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The synthesis of TiO_2 nanoparticles using sulfuric acid method with the aid of ultrasound

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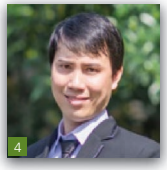


In this study, the authors report the synthesis of titanium dioxide (TiO_2) nanostructures by an ultrasound-assisted method using titanium dioxide particles and sulfuric acid. The synthesis process for titanium dioxide nanoparticles reported herein is simple and easy to reproduce. The structural and microstructural characterizations of titanium dioxide nanoparticles were accomplished using X-ray diffraction, scanning electron microscopy, transmission electron microscopy and Raman scattering spectroscopy. The titanium dioxide nanoparticles were spherical in shape, and the average size of the nanoparticles was in the range of 6–63 nm and depended on the annealing temperature. When the annealing temperature was lower than 650°C, the anatase phase ratio of titanium dioxide was 100%. However, a further increase in the annealing temperature resulted in a rapid increase in the content of the rutile phase. The anatase-to-rutile transformation temperature shifted to a very low level for the nanosize crystallites owing to the high surface energy of the particles. The successful fabrication of titanium dioxide nanosolution will open up new perspectives in the research on modifications and applications of titanium dioxide nanostructures.

Notation

D	particle size
k	A constant
β	line width at half maximum height
λ	wavelength
θ	diffraction angle

1. Introduction

Nanotechnology is an emerging technology, which can lead to a revolution in every field of science.[1] One of the most important nanomaterials, which have attracted a great attention due to their unique properties, is titanium dioxide (TiO_2). Due to its unique properties, nanosize titanium dioxide represents a promising research subject for various modern fields of science and technology, including microbiology, nanobiotechnology and fundamental medicine.[2] In 1972, Fujishima and Honda[2] discovered the phenomenon of the photocatalytic splitting of water on a titanium dioxide electrode under ultraviolet (UV) light. Since then, nanosize titanium dioxide has found wide applications in scientific, technological and environmental fields, including photocatalysis, electrochemistry, optics, microelectronics, production of dyes, ceramics, cosmetics, gas sensors, inorganic membranes, dielectrics, synthesis of mesoporous film coatings and catalysts for environmental cleaning processes.[2–5]

In order to prepare titanium dioxide nanostructured materials with desirable properties, several processes have been developed over the last decade. These methods can be classified as physical methods, including the low-pressure gas evaporation method, sputtering method, plasma method and high-energy ball milling, and chemical methods, such as the settling method, hydrolysis, spraying method, oxidation–reduction method, laser synthesis, hydrothermal method, sol–gel method and electrospark method.[2–6] The selection of a proper synthetic route in designing nanostructured materials is the most important issue in the development of new methodologies. In this study, the authors report the synthesis of titanium dioxide nanoparticles by using an ultrasound-assisted method to promote the reaction between titanium dioxide particles and sulfuric acid (H_2SO_4).

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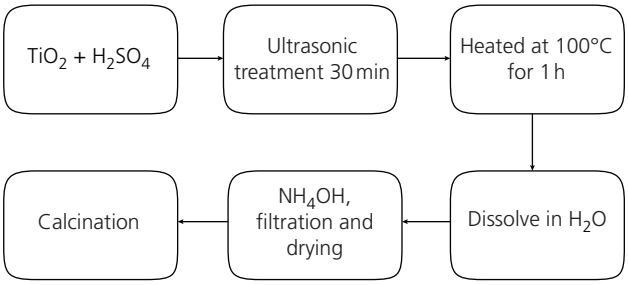


Figure 1. Schematic diagram of the synthesis of titanium dioxide nanoparticles by using ultrasound waves to promote the reaction between titanium dioxide particles and sulfuric acid

2. Experimental methods

Figure 1 shows the experimental set-up for the synthesis of titanium dioxide nanoparticles. The starting materials include anatase titanium dioxide powder (>99%), ammonium hydroxide (NH_4OH) (38%) and sulfuric acid (98%). In a typical synthesis, 10 g of anatase titanium dioxide particles were added to 20 ml of sulfuric acid. The composite mixture was transferred into a 250 ml beaker and treated with ultrasound (100 W, 28 kHz in Figure 2) for 30 min, and then it was hydrolyzed in distilled water at 100°C for 1 h as in Equation 1.

According to the 'cavitation' theory, extreme temperatures (>5000 K) and high pressures (>1000 atm) are generated during the bubble collapse, which forms 'hot spots'. The benefit of using ultrasonic waves in such reactions is to provide highly intensive mixing, particularly in viscous media. This leads to an acceleration effect in the chemical dynamics and reaction rates.[7] Titanium (IV) oxide reacts with sulfuric acid to produce titanium (IV) sulfate and water. The reaction occurring in the titanium dioxide nanoparticle formation can proceed as follows[6,8,9]

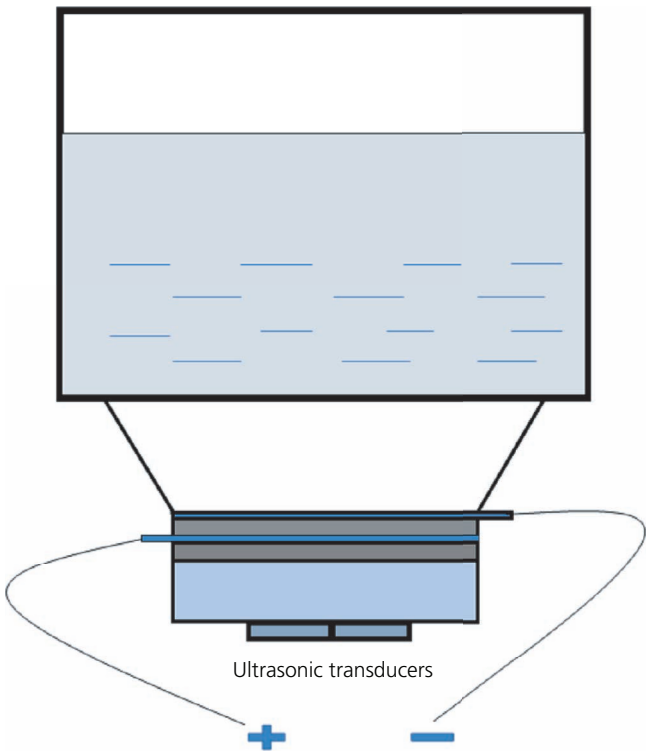


Figure 2. The synthesis tools of titanium dioxide nanoparticles by sulfuric acid method with the aid of ultrasound

$$TiO_2 + 2H_2SO_4 \xrightarrow{\text{ultrasonic energy} + 100^{\circ}C \text{ for } 1\text{ h}} H_2[TiO(SO_4)_2] + H_2O \quad (1)$$

$$H_2[TiO(SO_4)_2] \rightarrow TiOSO_4 + H_2SO_4 \quad (2)$$

$$TiOSO_4 + (n+1)H_2O \rightarrow TiO_2 \cdot nH_2O + H_2SO_4 \quad (3)$$

$$TiO_2 \cdot nH_2O \rightarrow TiO_2 + nH_2O \quad (4)$$

Ammonium hydroxide solution was used to adjust the pH of the compound from 8 to 11. In order to remove by-products, the final product was washed many times with distilled water at room temperature. After filtering and drying, the samples were annealed at 250, 350, 450, 550, 650 750, 850 and 950°C for 2 h. The crystal structure and microstructure of the calcined samples were examined by X-ray diffraction (XRD; D8 Advance), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Raman scattering spectra were also recorded using a Raman spectrometer (Jobin-Yvon Inc., Paris, France) at a backscattering configuration. The excitation laser was emitted from an argon ion (Ar^+) laser source with a wavelength of 488 nm and San output power of 11 mW.

3. Results and discussions

In this study, titanium dioxide nanostructures were synthesized. XRD was performed to examine the nanostructure and crystallinity of the pure titanium dioxide synthesized by the sulfuric acid method with the aid of ultrasound. As mentioned earlier, ultrasound promotes the reaction between titanium dioxide particles and sulfuric acid. It is believed to provide highly intensive mixing, particularly in viscous media. This leads to an acceleration effect in chemical dynamics and increases the rates of reactions.[7] According to Hassanjani-Roshana *et al.*,[10] ultrasound intensity plays a very important role in the morphological and dimensional properties of titanium dioxide nanoparticles. In this study, ultrasound intensity was found to control the dispersion of titanium dioxide particles in the sulfuric acid environment and helped in the breaking of chemical bonds in titanium dioxide particles to create new structures at a reaction temperature of 100°C in 1 h (Equation 1). He *et al.*[9] reported the extraction rate

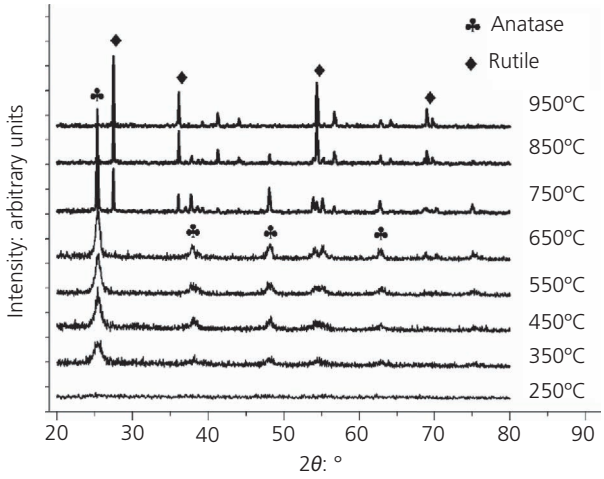


Figure 3. XRD of titanium dioxide nanoparticles at different annealing temperatures

of titanium as 92·62% under the conditions of a sulfuric acid mass fraction of 50%, an acid-to-slag ratio of 1·5:1, a reaction temperature of 160°C and a reaction time of 2·5 h. In this study, the XRD patterns of the as-prepared titanium dioxide samples showed an anatase-to-rutile phase transformation. This change in the phase was observed when the annealing temperature was increased from 250 to 950°C, as shown in Figure 3. Anatase titanium dioxide was formed after the annealing temperature was increased from 250 to 650°C. Figure 3 shows the presence of the peaks at 2θ values of 25·28, 37·78, 48·05, 55·01 and 62·61° originating by the reflections from the (101), (004), (200), (211) and (204) lattice planes of titanium dioxide anatase phases.[2,4,11] XRD showed the coexistence of anatase–rutile at a temperature higher than 650°C. When the heat treatment temperature was 750°C, an increment in the intensity of the rutile phase over the anatase phase was produced. It was observed that the presence of the peaks at 2θ values of 27·41, 36·05, 41·34, 54·32 and 68·99°, originated by the reflections from the (110), (101), (111), (211) and (301) lattice planes of titanium dioxide rutile phases.[4,7,11] The fact that higher temperatures resulted in lower amounts of anatase is due to the temperature threshold, as the complete anatase phase was converted into rutile when heat treatment was given at temperatures higher than 650°C.[4,11] In other studies, it has been reported that the anatase phase can be converted into the rutile phase at temperatures higher than 450°C.[10,12] Lower temperatures result in the formation of higher amounts of anatase, while higher temperatures result in rutile-rich structures, as shown in Table 1. The quantification of phase proportions usually is carried out by XRD.[7,13,14] Such analyses are often done using the method of Spurr and Myers,[13] which utilizes the ratio of the anatase (101) peak at 25·176° of 2θ to the rutile (110) peak at 27·355 of 2θ. The ratio of the intensities of these peaks, I_{101}/I_{110}, is used in an empirically determined formula (Equation 5) to give the weight fractions of anatase and rutile

$$\frac{\text{Anatase}}{\text{Rutile}} = 0{\cdot}79\frac{I_{101}}{I_{110}} \quad (5)$$

Table 1 shows that when the annealed temperature was lower than 650°C, the anatase phase ratio constituted up to 100%. However, a further increase in the annealed temperatures was accompanied by a rapid increase in the content of rutile phase. The anatase-to-rutile transformation temperature shifted to a very low temperature level for the nanosize crystallites because of the high surface energy of the particles. These results are consistent with the literature.[4] Viana *et al.*[15] reported that the crystallization peak of titanium dioxide nanoparticles in the range of 247–327°C, a characteristic of densification, is interrupted by a broad exothermic event between 650 and 800°C related to the anatase–rutile phase transition. These results were in accordance with Raman spectroscopic analysis mentioned in the next paragraph.

The crystallite size of the particles was estimated from the Debye–Scherrer equation (Equation 6) by using the XRD line broadening as follows[4,16]

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (6)$$

where D is the particle size, λ is the wavelength of the X-ray radiation (copper (Cu) Kα = 0·15406 nm), k is a constant taken as 0·94, θ is the diffraction angle and β is the line width at half-maximum height. The (1 0 1) plane diffraction peak is used for anatase, and the (1 1 0) plane peak, for rutile. Table 2 shows the particle size of titanium dioxide nanoparticles at different annealing temperatures. As shown in Table 2, the transition to rutile is accompanied by a significant grain growth, resulting in large rutile grains and small anatase grains, which would alter the

Table 1. Anatase/rutile ratios of titanium dioxide nanoparticles at different annealing temperatures

Temperature: °C	350	450	550	650	750	850	950
Anatase phase ratio: %	100	100	100	94·9	70·6	37·5	1·3
Rutile phase ratio: %	0	0	0	5·1	29·4	62·5	98·7

Table 2. Crystallite size of titanium dioxide nanoparticles at the different annealing temperatures

Temperature: °C	350	450	550	650	750	850	950
Particle size: nm	5·8	7·6	8·8	12·4	44·2	61·9	63·1

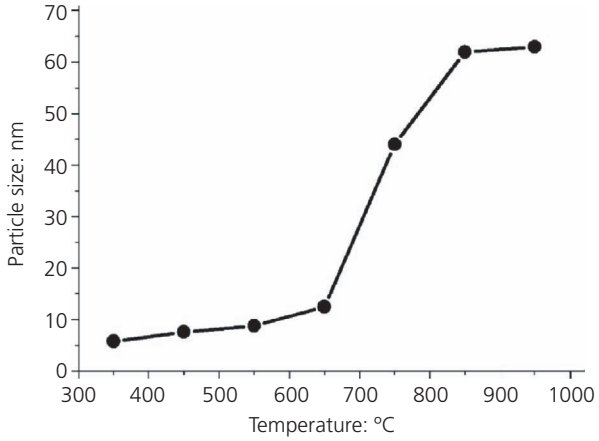


Figure 4. Particle size variation at different calcination temperatures

ratios of XRD peak intensities. As shown in Figure 3, the full width at half maximum of the anatase (101) diffraction peak decreased with increasing annealing temperature, suggesting that the average crystallite size of titanium dioxide nanoparticles was increased by thermal annealing. This result is in a good agreement with the literature.[14,16] The temperature dependence of the particle size of titanium dioxide nanoparticles on the different annealing temperatures is shown in Figure 4.

Raman spectroscopy was also used to characterize the obtained titanium dioxide nanoparticles; the phase purity of the titanium dioxide anatase and rutile[17–19] is shown in Figure 5. According to factor group analysis, anatase has six Raman-active modes such as A_{1g} (517 cm^{-1}), $2B_{1g}$ (397 and 517 cm^{-1}) and $3E_g$ (144, 197 and 640 cm^{-1}).[17,20,21] The titanium dioxide samples prepared by the sulfuric acid method with the aid of ultrasound annealing at 450°C (Figure 5(a)) showed four peaks at 146·45 cm^{-1} (E_g), 190·31 cm^{-1} (E_g), 394·99 cm^{-1} (B_{1g}), 514·51 cm^{-1} (A_{1g}) and 635·55 cm^{-1} (E_g), indicating the presence of titanium dioxide phase in accordance with the XRD results mentioned earlier. However, a further increase in the annealed temperatures resulted in a rapid increase in the content of the rutile phase. During the anatase–rutile transformation occurring in a heat treatment at 650°C (Figure 5(b)), the Raman spectrum of titanium dioxide nanoparticles showed eight allowed modes at 142·21 cm^{-1} (B_{1g}),

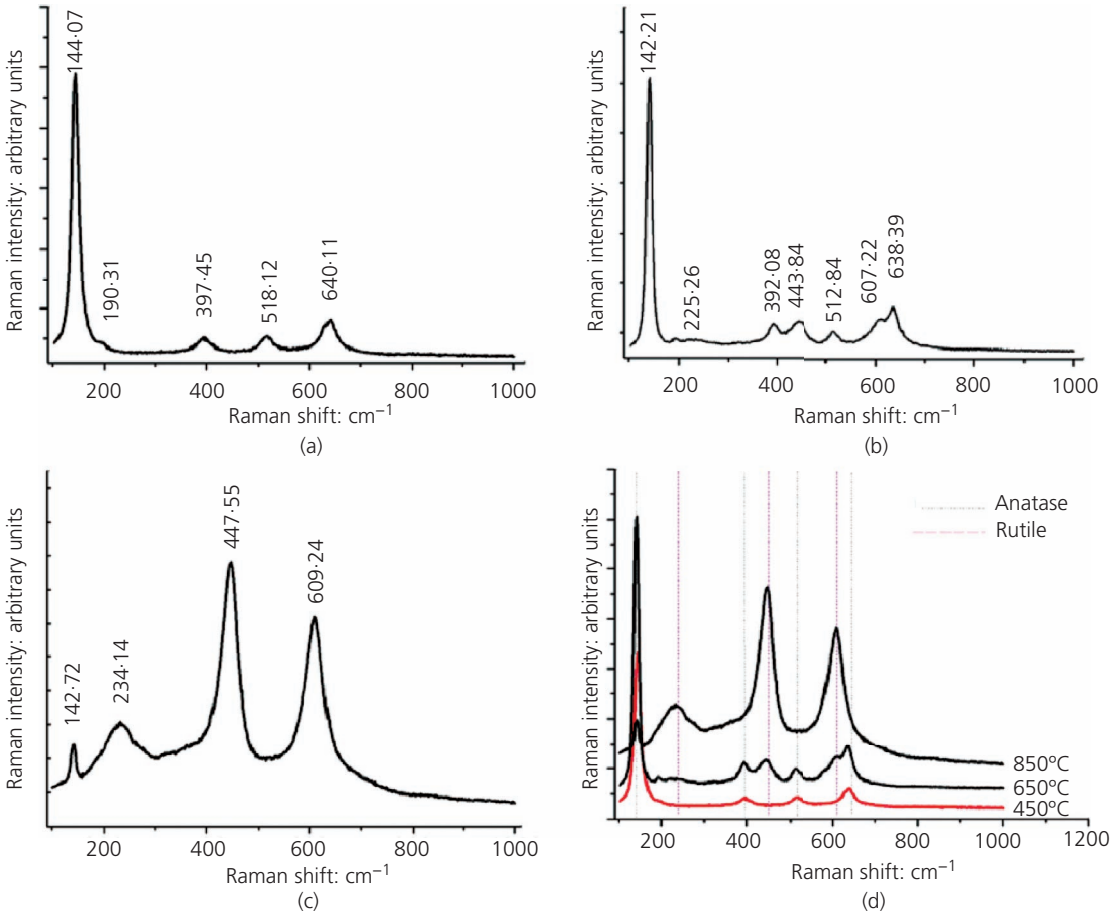


Figure 5. Raman spectra of titanium dioxide nanoparticles annealed at different temperatures for 2 h: (a) 450°C; (b) 650°C; (c) 850°C; (d) peak position of anatase and rutile

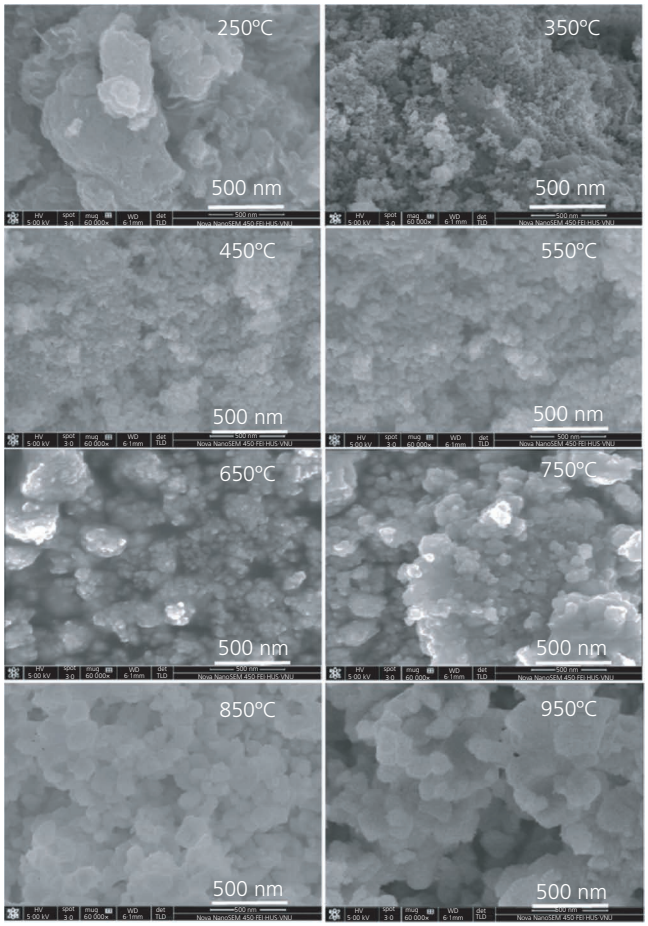


Figure 6. SEM image of the samples after annealing at different temperatures for 2 h

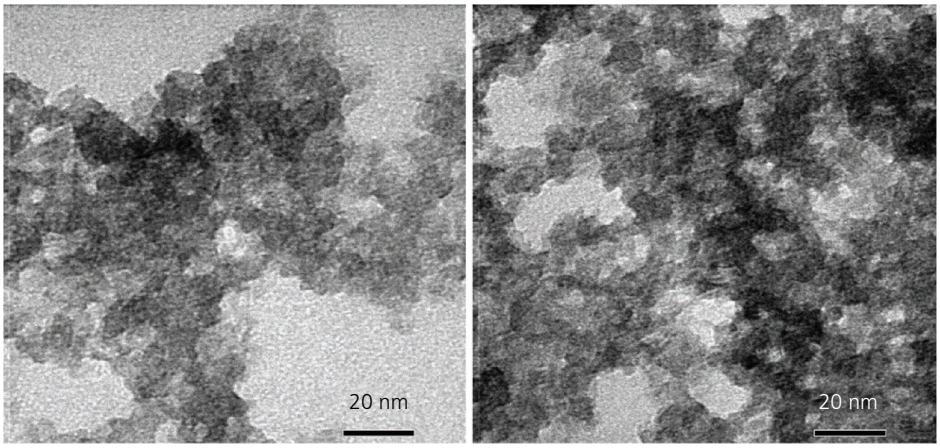
225·26 cm^{-1} (E_g), 392·08 cm^{-1} (B_{1g}), 443·84 cm^{-1} (E_g) and 607·22 cm^{-1} (A_{1g}), which are the characteristic peaks of a rutile titanium dioxide crystal system.[18,19] The E_g and A_{1g} modes located at 193·99 and 512·84 cm^{-1}, respectively, could be attributed to the anatase phase.[17] The Raman spectrum of the titanium dioxide sample heated at 850°C is given in Figure 5(c). The group theoretical analysis showed four Raman-active 'lattice vibrations', which were assigned as follows: 142·72 cm^{-1} (B_{1g}), 234·14 cm^{-1} (E_g), 447·55 cm^{-1} (E_g) and 609·24 cm^{-1} (A_{1g}), representing the characteristic peaks of a rutile titanium dioxide crystal system.[18,19] These results are in accordance with the mentioned XRD analysis.

Distinct shape and morphology were observed in the SEM micrographs of the samples calcined at different temperatures. It could be seen that at the high calcination temperatures, a larger particle size with spherical morphology could be obtained (Figure 6). The formed rutile showed a quite different behavior, having a larger size than the remaining anatase titanium dioxide nanoparticles.[4] This, in fact, reveals that the nucleation and growth of rutile phase would have been initiated at a temperature near 650°C. This result is in accordance with the mentioned XRD and Raman analysis.

In order to expand the applicability of titanium dioxide nanoparticles, the authors used titanium dioxide nanoparticles (Figure 7(a)) in the form of a solution (Figure 7(b)). Figure 8(a) is a TEM image showing titanium dioxide nanoparticles after annealing at 100°C for 1 h, and Figure 8(b) is a TEM image showing titanium dioxide nanosolution. These TEM images show that titanium dioxide nanoparticles are spherical and have a diameter smaller than 10 nm, which is in agreement with the crystallite size obtained from XRD.

(a) (b)

Figure 7. (a) Titanium dioxide nanoparticles after annealing at 100°C for 1 h; (b) titanium dioxide nanosolution



(a) (b)

Figure 8. TEM images of (a) the sample after annealing at 450°C for 2 h and (b) titanium dioxide nanosolution

4. Conclusion

The authors synthesized titanium dioxide nanoparticles by using ultrasound waves to enhance the reaction between titanium dioxide particles and sulfuric acid. A facile synthesis route for titanium dioxide particles was investigated. The titanium dioxide nanoparticles were appropriately characterized using UV–visible spectroscopy, Raman spectroscopy, XRD and SEM and TEM analyses. The results show that titanium dioxide nanoparticles are predominantly in a spherical form and the average size of the nanoparticles was in the range of 6–63 nm and depended on the annealing temperature. The results also show that the amorphous titanium dioxide nanoparticles were crystallized to the anatase nanophase at 250°C and a diffuse phase transition from anatase to rutile occurred between 650 and 950°C. The fabrication of titanium dioxide nanosolution can be of great interest for the research on modifications and applications of titanium dioxide nanostructures.

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