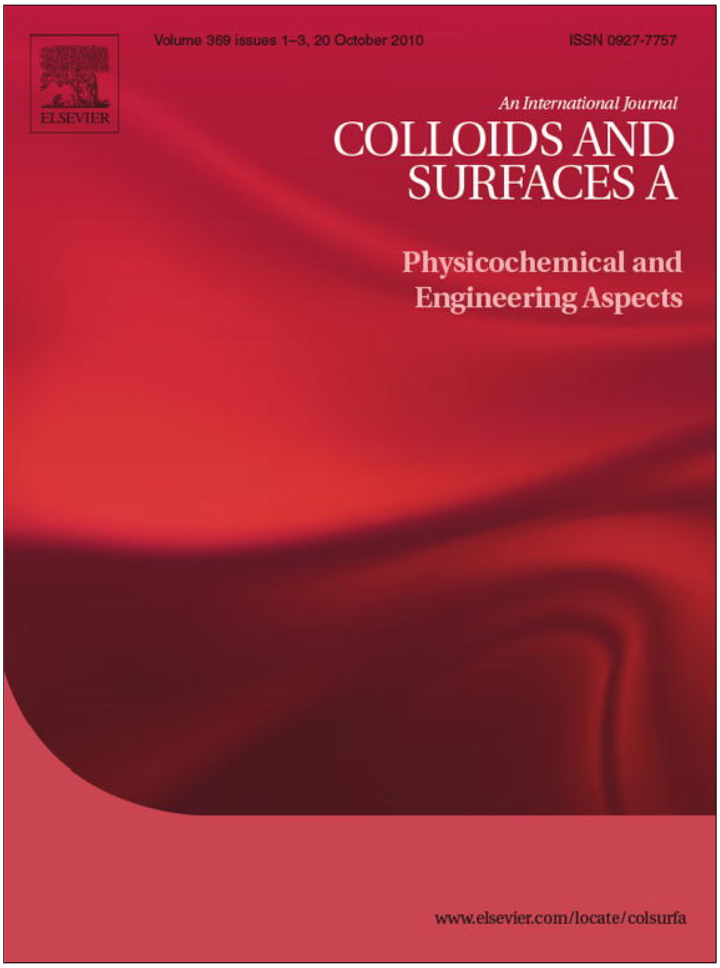
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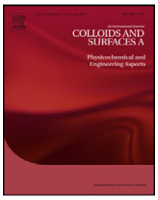

Room temperature synthesis of titanium dioxide nanoparticles of different phases in water in oil microemulsion

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ABSTRACT

We report the synthesis of crystalline titanium dioxide nanoparticles of two different phases (rutile and anomalous pseudobrookite) at room temperature by a novel microemulsion technique. In this method, one of the reactants (titanium tetrachloride) is dissolved in the continuous organic phase, whereas the second reactant (ammonium hydroxide) is added as an aqueous solution. The site of the reaction has been controlled by using two different addition methods for the second reactant. The size and the crystalline phase of the titanium dioxide nanoparticles varied according to the site of the reaction between the two reactants. Reaction in the aqueous core gives rutile titanium dioxide nanoparticles having an average size of 4.2 nm verified by X-ray diffraction and FTIR. The reaction in the organic phase gives rise to crystalline anomalous pseudobrookite titanium dioxide nanoparticles of much larger size (10–40 nm). This anomalous pseudobrookite structure is thermally unstable and converts to rutile on high temperature treatment.

1. Introduction

Titanium dioxide (TiO_2) is an important non-toxic pigment used in the manufacture of many everyday substances such as paints and cosmetics. It exists mainly as three crystalline polymorphs – anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [1]. In the past 20 years, TiO_2 nanoparticles have become important due to their numerous applications. TiO_2 has excellent photocatalytic oxidative properties that depend on the crystallinity and crystal form [2]. The photocatalytic activity of TiO_2 is used for cleaning polluted air and water [3,4]. It also exhibits some unique dielectric and chemical properties that can be utilized in various technological and engineering applications such as ceramic membranes, humidity sensors [5], gas sensors [6], absorbents and pigments [7]. It is currently being used in solar cells and lithium-based batteries [6]. Optical properties of TiO_2 have also been proposed due to their high refractive index and stability [8].

Microemulsion routes [7–15] have been used to prepare TiO_2 nanoparticles through a host of precursor materials like titanium tetraisopropoxide (TTIP) [7,9] titanium tetrachloride ($TiCl_4$) [10] titanium butoxide (TB) [11,13] and titanium ethoxide [12]. Water-in-CO_2 microemulsions have also been used to prepare titanium dioxide nanoparticles, as CO_2 is non-toxic, non-flammable, highly volatile, inexpensive and environmentally benign [16]. Microemulsions are used as they provide a micro-heterogeneous medium for the generation of nanoparticles [7]. The surfactant-stabilized micro-cavities provide a cage-like effect that influences particle nucleation, growth and agglomeration [17]. The size scale of these nanoreactors is in the range of 1–10 nm. This is a dynamic system at the micellar level. The micelles collide with each other and exchange their contents rapidly, which is essential for carrying out chemical reactions [17].

Work on titanium dioxide nanoparticle synthesis using water in oil microemulsion has focused extensively on using a two-microemulsion method [10], in which, mixing of two microemulsions with two reactants dissolved in the aqueous core of the microemulsion leads to formation of titanium dioxide nanoparticles by intermicellar exchange. The produced nanoparticles are amorphous and convert to anatase on heating at 600–750 °C and to rutile above 900 °C. In this paper, we demonstrate the use of a novel method to produce highly monodisperse crystalline titanium dioxide nanoparticles using the organic phase of the microemulsion as one of the reactant phases. The site of the reaction is controlled by carrying out the reaction via two different synthetic routes. The size and the crystalline phase of the TiO_2 nanoparticles vary according to the site of the reaction.

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Table 1
Weight fraction of the various components of the microemulsion.

Chemical	Weight fraction
Cyclohexane	0.62
Hexanol	0.13
Triton X-100	0.19
Ammonium hydroxide solution (13.4 M)	0.04
Titanium chloride	0.02

2. Materials and methods

2.1. Materials

All chemicals were used as purchased unless mentioned. Cyclohexane and ammonium hydroxide (13.4 M) solution were bought from Merck Ltd. Cyclohexane was refluxed with calcium hydride to remove moisture and stored in the presence of zeolites before use. Titanium tetrachloride ($TiCl_4$) and methanol were purchased from Spectrochem Pvt. Ltd. Triton X-100 (TX-100) and hexanol were purchased from S.D. Fine Chemicals Ltd. and were used without further processing. Butanol was purchased from Thomas Baker Chemicals Ltd. Chloroform was used as purchased from Qualigens Fine Chemicals.

2.2. Methods

40.47 g of TX-100 was mixed with 31 ml of hexanol in a clean and dry 250 ml standard flask to form a blend. This blend was then dissolved in cyclohexane to form 250 ml of 0.25 M stock TX-100 solution. The TX-100:hexanol molar ratio was maintained at 1:4. Titanium dioxide nanoparticles have been synthesized by basic hydrolysis of titanium chloride in the water in oil microemulsion. Two different synthetic routes were used for obtaining the titanium dioxide nanoparticles. Fig. 1a and b shows the flow charts for preparation of titanium dioxide nanoparticles by Route 1 and Route 2, respectively. The composition of the final microemulsion was maintained constant in both the methods. The composition of the various components of the microemulsion is given in Table 1.

2.2.1. Route 1

To 12.25 ml of the TX-100 stock solutions, 0.25 ml titanium chloride was added with constant stirring to obtain a faint yellow solution (solution 1).

To 11.55 ml of TX-100 stock solutions, 0.95 ml of 13.4 M aqueous ammonium hydroxide solution was added with stirring to obtain transparent microemulsion (μE 1). The μE 1 was then added to solution 1 with constant stirring, to obtain a transparent microemulsion (μE 2). This was incubated at 27 °C for 48 h. At the end of this period a layer of white precipitate settled at the bottom. Titanium dioxide nanoparticles thus formed were separated by centrifugation at 10,000 rpm for 15 min. The nanoparticles were washed with a mixture of 1:1 chloroform/methanol (v/v) twice and then only with methanol and dried at 80–100 °C in an oven for 4 h before characterization.

2.2.2. Route 2

To 23.80 ml stock TX-100 solution, 0.25 ml of titanium tetrachloride was added with constant stirring to obtain a faint yellow solution. 0.95 ml of 13.4 M aqueous ammonium hydroxide solution was then added drop wise to the yellow solution directly. In this case the precipitate is formed instantaneously due to reaction between ammonium hydroxide and $TiCl_4$. The solution was incubated for 48 h to ensure completion of reaction. The particles were then separated, washed and dried in the same manner as in Route 1.

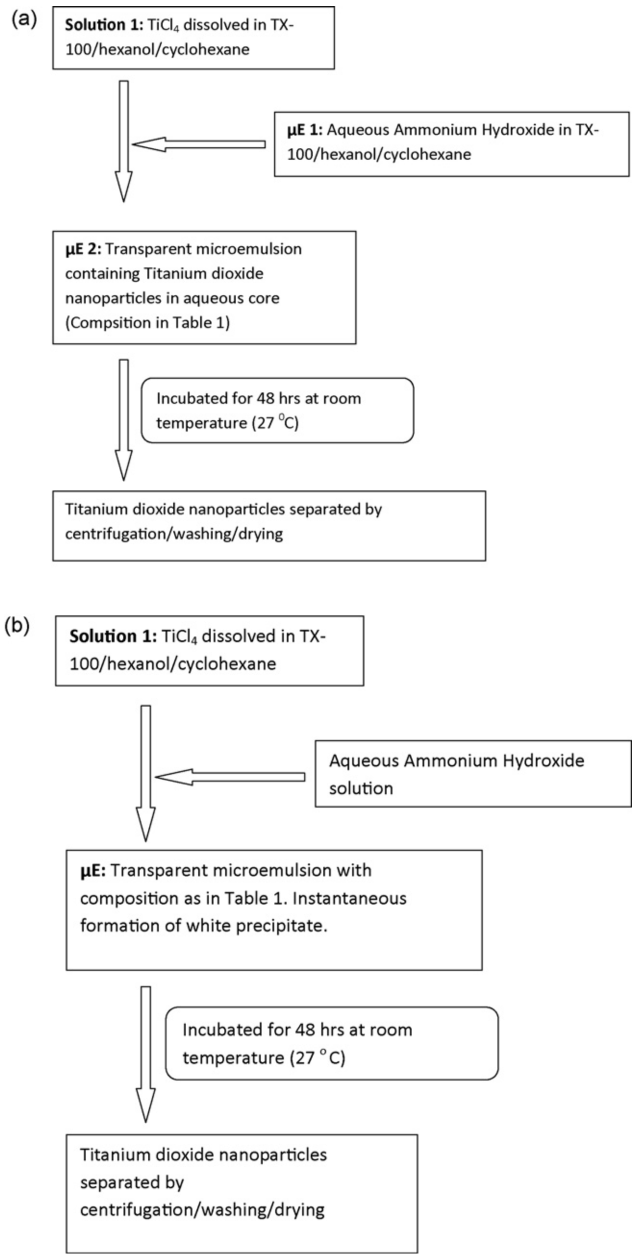

Fig. 1. Schematic for synthesis of titanium dioxide nanoparticles: (a) Route 1 and (b) Route 2.

2.2.3. Control experiment

We also carried out a control experiment where titanium dioxide nanoparticles were synthesized in the organic phase without the surfactant. To a solution of 0.25 ml of $TiCl_4$ in 23.80 ml of cyclohexane, we added 0.95 ml of aqueous ammonium hydroxide solution and observed the instantaneous formation of a white precipitate, which was washed and dried as described above. These titanium dioxide particles formed in the bulk were termed *Organic Phase* TiO_2.

2.3. Characterization techniques used

The phase of the nanoparticles thus formed was characterized by XRD spectra using a PW3040/60 X'pert PRO console in continuous scanning mode using Cu K_α radiation ($\lambda = 1.5425$ Å) at 40 kV and 30 mA with a step size of 0.001° over a range of 5–90° at 25 °C.

Transmission Electron Microscope (TEM) micrographs were taken using a Philips CM 200 with tungsten filament with a resolution of 0.23 nm and an operating voltage of 200 kV. Samples for TEM were prepared by dispersing the titanium dioxide nanoparticles in butanol and sonicating for 30 min before being sprayed on 3 mm copper grids. Image analysis was carried out using the software Image J.

Fourier transform infrared spectroscopy (FTIR) was carried out on a spectrophotometer from 400 to 4000 cm^{-1}. A small amount of sample was added to KBr in an approximate mass ratio of 1:100 (sample:KBr) and pressed to form a thin pellet, which was tested at room temperature.

3. Results and discussion

In our study one of the reactants titanium chloride was dissolved in the organic phase of the TX-100 stock solution (solution 1). In Route 1, aqueous solution of ammonium hydroxide was added to solution 1 in microemulsion form (Fig. 1a). This prevents the reaction between ammonium hydroxide and titanium chloride in the organic phase, as the ammonium hydroxide present in the aqueous core of the microemulsion cannot diffuse out into the organic phase. On mixing the two we get a transparent microemulsion and do not observe any instantaneous formation of precipitate. The titanium chloride that diffuses slowly into the aqueous core reacts with the ammonium hydroxide present in these cores to form titanium dioxide nanoparticles, hereby termed as *Aqueous phase* TiO_2. The reaction takes about 48 h for completion and a thin layer of titanium dioxide nanoparticles settle at the bottom at the end of this period.

Fig. 2a and b shows the TEM images of the *Aqueous phase* TiO_2 nanoparticles synthesized by Route 1. The particles are spherical in shape and the average size of the particles (50 particles) measured using the software Image J is 4.2 nm. The particle size distribution (Fig. 3) shows that particles are reasonably monodispersed.

Fig. 4 is the XRD spectra of the *Aqueous phase* TiO_2 nanoparticles synthesized by Route 1. The well-formed peaks show that the nanoparticles formed within the aqueous environment of the reverse micelles are crystalline and the phase is identified as being rutile [JCPDS No. 88-1172]. The broadening of the peaks clearly shows the small size of the nanoparticles [18,19]. The size of the nanoparticles was also determined from the full width at half maximum (fwhm) of the peak of highest intensity, using Scherrer equation [20]. The particle size obtained was 4.8 nm, which matched well with the average size (4.2 nm) of these nanoparticles measured from the TEM micrographs using the software Image J.

Fig. 5 shows the FTIR spectra of the rutile nanoparticles synthesized by Route 1. The broad peak around 619 cm^{-1} is that for the Ti–O bond in rutile titanium dioxide. This matches well with the value reported in literature [21] for rutile titanium dioxide. The other peaks in the FTIR spectra are due to absorbed organic molecules on the surface of nanoparticles.

The synthesis of nanoparticles by Route 1 was repeated thrice under identical experimental conditions and rutile nanoparticles of average size ∼4 nm were obtained in each case.

In synthesis of nanoparticles by Route 2, titanium chloride was dissolved in the organic phase of the TX-100 microemulsion as in the case of Route 1 and aqueous ammonium hydroxide solution was added drop wise. In this case there is instantaneous formation of precipitate. TEM image (Fig. 6) of the titanium dioxide nanoparticles synthesized by Route 2 clearly reveal the presence of two types of nanoparticles. First there are small spherical nanoparticles having average size of 4.5 nm (measured by software Image J). As indicated by the arrows in Fig. 6, we also observe a second type of nanoparticles, which are relatively large (10–40 nm) and irregularly shaped.

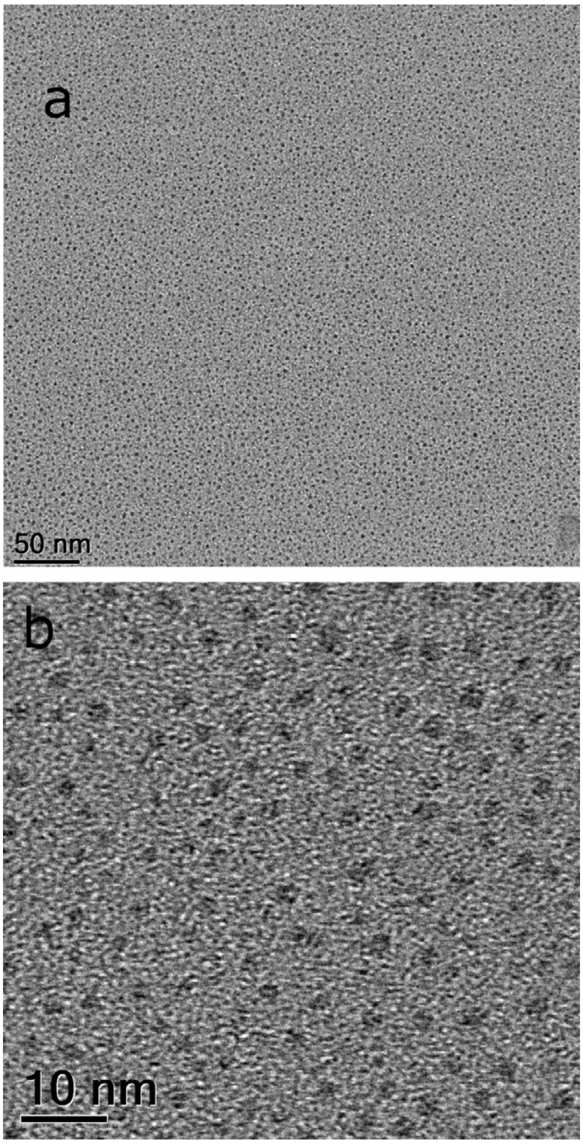

Fig. 2. TEM image of titanium dioxide nanoparticles synthesized by Route 1. Scale (—) (a) 50 nm and (b) 10 nm.

We conclude from Fig. 6 that two different types of nanoparticles are formed in Route 2. The smaller nanoparticles are similar in shape and size to the rutile nanoparticles formed in Route 1. The observation of two types of particles in the TEM image and the fact that reaction occurs instantaneously, led us to hypothesize that these two particles could possibly originate in the two different

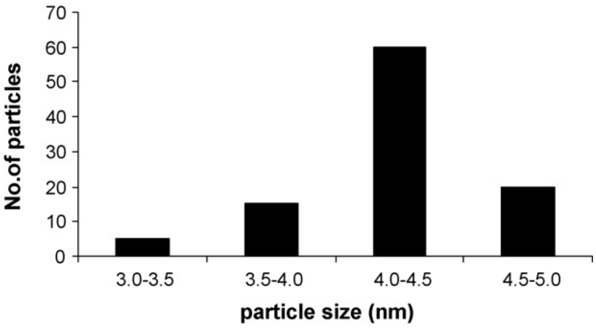

Fig. 3. Particle size distribution for titanium dioxide nanoparticles synthesized by Route 1.

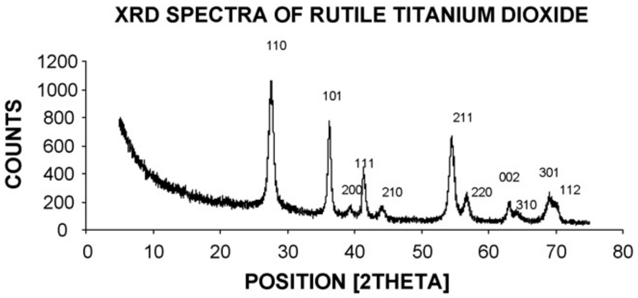

Fig. 4. XRD spectra of rutile titanium dioxide synthesized by Route 1.

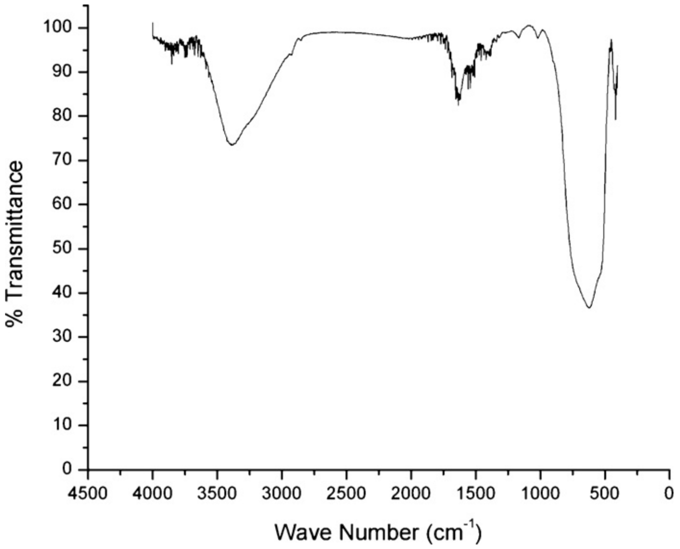

Fig. 5. FTIR spectra of titanium dioxide nanoparticles synthesized by Route 1.

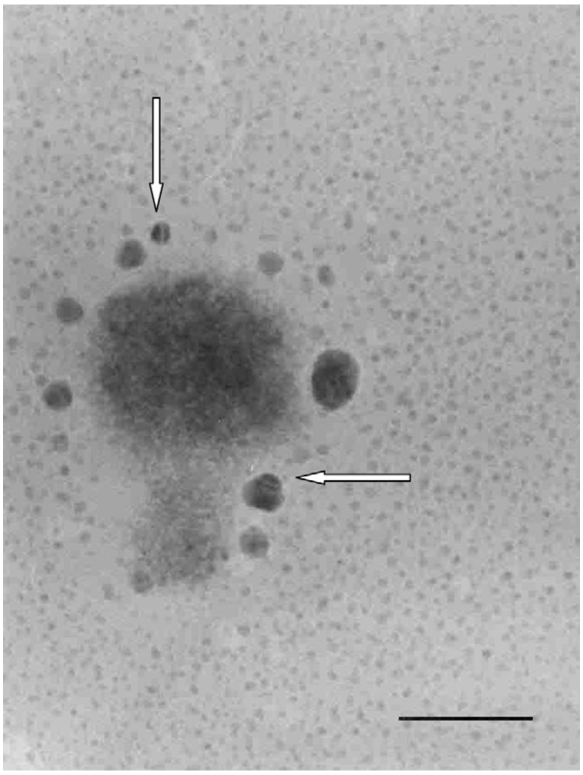

Fig. 6. TEM image of titanium dioxide nanoparticles synthesized by Route 2. Scale (—) 100 nm.

phases – the organic phase (irregular shaped, large 30–40 nm sized nanoparticles) and aqueous core of the reaction mixture (spherical, small 4.2 nm sized nanoparticles).

Fig. 7 shows the XRD spectra of the titanium dioxide nanoparticles synthesized by Route 2. The standard peaks for rutile (JCPDS No. 88-1172), anatase (JCPDS No. 1271) and pseudobrookite [8]

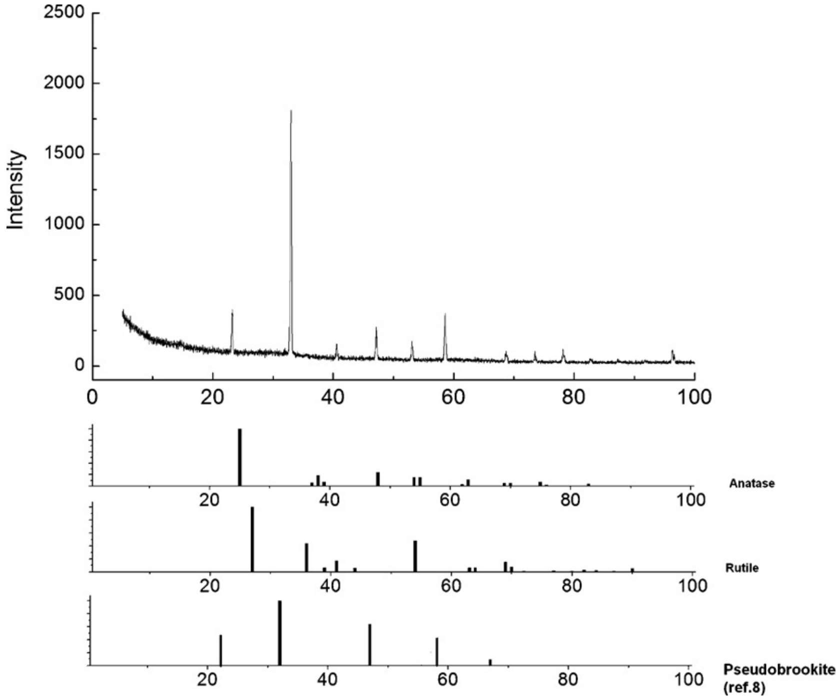

Fig. 7. XRD spectra of titanium dioxide nanoparticles synthesized by Route 2. Standard peaks for rutile (JCPDS No. 88-1172), anatase (JCPDS No. 1271) and pseudobrookite [8] are shown at the bottom.

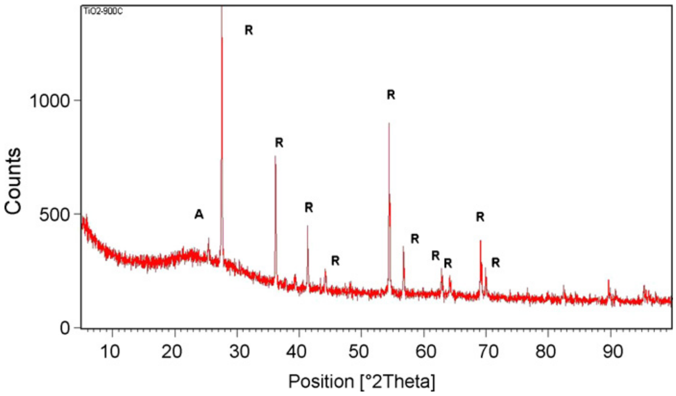

Fig. 8. XRD spectra of titanium dioxide nanoparticles synthesized by Route 2 and heated at 900 °C for 4 h. (R) Rutile peaks and (A) anatase.

are also shown for reference. The well-formed XRD peaks indicate that the nanoparticles are crystalline. As compared to the peaks observed for rutile titanium dioxide in Route 1, the peaks are narrow indicating the larger size of the nanoparticles. The size of the nanoparticles calculated from the fwhm values of the peak of highest intensity is 33.1 nm which correlate well with the size of the larger nanoparticles measured from the TEM images. As can be seen from Fig. 7, the peaks obtained in the XRD pattern do not match either anatase or rutile phase. However, the peaks match the orthorhombic distorted brookite structure reported in literature [8] and such anomalous distorted crystal structures of brookite are termed as 'pseudobrookite' [8]. In order to verify the reproducibility of this results, the experiment was repeated three times and identical results were obtained in all cases.

To test the thermal stability of our sample we also heated the TiO_2 nanoparticles prepared by Route 2 at 900°C for 4 h, following which the anomalous structured nanoparticles converted to rutile (Fig. 8). The orthorhombic brookite phase of titanium dioxide is known to be thermally unstable and converts to anatase and rutile at higher temperature [22].

The FTIR spectra of the titanium dioxide nanoparticles obtained by Route 2 is shown in Fig. 9. As in the case of rutile, a broad peak due to Ti–O bond stretching is observed in pseudobrookite titanium dioxide samples obtained by Route 2, but in this case the peak is shifted to a lower wavelength (around 495 cm^{-1}).

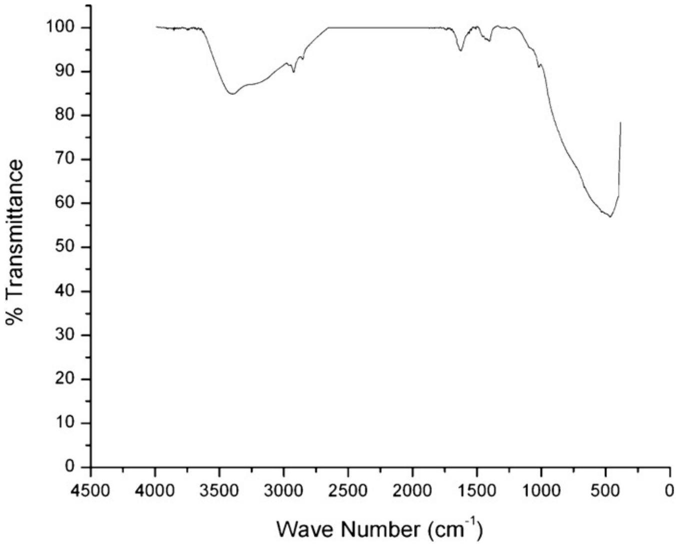

Fig. 9. FTIR spectra of titanium dioxide nanoparticles synthesized by Route 2.

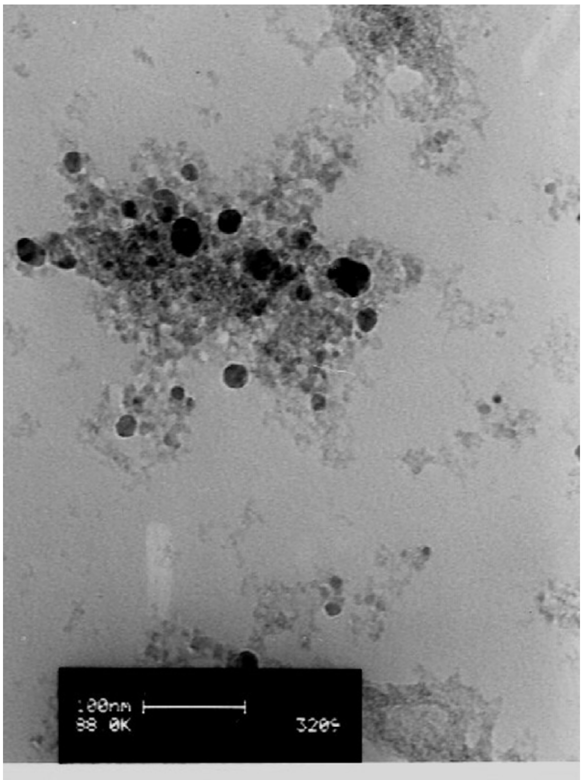

Fig. 10. TEM image of titanium dioxide nanoparticles synthesized in the organic phase (control experiment). Scale (—) 100 nm.

We have already confirmed by Route 1 that the nanoparticles obtained in aqueous core are rutile, spherical in shape and size is about 4.2 nm. Now we designed a control experiment to study the characteristics of nanoparticles formed in the bulk organic phase. Upon adding aqueous ammonium hydroxide solution to a solution of titanium chloride dissolved in cyclohexane, we observed instantaneous reaction and precipitation. A TEM image of the precipitate, termed *Organic Phase* TiO_2, obtained from this reaction is shown in Fig. 10. We note that the shape and size of these particles (size range 30–40 nm) are similar to those indicated by the arrows in Fig. 6. The XRD spectrum of the Organic Phase TiO_2 obtained from Control 1 (Fig. 11) shows exactly the same peaks as observed in case of titanium dioxide nanoparticles synthesized in the microemulsion by Route 2.

Based on these observations from TEM images and XRD spectra, we propose a possible mechanism for nanoparticle synthesis by Route 2. In this method, one of the reactants ($TiCl_4$) is present in the continuous phase while the other reactant aqueous ammonium hydroxide solution is added drop wise, resulting in instantaneous formation of a precipitate. This instantaneous precipitation coupled with the presence of two types of nanoparticles indicates that there are two dominant mechanisms for nanoparticle synthesis. We propose that some of the ammonium hydroxide before it enters the reverse micellar core, may react with the $TiCl_4$ in the continuous organic phase during the process of micelle swelling, giving rise to anomalous pseudobrookite TiO_2 nanoparticles. As observed in these TEM images, nanoparticles formed in the continuous organic phase are irregular shaped, crystalline and about 30–40 nm. Once the ammonium hydroxide solution enters the reverse micellar core, it reacts with $TiCl_4$ diffusing into the aqueous core to produce the small nanoparticles (rutile). We can explain the absence of peaks corresponding to the rutile phase in the XRD spectra of nanoparticles synthesized by Route 2 by considering the relative extents

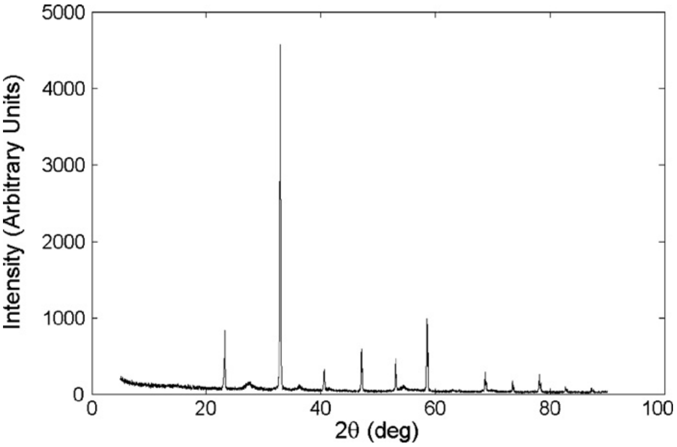

Fig. 11. XRD spectra of titanium dioxide nanoparticles synthesized in organic phase (control experiment).

of reaction occurring in the two phases. We believe that organic phase reaction may be significant at short time scales and that conversion of TiO_2 formed in the aqueous core to nanoparticles via nucleation may be significant only at larger time scales and that at the time of imaging, the amount of rutile nanoparticles may be small compared to those of pseudobrookite. This is because the rutile nanoparticles are formed in the aqueous core of the microemulsion whereas pseudobrookite particles are formed in the bulk organic phase. Alternately, it is possible that the residual surfactant on the small nanoparticles formed in the aqueous core could also diminish the intensity of the signals arising from the rutile nanoparticles, explaining the absence of the rutile peaks in the XRD spectrum of nano-titanium dioxide particles obtained by Route 2.

In Route 1 the reaction takes place entirely inside the reverse micellar core. Inside the reverse micellar core, the nanoparticle formation mechanism is based on nucleation and growth [17]. The reverse micellar core acts like 'nanoreactor'. In the reverse micellar core, the growth is mediated by the intermicellar exchange of materials and growth of the nanoparticles inside the reverse micellar core is restricted by the surfactant layer. The surfactant layer acts like cage and prevents the aggregation of the nanoparticles in the reverse micellar core [23] resulting in small nanoparticles of average size 4.2 nm.

In Route 2, part of the reaction takes place inside the reverse micellar core giving rise to small nanoparticles similar to the rutile nanoparticles obtained by Route 1 and part of the reaction that takes place in the organic phase gives rise to larger nanoparticles (30–40 nm). Inside the micelles the size of the nanoparticles is restricted by surfactant layer whereas outside the micelles the growth is restricted by local availability of materials due to very low solubility of ammonium hydroxide in cyclohexane.

We thus obtain pure spherical monodispersed crystalline rutile titanium dioxide of average size 4.2 nm by Route 1 and by Route 2 we get a mixture of anomalous pseudobrookite titanium dioxide of much larger size (33.2 nm) in the continuous phase and small size (4.5 nm) rutile nanoparticles in the aqueous phase. The anomalous pseudobrookite phase obtained is thermally unstable and converts to rutile on heating.

4. Conclusion

We have synthesized crystalline titanium dioxide nanoparticles of two different phases via a novel microemulsion route. The size and the crystalline phase of the TiO_2 nanoparticles vary according to the site of the reaction. Reaction in the aqueous core gives rutile titanium dioxide nanoparticles having an average size of 4.2 nm verified by X-ray diffraction and FTIR. Our study demonstrates a method to synthesize rutile titanium dioxide at room temperature that is usually obtained at higher temperature.

The reaction in the organic phase gives rise to crystalline anomalous pseudobrookite titanium dioxide nanoparticles of much larger size (10–40 nm). This anomalous pseudobrookite structure is thermally unstable and converts to rutile on high temperature treatment.

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