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Ceramics International 38 (2012) 1905–1913

CERAMICS INTERNATIONAL

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Studies on influence of reflux time on synthesis of nanocrystalline TiO_2 prepared by peroxotitanate complex solutions

Arti Bandgar [a], Sandip Sabale [a,b,c,*], S.H. Pawar [a]

[a] Center for Interdisciplinary Research, D.Y. Patil University, Kolhapur 416 006, MS, India

[b] P.G. Department of Chemistry, Jaysingpur College, Kolhapur 416 101, MS, India

[c] School of Life Sciences, Shanghai University, Shanghai 200444, China

Received 11 May 2011; received in revised form 9 October 2011; accepted 10 October 2011
Available online 15 October 2011

Abstract

Aqueous peroxotitanate complex (PTC) precursor was used to obtain phase pure anatase nanocrystaline TiO_2. A wet chemical synthesis route was used in which number of aqueous solutions of PTC was refluxed for different time intervals to study the effect of reflux time on final product. Several characterization techniques were used such as DSC–TGA, XRD, UV–Vis, SEM and TEM. The study revealed that there is a significant influence of reflux time on structural, morphological and optical properties of TiO_2. As reflux time of PTC has been increased, crystallite size found to be increased. Also, surface morphology of TiO_2 nanoparticles changed from ‘hexagonal shape’ to ‘rice like’ shape and further in ‘ellipsoid rod like’ shape. Optical band gap energy and refractive index incurred to be altered with respect to reflux time of PTC. Detailed study of refluxed PTC solutions has been reported for the first time in the literature.

Keywords: PTC; Nano TiO_2; Reflux; Crystallite size; Morphology

1. Introduction

Titanium dioxide has been reported as of great importance counting its wide range of practical applications in the field of industry and technology. It is indispensable to control the particle size, morphology, and crystalline phase of the TiO_2 nano particles as their applications demand highly pure titania with controlled surface properties. Different physical properties associated with each phase of TiO_2 (anatase, brookite, rutile) acquainted their different applications. In this respect, it is beneficial as well as important to develop new improved routes of synthesis through which crystalline structure, size and shape of TiO_2 nanocrystals can be monitored. The literature contains several studies on the synthesis, phase evolution and particle morphology of TiO_2 nanocrystals [1]. Some of the methods have been reported for synthesis of TiO_2 from peroxotitanate complex [2–5] which is a crucial part of few of the chemical reactions involving synthesis of TiO_2. Peroxotitanate complex can be a good and effective precursor to prepare nano TiO_2. These peroxo complexes are of certain types depending on the pH of their particular reaction [6,7]. There are some reports commenting on the composition of PTC and its chemical structure considering their synthetic conditions [8,9]. Among the all synthetic methods for preparation of nanocrystalline TiO_2, some of the methods refer to the reflux treatment used as a step in their experimental part [10,11]. This treatment is experienced in chemical synthesis methods also and it has been proven useful to obtain nanocrystalline metal oxides [12–15]. Considering all the above aspects, it was decided to carry out detailed study of peroxotitanate route of chemical synthesis of TiO_2 giving reflux treatment. The objective was to know about, whether refluxed solutions of aqueous peroxotitanate complex can affect the crystallinity of the nano TiO_2 and is it possible to perceive the size of TiO_2 nanocrystals prior to the actual experiment and can nano TiO_2 be prepared with desired size. The authors were also interested in studying the morphological and optical properties of TiO_2 prepared by refluxed PTC solutions.

In the present investigation, the systematic effort has been made to synthesis nanocrystalline TiO_2. The effect of time

* Corresponding author at: Center for Interdisciplinary Research, D.Y. Patil University, Kolhapur 416 006, MS, India. Tel.: +91 231 2601202/2601235; fax: +91 231 2601595.

E-mail address: sandip_ana@rediffmail.com (S. Sabale).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.019

variable refluxed aqueous PTC on TiO_2 synthesis has been studied in detail. To the best of the researchers' knowledge, the detailed study of refluxed aqueous solutions of PTC is reported for the first time in the literature.

2. Materials and methods

2.1. Preparation of peroxo titanate complex (PTC)

Titanous (III) chloride [Sigma–Aldrich] is dissolved in distilled water and precipitated by adding aqueous ammonia [Thomas Baker 15%] solution. The precipitate was washed for several times until the most of the Cl^- and NH_4^+ ions were removed. Then it was peptized with hydrogen peroxide [Loba Chemie (30% w/v)] to get peroxo titanium complex (PTC) solution.

2.2. Preparation of titanium gel

The titanium gel was obtained by controlled heating of the prepared aqueous PTC solution. Direct heating of this titanium gel gave anatase TiO_2 powder (without reflux) which was annealed at 400 °C further.

2.3. Preparation of refluxed PTC solutions

The refluxed solutions of PTC were obtained by refluxing PTC solution with varying time of reflux treatment. Samples of refluxed PTC such as 1–10, 12, 14, 16, 18, 20, and 24 h respectively were prepared.

2.4. Preparation of TiO_2 nanocrystals

Refluxed aqueous solution of PTC converted to nano anatase TiO_2 powder after controlled heating and annealed at 400 °C. The all reagents used to prepare nano TiO_2 were of analytical grade and double distilled water was used throughout the experiment.

2.5. Characterization techniques

DSC–TGA study of the titanium gel was carried out using Perkin Elmer SDT Q600V 20.9 build 20; in the range 0–100 °C. The studies of optical properties of PTC, Titanium Gel and nano TiO_2 were carried out using JASCO V-670 UV–VIS–NIR spectrophotometer with wavelength range from 200 to 800 nm at room temperature. The cystallinity of titanium gel and nano TiO_2 was identified by X-ray diffractometer of BRUKER AXS using graphite monochromatic copper radiation (CuKα) at 40 kV, 25 mA over the 2θ range 10–100°. The surface morphology of nano TiO_2 was observed by scanning electron microscopy (SEM) using JEOL JSM 6360 and transmission electron microscopy (TEM) using Hitachi H-7000 operating at 100 kV with a resolution not less than 3 nm.

3. Results and discussion

3.1. Formation of peroxotitanate complex

The PTC was formed by precipitation of titanous(III) chloride with aqueous ammonia followed by oxidation with hydrogen peroxide resulting into a transparent yellow solution of Ti(III)–H_2O_2. The exact composition of PTC is still unknown even after number of efforts [16–18] has been made to identify structure and chemical composition of PTC. The controlled heating of this solution gives titanium gel [19] which is in the TiOOH matrix form [20]. Further heating of this gel gives nanocrystalline TiO_2 (Fig. 1).

The possible reaction is as follows:

$$TiCl_3 + 3NH_4OH \xrightarrow{\text{yields}} Ti(OH)_3\downarrow + 3NH_4Cl$$

$$\begin{aligned} Ti(OH)_3 + H_2O_2 &\rightarrow \text{Solution of Ti(III)} \\ &- H_2O_2 \ \text{Complex} \rightarrow \frac{\Delta}{\text{Decomposition of } H_2O_2} \\ &\times \text{Titanium gel}/(\text{TiOOH matrix}) \xrightarrow{\Delta} TiO_2 \ \text{nanoparticles} \end{aligned}$$

3.2. DSC–TGA studies of peroxo titanium gel

To investigate the effect of the temperature on the peroxo titanium gel the DSC–TGA study was carried out. The TGA of the PTC was carried out from room temperature to 1000 °C in flowing ambient air. The TGA curve (Fig. 2) shows that there is a large weight loss of 93.11% observed between room temperature to 150 °C which was mostly due to the removal of water from the gel. There was gradual increase in weight loss from 150 °C to 450 °C and afterwards it was almost constant. DSC studies (Fig. 2) were also carried out from the room temperature to 1000 °C. There was observed an endothermic peak between 100 and 150 °C which coincides with the first major weight loss in TGA curve due to the removal of water. But this peak splits into two regions, 100–125 °C and a sharp

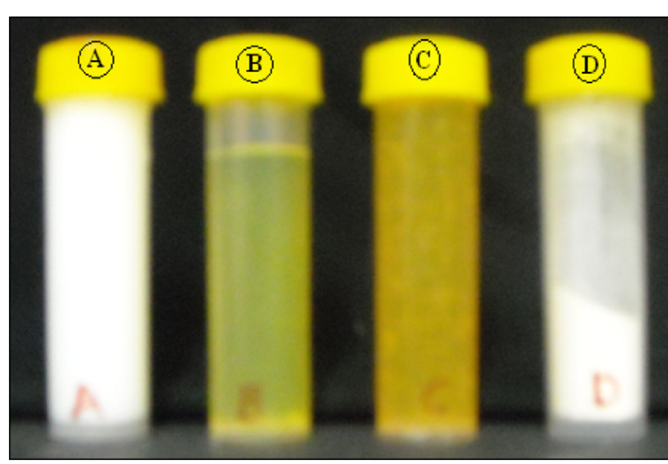

Fig. 1. Photographic presentation of different stages of formation of nanocrystalline TiO_2 (A: Ti $(OH)_3$ dispersion; B: Ti-peroxotitanate complex; C: titanium gel and D: TiO_2 powder).

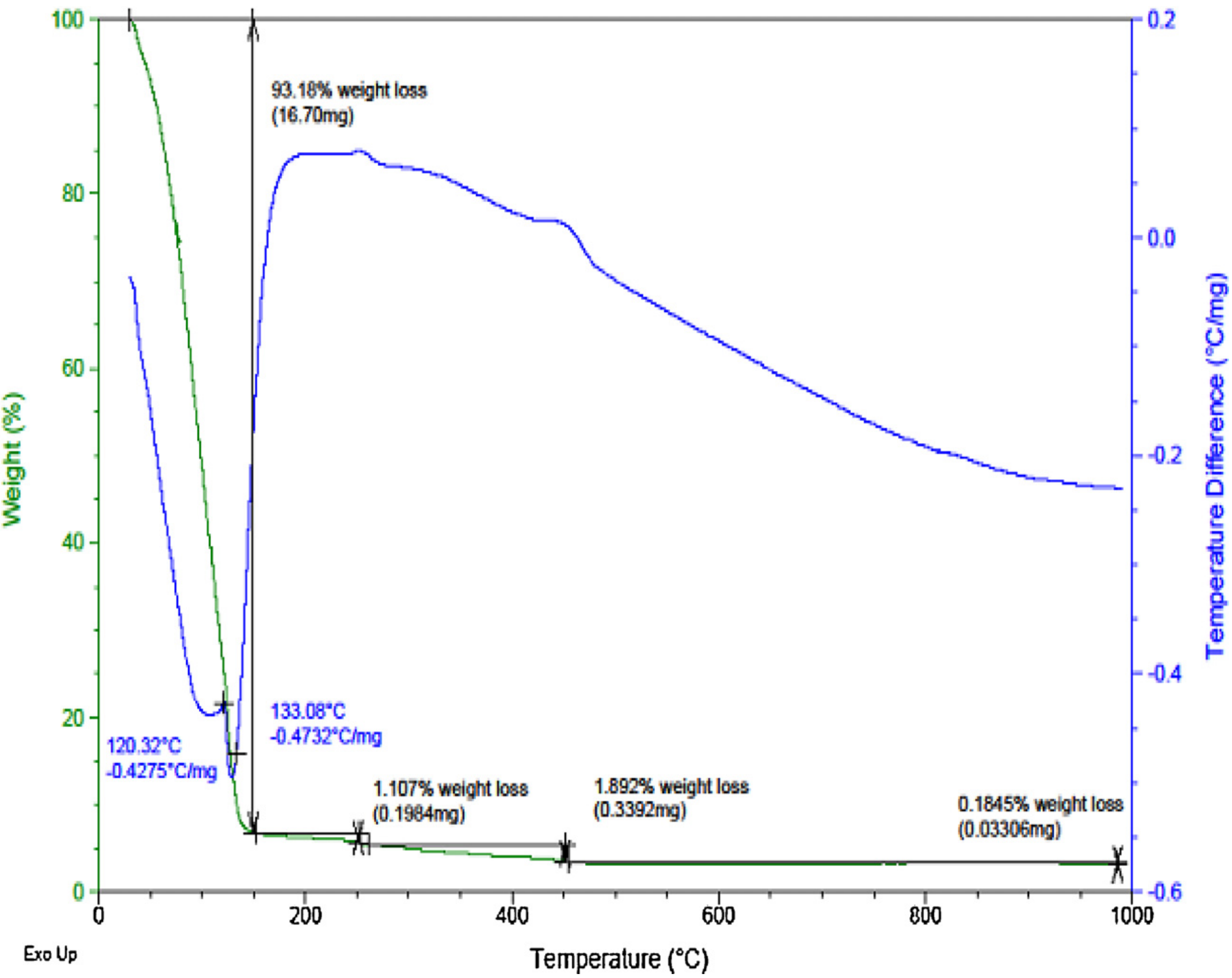

Fig. 2. DSC–TGA curve of peroxotitanium complex.

peak at 125–130 °C which may be due to the removal of water from PTC while formation of titanium gel and chemical conversion of PTC to the nano TiO_2 respectively. The observed exothermic peaks at 250 °C and 400 °C are attributed to oxide formation and phase transformation of titanium respectively.

3.3. Structural properties

3.3.1. XRD studies of titanium gel and nanocrystalline TiO_2 without reflux treatment

The X-ray diffraction measurements were performed for titanium gel and TiO_2 without reflux in the 2θ range from 20 to 80° to determine their crystallinity and size. Diffraction patterns for both were compared with reference to JCPDS database. The XRD pattern (Fig. 3) of titanium gel shows it is amorphous in nature while TiO_2 prepared by titanium gel shows crystalline phase pure anatase and is in good agreement with the standard spectrum (1 0 1) (Ref. No. 00-021-1272, Anatase, Syn). It was observed that titanium gel forms anatase TiO_2 after direct heating because of decomposition of titanium gel into anatase nano crystals.

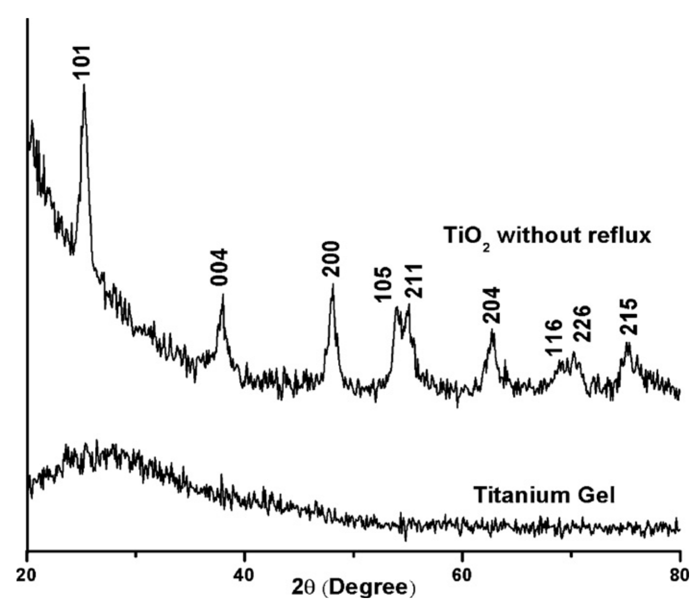

Fig. 3. XRD pattern of titanium gel and nanocrystalline TiO_2 without reflux treatment prepared from aqueous PTC solutions.

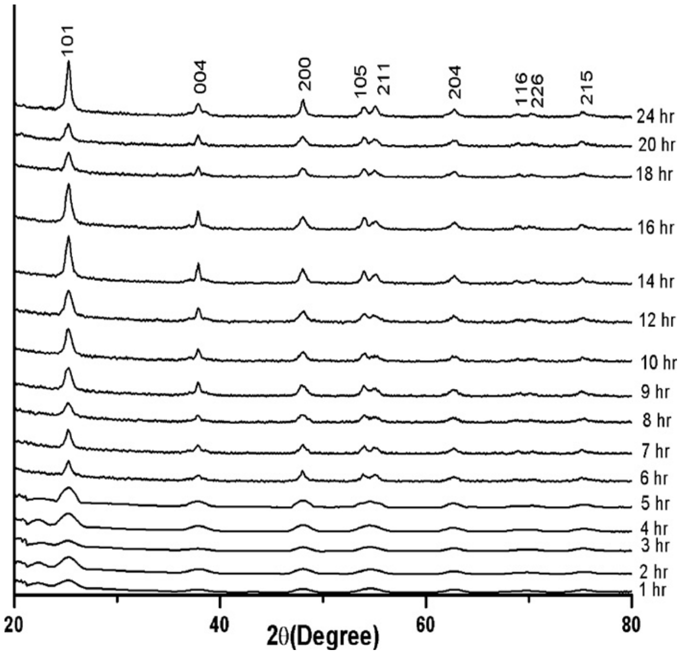

Fig. 4. XRD patterns of nano TiO_2 prepared from refluxed aqueous PTC solutions at different time intervals.

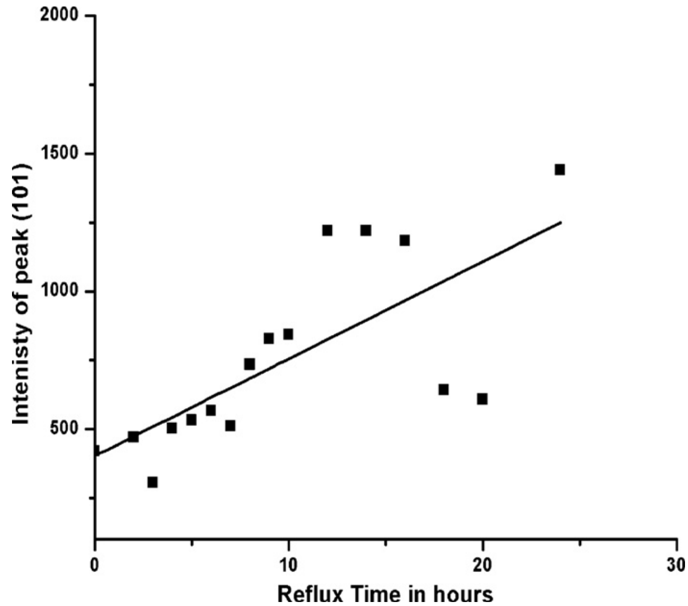

Fig. 5. Variation of intensity of peak 1 0 1 with change in reflux time.

3.3.2. XRD studies of nanocrystalline TiO_2

The X-ray diffraction patterns were recorded in the 2θ range from 20 to 80° to determine crystallite size of several nano samples containing TiO_2 with varying reflux time as shown in Fig. 4. The XRD patterns show the formation of anatase TiO_2 matched with standard JCPDS data (1 0 1) (Ref. No. 00-021-1272, Anatase, Syn) for all nano samples prepared from aqueous refluxed PTC solutions. No characteristic peaks of other impurities were noticed in the XRD results, indicating that the product has high crystallinity and purity. The crystallite size of nano TiO_2 is calculated using Scherrer's Equation (Eq. (1)) and the calculated values are given in Table 1,

$$D = \frac{K\lambda}{\beta\cos\theta}\left(\frac{360}{\pi}\right) \tag{1}$$

where K is Scherrer constant and is taken as 0.9.

From the XRD patterns it was observed that increase in reflux time of PTC affects the diffraction peak intensity of 1 0 1 peak of TiO_2 as shown in Fig. 5. Intensity of peak 1 0 1 goes on increasing with decrease in peak broadening which suggests that these TiO_2 powders were composed of irregular polycrystalline structures showing the remarkable influence

Table 1
Change in crystallite size (D), band gap (E_g), maximum wavelength of absorption (λ_{max}), intensity of absorption and refractive index with variation in reflux time of PTC.

Reflux time (h)	D (nm)	E_g (eV)	λ_{max} (nm)	Absorption intensity (au)	Refractive index (au)
0	9.77	2.96	349	0.803	1.563
1	3.97	2.92	352	0.815	1.550
2	5.02	2.94	345	0.772	1.559
3	6.12	2.94	353	0.870	1.569
4	5	2.99	354	0.827	1.566
5	6.31	2.92	347	0.832	1.565
6	12.98	2.88	354	0.825	1.566
7	12.66	3.01	347	0.843	1.567
8	9.58	3	343	0.844	1.570
9	10.35	3.02	339	0.868	1.570
10	10.87	3.06	336	0.863	1.570
12	10.39	3.08	331	0.877	1.571
14	12.59	3.1	334	0.855	1.570
16	12.54	3.1	331	0.836	1.570
18	12.70	3.11	328	0.836	1.570
20	12.10	3.05	327	0.841	1.569
24	14.95	3.2	327	0.765	1.567

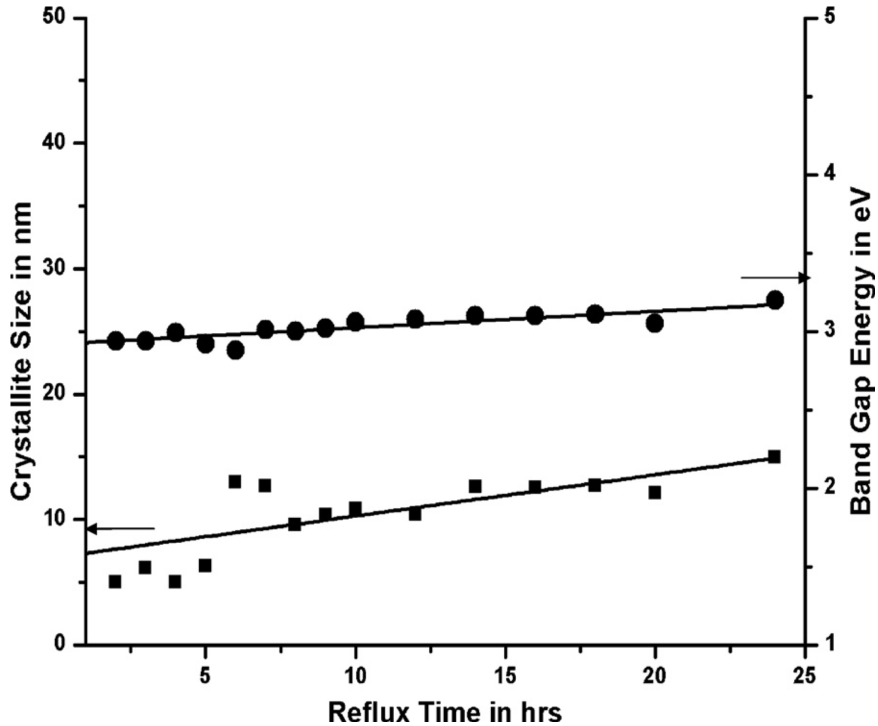

Fig. 6. Variation of crystallite size (■) and band gap energy (•) of nano TiO_2 dependent on change in reflux time.

of reflux time on aqueous PTC solutions. It is stated that decomposition of PTC into anatase TiO_2 crystals takes place when PTC is refluxed [10] which changes crystallite size of TiO_2 in a regular fashion and it is noted that crystallite size goes on increasing when refluxing time increases. Due to variance in reflux time; changing crystallite size has resulted shift in band gap energy of TiO_2. Calculated values of crystallite sizes and band gap energies are plotted in Fig. 6 indicating the gradual increasing trends observed altogether for both.

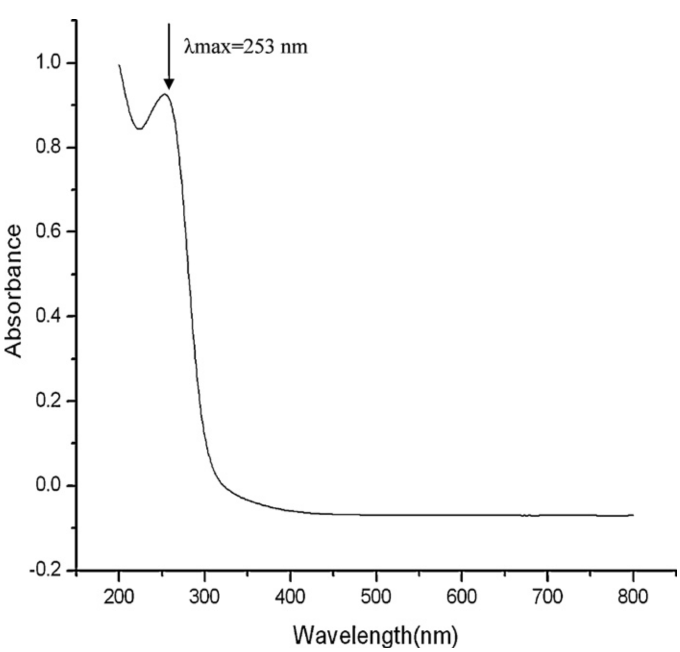

Fig. 7. Absorbance spectrum of aqueous PTC solution.

3.4. Optical properties

Optical band gap energies and refractive indices were calculated from the optical absorption spectra of PTC solution, titanium gel and nano TiO_2 samples which has been sounded out the impact of reflux time of PTC on optical properties of TiO_2 nanopowder and mentioned below.

3.4.1. Refractive index

The analytical method has been used for the calculation of refractive index [21] 'n' of nano samples of TiO_2 (Table 1)

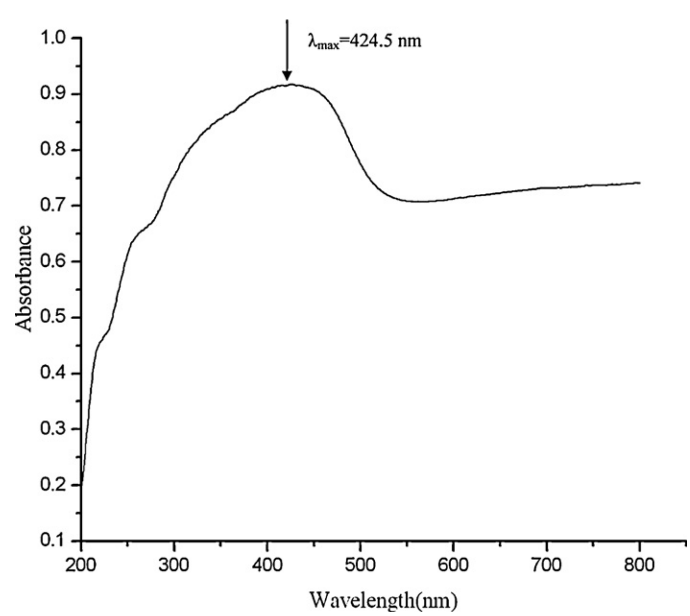

Fig. 8. Absorbance spectrum of hydrous titanium gel/TiOOH matrix.

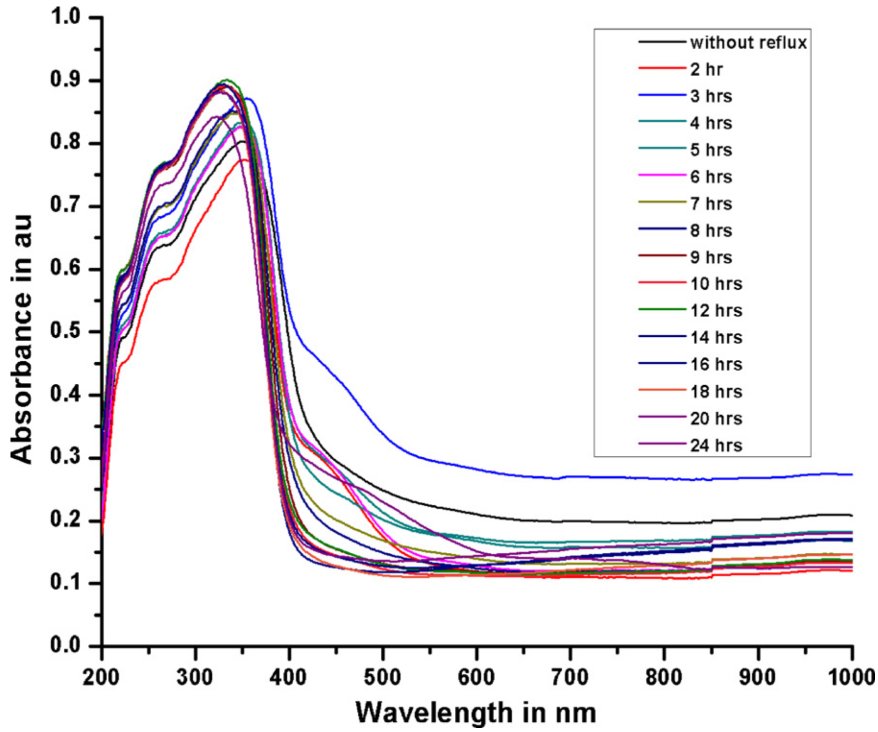

Fig. 9. Absorbance spectra of nano TiO_2 prepared from refluxed aqueous PTC solutions for different time intervals.

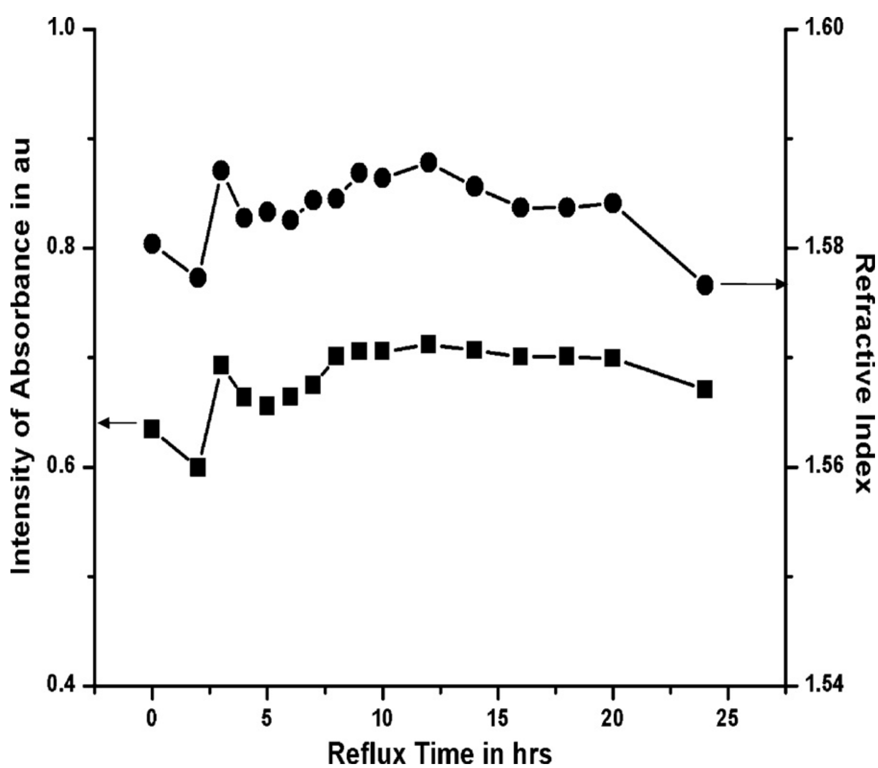

Fig. 10. Variation in intensity of absorption (•) and refractive index (■) with change in reflux time of PTC.

using Eq. (2),

$$n = \left[\frac{n_s^2 T_f + n_s(1+\sqrt{R_f})^2}{T_f + n_s(1-\sqrt{R_f})^2}\right]^{1/2} \tag{2}$$

where n = refractive index of the material; n_s = refractive index of the quartz; T_f = transmittance of the material; R_f = reflectance of the material.

3.4.2. Optical band gap

The band gap [22] study (Table 1) of prepared nano TiO_2 powder was carried out from the absorption data. The graph of $(\alpha_t h\upsilon)^{1/2}$ as a function of $h\upsilon$ from which the band gap energy was calculated using Eq. (3),

$$\alpha = \frac{[\alpha_0(h\upsilon - E_g)^n]}{h\upsilon} \tag{3}$$

where E_g is the separation between bottom of the conduction band and top of the valence band, α is absorption of the gel/ TiO_2 powder and α_0 is absorption coefficient, $h\upsilon$ is the photon energy and n is constant. The value of n depends on the probability of transitions; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transition respectively.

The UV absorption spectra of PTC (Fig. 7), titanium gel (Fig. 8) and TiO_2 (Fig. 9) were measured between 200 and 800 nm. The Fig. 7 is pointing out the absorbance spectra of aqueous PTC solution which shows maximum absorbance in UV region and has negligible absorbance for visible region. The Fig. 8 shows the absorbance spectra of titanium gel. It is mattering that, titanium gel has shown absorption in both UV and visible region which may be due to yellow and transparent nature of titanium gel. The band gap energy and refractive index calculated for titanium gel is 2.39 eV and 1.57 respectively. Most interesting evidence found for titanium gel showing higher absorption in both UV as well as visible region, however, nano TiO_2 prepared from this titanium gel without reflux shows maximum absorption only in UV region which is almost decreased for visible region. For various nano TiO_2 obtained from refluxed PTC aqueous solutions, it was observed that the absorption changes with change in reflux time. It is due to the varying rate of decomposition of anatase crystals within refluxing; and refluxing time affected on size of nanoparticles resulting variation in band gap energies of TiO_2

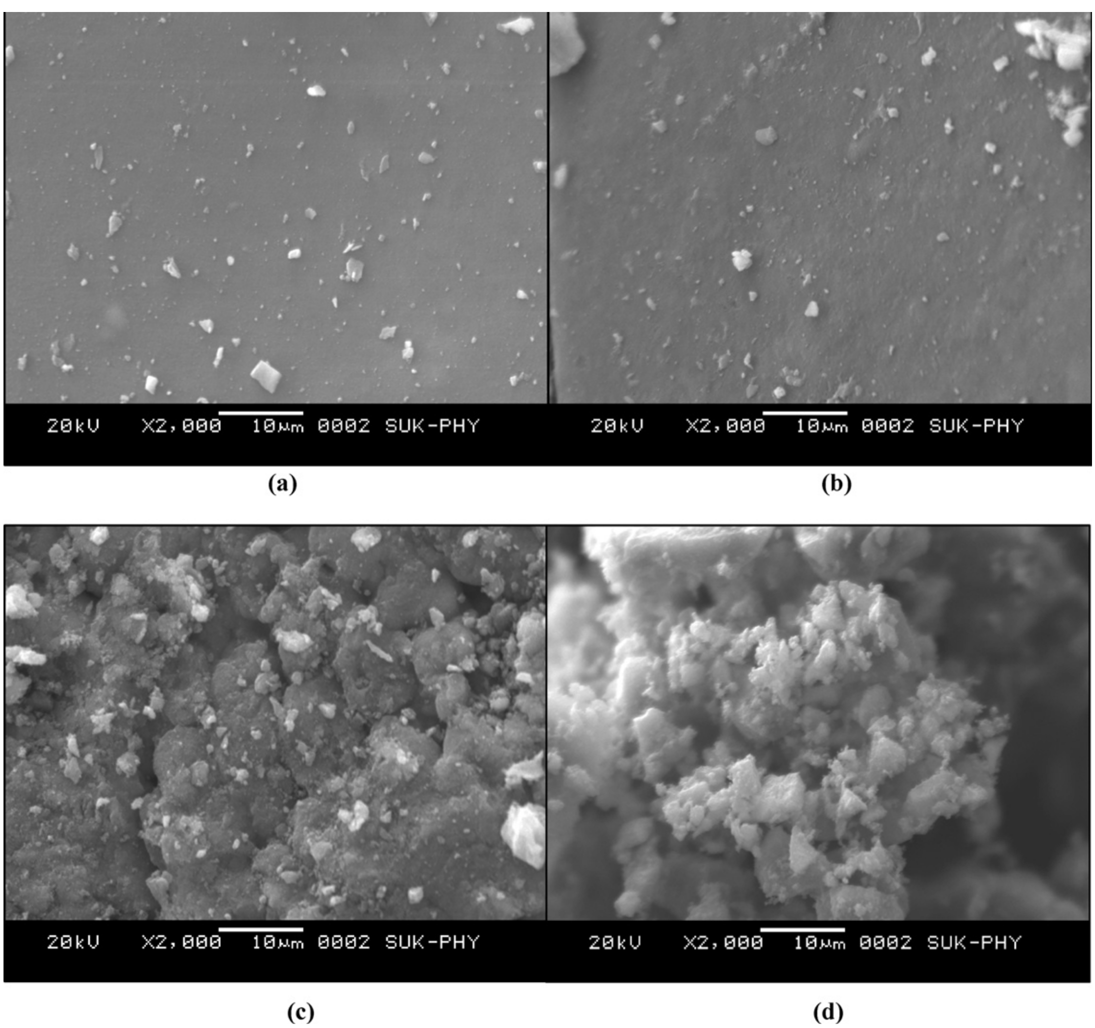

Fig. 11. SEM images of nanocrystalline TiO_2 powder annealed at 400 °C (a) without reflux and (b) 3 h (c) 12 h (d) 24 h with reflux respectively.

and change in absorption properties too. The spectra showing maximum absorption in UV region is seen to be decreased in visible region. Also, the impact is found on intensities of absorption values and refractive indices due to effect of reflux time on PTC (Fig. 10).

3.5. Morphological properties of nanocrystalline TiO_2

3.5.1. SEM analysis

Highly agglomerated TiO_2 nanoparticles were observed in SEM image of sample without reflux and shown in (Fig. 11a). It is because, very fine particles of TiO_2 have tendency to agglomerate easily and it forms nanocrystals of TiO_2. SEM pictures for refluxed TiO_2 samples indicate that grain growth of all anatase samples occurred having finer crystallinity during reflux experiments; and are shown in Fig. 11b–d with reflux of 3, 12 and 24 h respectively. Average crystallite size increased roughly with increase in reflux time of PTC carried from 1 to 24 h. It is due to increasing thermal energy within reflux itself causing the process of decomposition of PTC into anatase crystals. Protracted reflux treatment provides more thermal energy to the PTC solutions and it results into increasing size and crystallinity of the nanoparticles.

3.5.2. TEM analysis

The most striking revelation in the TEM images, however, is that reflux has pronounced effect on particle morphology and distribution. Specifically, the particle sizes and shapes appear to shift from hexagonal crystals for without reflux with large number of nano particles of the diameter below than 10 nm to bimodal distribution consisting rice shaped nano particles of the diameter around 20 nm at 12 h of reflux treatment. And further nano particles have gone under irregular distribution with ellipsoid rod like structure for 24 h of reflux varying the

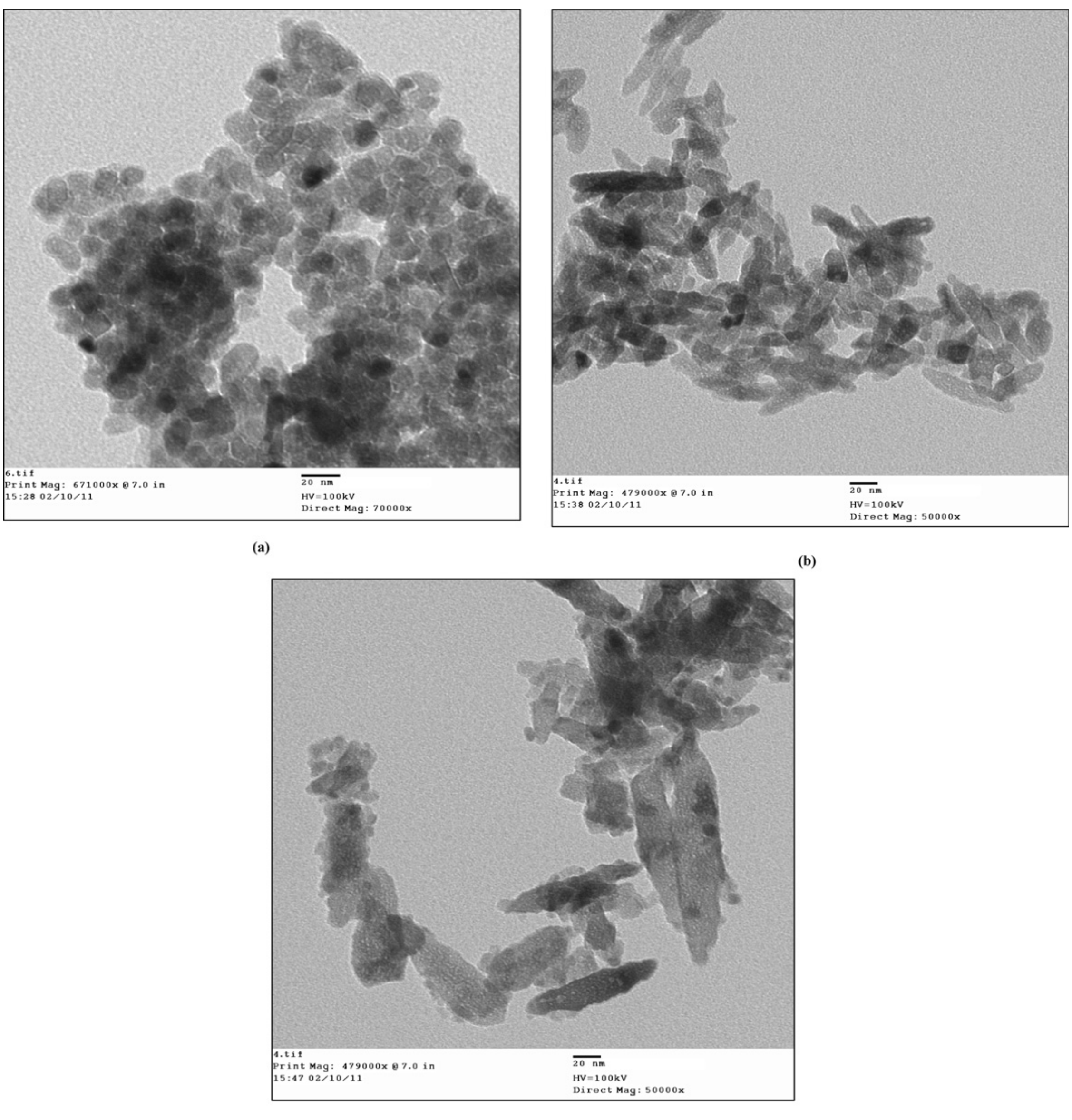

Fig. 12. TEM images of nanocrystalline TiO_2 powder annealed at 400 °C (a) without reflux and (b) 12 h (c) 24 h with reflux respectively.

diameter range slightly about 20 nm. The appearance of larger particles with new morphology at the latter suggests that the increased reflux time of PTC is conductive to grain growth via a reflux mechanism, in which larger particles are grown in expense of smaller particles which is in good agreement with the XRD results (Fig. 12).

4. Conclusions

In this paper, we reported that the decomposition of peroxotitanate complex into anatase TiO_2 nano crystals took place during the refluxing; depending on the increasing reflux time which has been affected ultimately the structural, morphological and optical properties of TiO_2. Peroxotitanate complex (PTC) is used as precursor and aqueous solutions of PTC were refluxed for different reflux time intervals which showed that increase in the reflux time causes variation in the crystallite size of TiO_2 in a systematic manner playing a substantial role in the formation of nano TiO_2 with changing band gap energies and refractive indices. It gives phase pure anatase TiO_2 nano crystals having different surface morphologies such as hexagonal, rice like and ellipsoid rods like structures depending upon time of refluxed PTC solution. The detailed data of influence of reflux time on PTC is useful to monitor the size, shape and band gap energies of nano TiO_2 which has been reported for the first time in the literature. Authors have developed a simple, fast and cost-effective method for controllable synthesis of nano TiO_2 under mild chemical reaction conditions without using an expensive experimental technique is an advantageous contribution to the work.

Acknowledgements

We acknowledge the financial support of BRNS-DAE and DRDO to the research. The authors are thankful to Dr. B.A. Kakade for valuable discussions throughout the research.

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