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Archives of Applied Science Research, 2012, 4 (2):1183-1190
(http://scholarsresearchlibrary.com/archive.html)

ISSN 0975-508X
CODEN (USA) AASRC9

Synthesis and characterization of nano-TiO_2 via different methods

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ABSTRACT

In this paper, we report the comparison between TiO_2 nanoparticles prepared via two different routes; i) via sol-gel route and ii) by hydrothermal method. It was found that when prepared under the same ambient conditions viz temperature, pressure etc. and keeping all the parameters same viz precursors, mole ratio, solvent etc; the nanoparticles prepared via sol-gel route were highly crystalline and had smaller crystallite size (~ 7 nm) as compared to the one prepared by hydrothermal method (~ 17 nm). The crystallinity and the crystallite size were examined by XRD and TEM. The band gap values of the TiO_2 nanoparticles were calculated to be 3.54 and 3.43 eV. Photoluminescence (PL) was also recorded for the two types of particles and results have been analyzed.

Keywords: sol-gel, hydrothermal, optical properties, nanomaterials, size effect.

INTRODUCTION

In the recent years, scaling optical and electronic properties of nanomaterials, which become strongly size dependant focused attention on the preparation of nanoparticle semi-conductors [1]. TiO_2 is the promising material as semi-conductor having high photochemical stability and low cost. Well-dispersed titania nanoparticles with very fine sizes are promising in many applications such as pigments, adsorbents and catalytic supports [2-4]. In almost all of these cases, when the particle size is reduced greatly, especially to several nanometer scales, due to the large surface-to-volume ratio, some novel optical properties can be expected [5]. It is not surprising; therefore, that much research has been focused upon the reduction of particle size. It was usually found that different routes often produce different results [6-8]. So it is necessary for us to investigate in detail the methods which may have important effect upon the particle size.

In the present work, we have synthesized TiO_2 nanoparticles via two different routes (sol-gel route and hydrothermal method) and tried to analyze the two on the basis of their crystallinity, crystallite size, band gap and structural properties. X-ray diffraction (XRD) is used to calculate crystallite size. Transmission electron micrograph (TEM) and Scanning electron micrograph (SEM) images are shown to clearly see the particle size and grain size respectively.

MATERIALS AND METHODS

Experimental Procedure

Sol-gel route

All the reagents used were of analytical grade and no further purification was done before use. The sol-gel synthesized TiO_2 was obtained from Titanium (IV) isopropoxide (TTIP) was dissolved in absolute ethanol and distilled water was added to the solution in terms of a molar ratio of Ti: H_2O=1:4. Nitric acid was used to adjust the pH and for restrain the hydrolysis process of the solution. The solution was vigorously stirred for 30 min in order to form sols. After aging for 24 hrs, the sols were transformed into gels. In order to obtain nanoparticles, the gels were dried under 120^{o}C for 2 hr to evaporate water and organic material to the maximum extent. Then the dry gel was sintered at 450^{o}C for 2hrs were subsequently carried out to obtain desired TiO_2 nanocrystalline.

Hydrothermal method

Analytical grade titanium tetrachloride was adopted as the source material and sodium hydroxide as mineralizer. An aqueous solution of titanium was obtained by mixing one molar stoichiometric ratio of TTIP in 50 ml of distilled water. The solution 2-3 mol of NaOH with stirring at several minutes, resulting in a white colloidal sol. The final volume was adjusted to 90 ml using distilled water. Therefore, 90ml sol was transferred to a 100 ml Teflon lined auto clave vessel. The sealed vessel was heated to 240^{o}C for 12 hrs and the resultant precipitate was dried at 450^{o}C for 2 hrs to obtain TiO_2 nanoparticles.

The XRD pattern of TiO_2 was obtained using a X-ray diffractometer Schimadzu model: XRD 6000 with CuKα radiation in the range of 20-70^o (λ=0.154nm). Transmission Electron Microscope (TEM) studies were carried out on the sample using a model JEOL-2010 microscope with an accelerating voltage of 100kV. The surface morphologies of TiO_2 samples were studied using the Hitachi S-4500 Scanning Electron Microscope (SEM). UV-Vis absorption spectra TiO_2 were recorded using a Varian Cary 5E spectrophotometer at room temperature in the range of 200-700nm.The photoluminescence (PL) spectra of TiO_2 were recorded by the Perkin-Elmer lambda 900 spectrophotometer with a Xe lamp as the excitation light source.

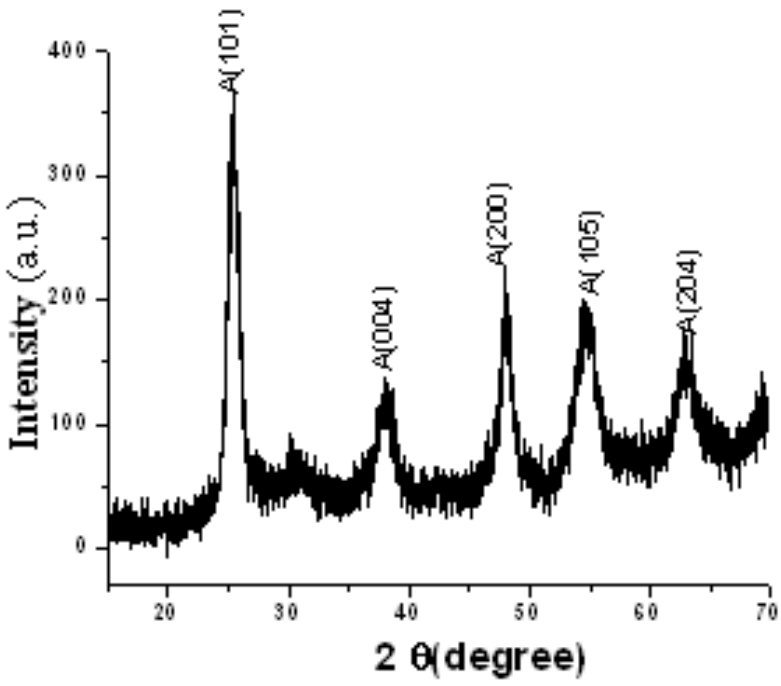

Fig.1 (a) XRD pattern of TiO_2 nanoparticles synthesized via sol-gel route

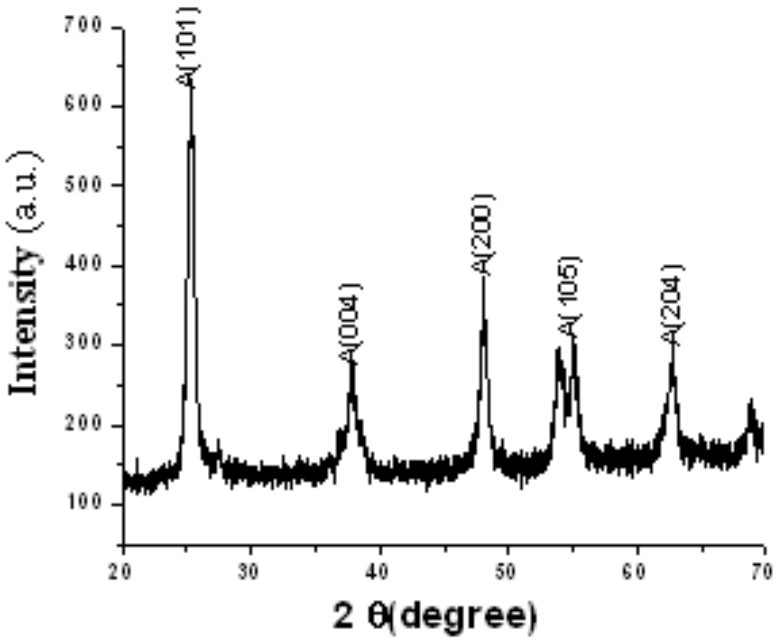

Fig.1 (b) XRD pattern of TiO_2 nanoparticles synthesized via hydrothermal method.

RESULTS AND DISCUSSION

The XRD patterns of the nanoparticles obtained by sol-gel route and hydrothermal method are shown in Fig. 1(a) and 1(b) respectively. The nanoparticles synthesized by both methods showed crystalline nature with 2θ peaks lying at $2\theta=25.25^o$ (101), $2\theta=37.8^o$ (004), $2\theta=47.9^o$ (200), $2\theta=53.59^o$ (105) and $2\theta=62.36^o$ (204). The preferred orientation corresponding to the plane (101) is observed in both the samples. All the peaks in the XRD patterns can be indexed as anatase phases of TiO_2 and the diffraction data were in good agreement with JCPDS files # 21-1272 [9]. Crystallite size was obtained by Debye-Scherrer's formula given by equation

$$D=K\lambda/(\beta\cos\theta)$$

where D is the crystal size; λ is the wavelength of the X-ray radiation (λ=0.15406 nm) for CuKα; K is usually taken as 0.89; and β is the line width at half-maximum height [10]. The crystallite size obtained using this formula is 7 nm for sol-gel derived particles and 17 nm in case of hydrothermal method derived particles.

TEM images of sol-gel derived nanoparticles are shown in Fig. 2a. Clear spherical and non-homogeneous structures can be seen in the Fig. 2a having diameter ~ 9 nm. Selected area diffraction is shown in inset of Fig. 2a which clearly indicates that the TiO_2 nanoparticles are highly crystalline in nature. TEM image and selected area diffraction pattern of the hydrothermal derived nanoparticles are shown in Fig. 2b respectively. Selected area diffraction pattern of the nanoparticles indicates that the TiO_2 nanoparticles prepared via hydrothermal method are crystalline in nature. However, in this case no diffraction rings are aligned as in the case of sol-gel derived nanoparticles. No clear spherical structures can be seen in the TEM image. Nanoparticles obtained in this case are adhering to one another. Agglomeration of nanoparticles is more in this case than the former one. As can be seen from the TEM image that the average particle size is ~ 19 nm, which is in agreement with the crystallite, size obtained from XRD.

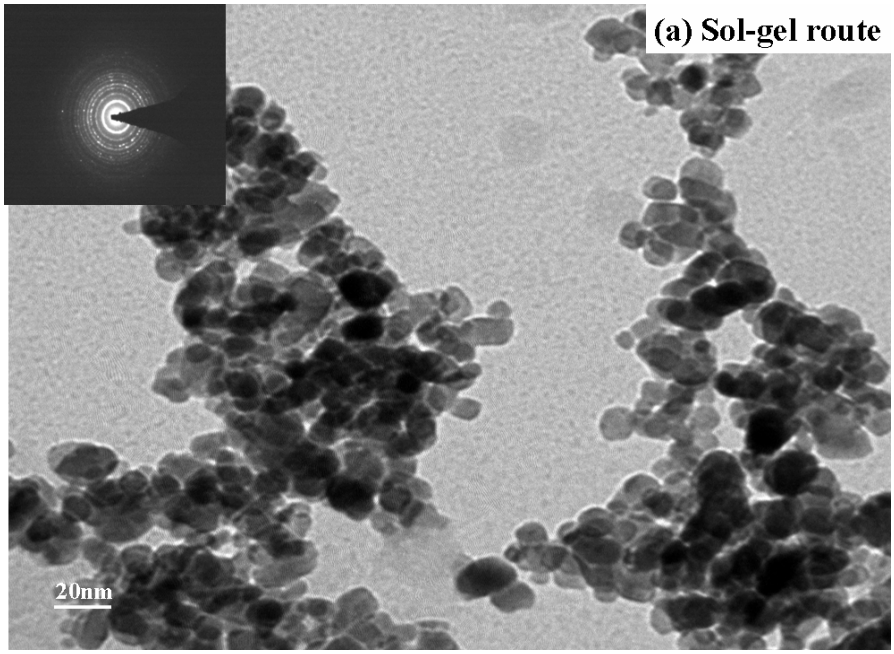

Fig.2 (a) TEM images of TiO_2 nanoparticles synthesized via sol-gel route

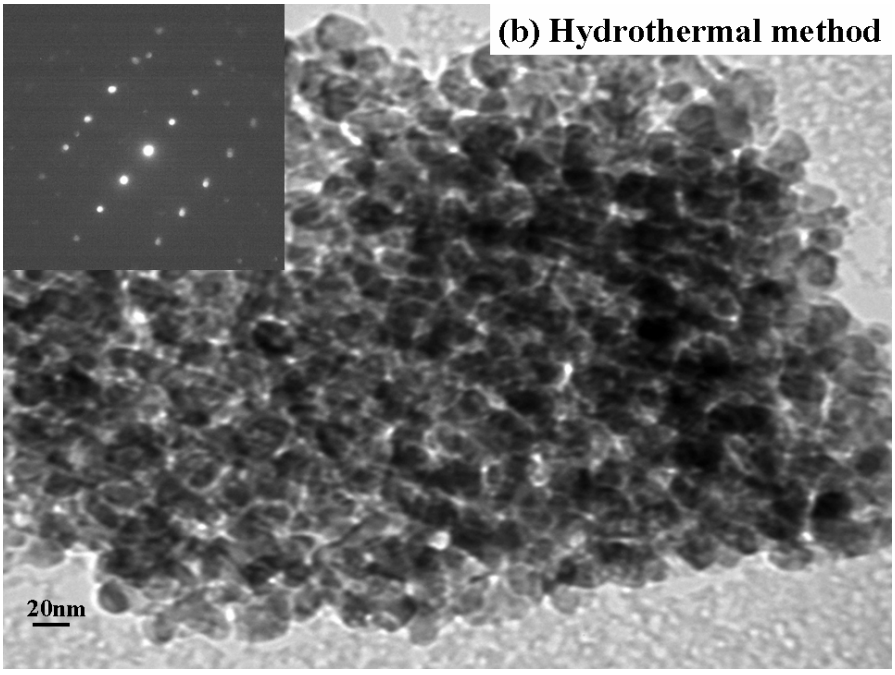

Fig.2 (b) TEM images of TiO_2 nanoparticles synthesized and hydrothermal method.

SEM images of the nanoparticles prepared via both the routes are shown in Fig. 3. Fig. 3a shows the SEM image of sol-gel derived nanoparticles. Clear nanostructures can be seen having grain size of ~ 30 nm. The crystallite size as observed from TEM in this case is ~ 8 nm. This shows that one grain in sol-gel derived nanoparticles is approximately equal to three crystallites. So it is clear that the nanoparticles seen by SEM image consist of a number of crystallites which are seen by TEM image. SEM image of nanoparticles prepared by hydrothermal method is shown in Fig. 3b. Grain size in this case is ~ 100 nm. Crystallite size as seen from TEM image is ~ 19 nm in this

case. This shows that one grain in hydrothermal derived nanoparticles consists of approximately five crystallites. XRD results are confirmed by the combined study of these SEM and TEM images.

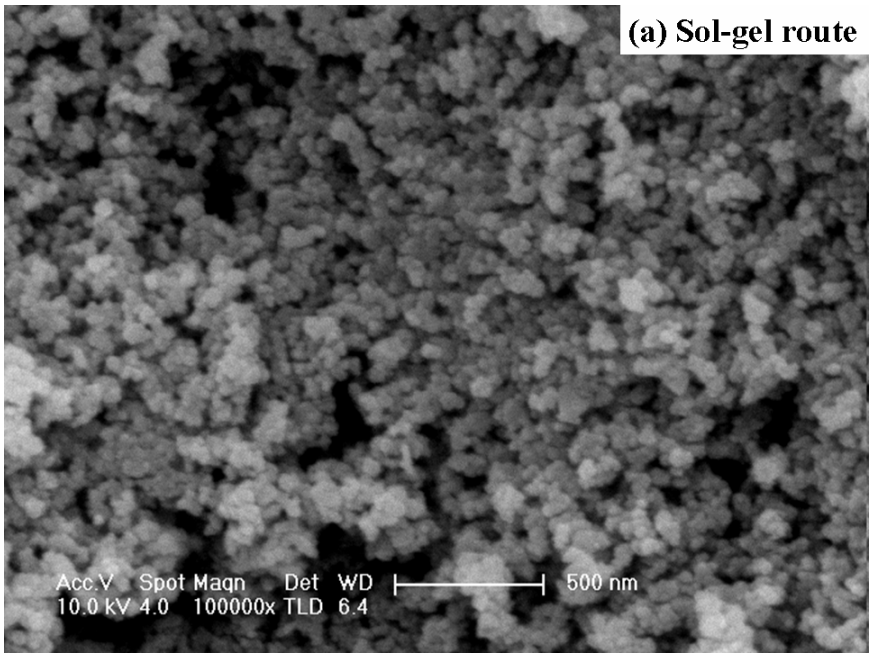

Fig.3 (a) SEM micrographs of TiO_2 nanoparticles synthesized via sol-gel route

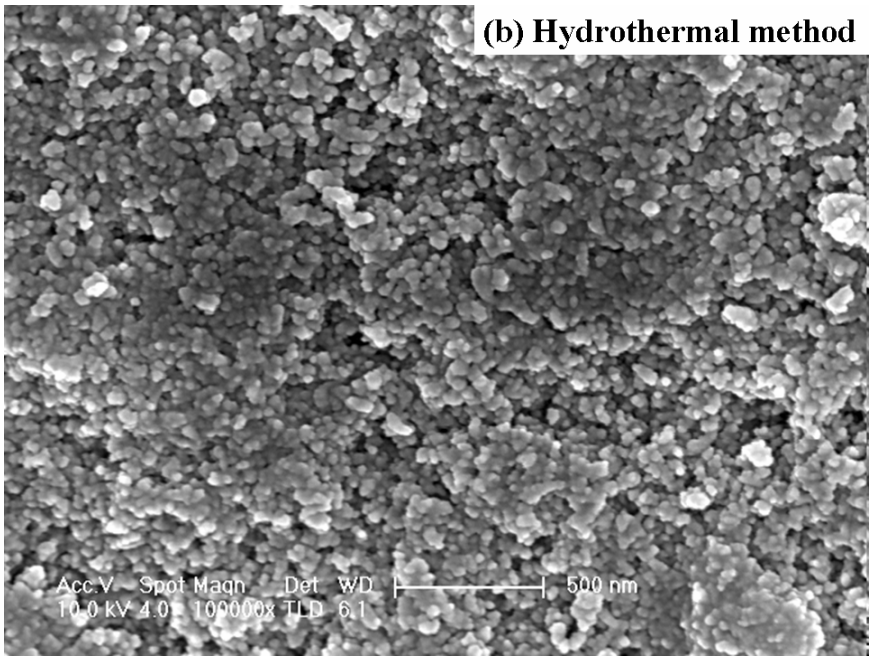

Fig.3 (b) SEM micrographs of TiO_2 nanoparticles synthesized via hydrothermal method.

The optical absorbance coefficient α of a semiconductor close to the band edge can be expressed by the following equation:

$$\alpha = A(h\upsilon - E_g)^{n}/ h\upsilon$$

Where α. is the absorption coefficient, E_g is the absorption band gap, A is constant, n depends on the nature of the transitions, n may have values ½, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. In this case n=1/2 for direct allowed transition [11]. The absorption spectra of TiO_2 nanoparticles are shown in Fig.4 (a). The absorption band edges were estimated around 351 and 362 nm (about 3.54 and 3.43eV). The band gap energy can be determined by extrapolation to the zero coefficients, which is calculated from the above equation. The intercept of the tangent to the plot $(\alpha h\upsilon)^2$ versus $h\upsilon$ (Fig.4b) gives a good approximation of the band gap energy for this direct band gap material.

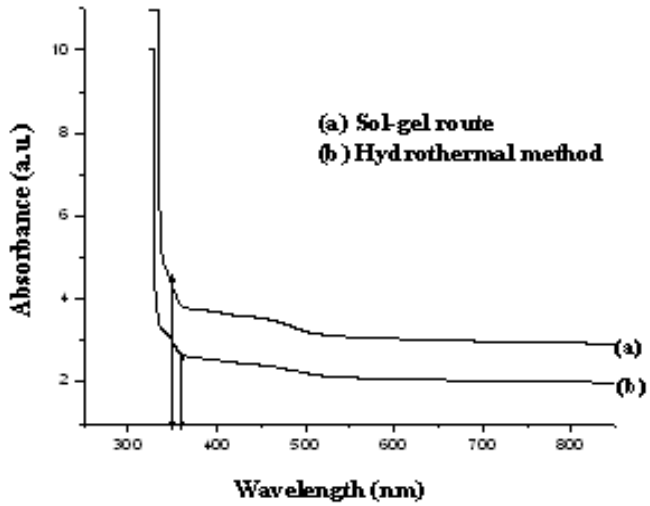

Fig.4 (a) UV-vis absorption spectra of TiO_2 nanoparticles via different method.

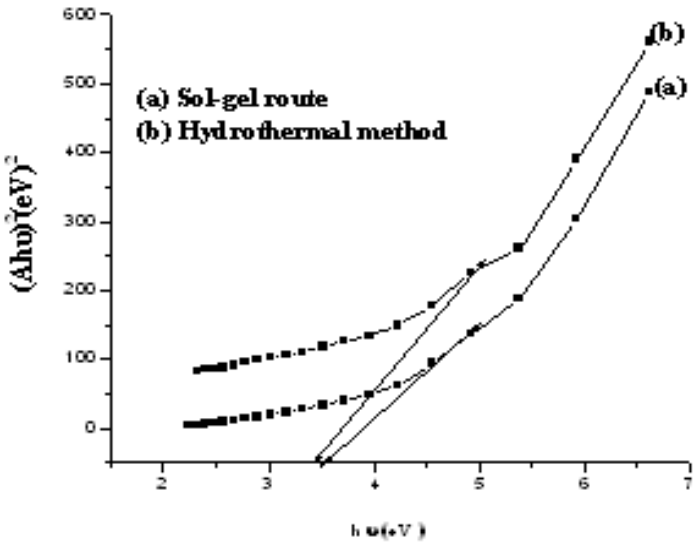

Fig.4 (b) Band gap obtained by extrapolating the linear portion of the $(Ah\upsilon)^2$ versus $h\upsilon$ curve

The band gap energies (Eg) of as-prepared TiO_2 nanoparticles (3.54 and 3.43eV) which are larger than the value of 3.2 eV for the bulk TiO_2. This can be explained because the band gap of the semiconductors has been found to be particle size dependent [12]. The band gap increases with decreasing particle size and the absorption edge is shifted to a higher energy (blue shift) with decreasing particle size. Considering the blue shift of the absorption position from the bulk TiO_2, the absorption onset of the present samples can be assigned to the direct transition of electrons

in the TiO_2 nanocrystals. The band gap values validates our crystallite size results according to which smaller crystallite size should have larger band gap (7 nm, 3.54 eV for sol-gel derived nanoparticles) and large crystallite size should have smaller band gap (17 nm, 3.43 eV for hydrothermal derived nanoparticles).

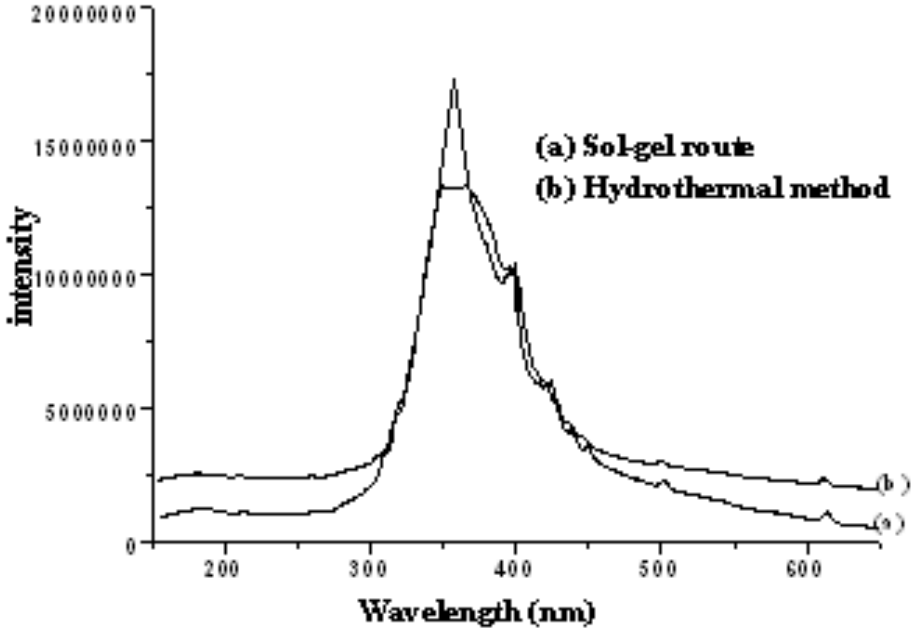

Fig.5 Photoluminescence of TiO_2 nanoparticles obtained via different method

Photoluminescence (PL) spectra of the nanoparticles obtained by both the processes are shown in Fig. 5. The first peak in PL spectra between 320-400 nm corresponds to the direct recombination between electrons in the conduction band and holes in the valence band [13]. TiO_2 nanoparticles prepared via sol-gel method show high luminescence than hydrothermal derived nanoparticles. This could be due to the chemical instability caused during the fabrication process. As can be seen from the PL spectrum of sol-gel derived nanoparticles, the intensity peak is observed at 354 nm. If we calculate the band gap value from this wavelength, it comes out to be 3.5 eV. The PL intensity peak in case of hydrothermal derived nanoparticles is observed at 359 nm. From this value, band gap comes out to be 3.45 eV.

CONCLUSION

TiO_2 nanoparticles were prepared via sol-gel and hydrothermal methods. The TiO_2 nanoparticles prepared via sol-gel route were highly crystalline and had smaller crystallite size (~ 7 nm) as compared to the one prepared by hydrothermal method (~ 17 nm). The band gap of the synthesized nanoparticles was found to be size dependent. Photoluminescence (PL) study confirms the results obtained by XRD and TEM.

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