^o, 47.8^o, 54.1^o, 62.5^o, 69.4^o and 75.5^o with (101), (004), (200) , (105), (211), (204) and (116) diffraction planes, respectively are in accordance with the TiO_2 anatase phase. It can be seen the peak position at 27.5^o corresponds to the plane (110) of rutile form. The mean size of the ordered TiO_2 nanoparticles has been estimated from full width at half maximum (FWHM) and Debye-Sherrer equation.[38]

Where, 0.89 is the shape factor, λ is the x-ray wavelength, B is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle. The mean size of as-prepared TiO_2 nanoparticles was 5.5 nm from this Debye-Sherrer equation.

Scanning electron microscope (SEM) was used for the morphological study of nanoparticles of TiO_2. These figures show that high homogeneity emerged in the samples surface by increasing annealing temperature. With increasing temperature the morphology of the particles

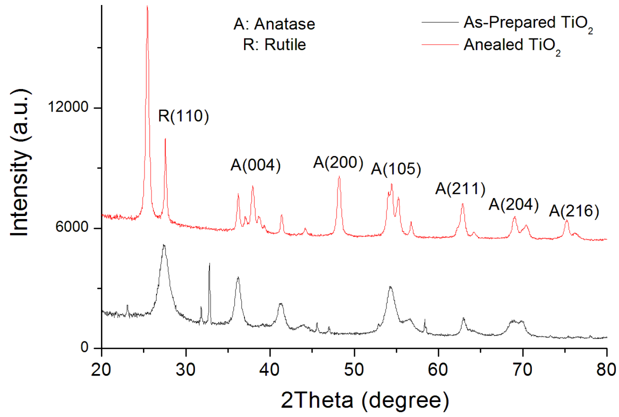

Figure 1. XRD pattern of as-prepared and annealed TiO_2 nanoparticles

changes to the spherical shape and nanopowders were less agglomerate. Figure 2(a) shows the SEM image of the as-prepared TiO_2 nanoparticles with spherical shape prepared by wet chemical method. Figure 2(b) shows the SEM image of the annealed TiO_2 nanoparticles. The TiO_2 nanoparticles formed were not agglomerated. The spherical shaped particles with clumped distributions are visible through the SEM analysis. The average crystallite size of annealed nanocrystals is about 25 nm. Figure 3 indicates the commercial TiO_2 nanoparticles.

The transmission electron microscopic (TEM) analysis was carried out to confirm the actual size of the particles, their growth pattern and the distribution of the crystallites. 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 with a diameter of 5nm. The principal novelty of the procedure developed is that it results in nanoparticles of TiO_2, with a regular distribution, uniform size and spherical shape because of HNO_3 stabilizer.[39,40]

4 Conclusion

Titanium dioxide nanoparticles were successfully prepared by simple and new wet synthesis method. Anatase TiO_2 is obtained from wet synthesis method and rutile phase is obtained when it is calcined at 600 ^{o}C. The average size of annealed TiO_2 is about 25 nm. TEM studies show spherical structure of TiO_2 nanoparticles with size of 5nm for smallest particle. SEM images showed that with increasing temperature the morphology of the particles changes to the spherical shape and nanopowders were less agglomerate. XRD pattern of TiO_2 nanoparticles indicated the structure of tetragonal anatase phase without annealing and rutile phase with annealing process at 600 ^{o}C.

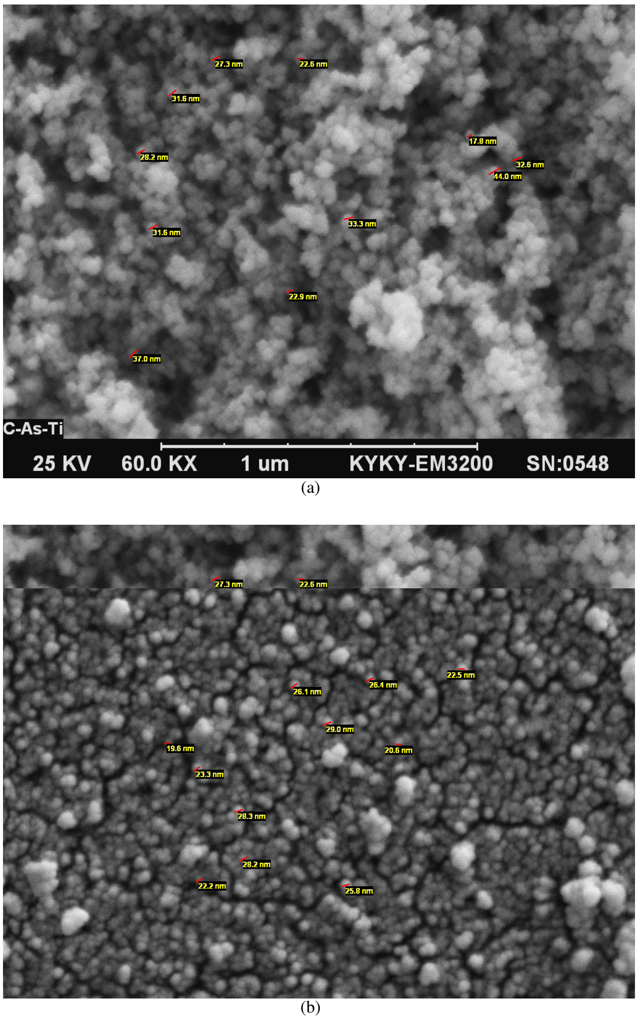

Figure 2. SEM images of the (a) as-prepared (b) annealed at 600^0C

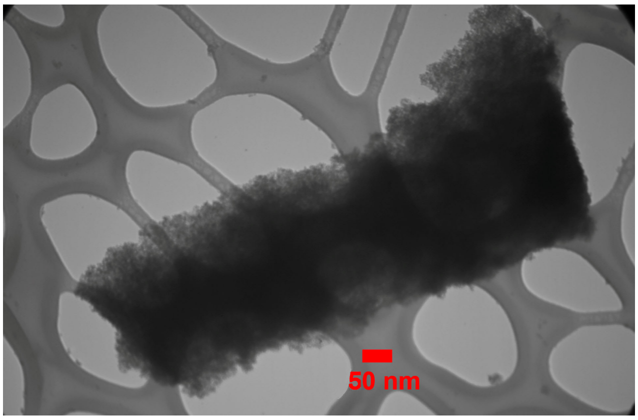

Figure 3. TEM image of the as-prepared TiO_2 nanoparticles

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