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Hydrothermal synthesis of aqueous nano-TiO_2 sols

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A poorly crystalline nano-anatase precursor with the crystallite sizes of about 3.5 nm was prepared via reprecipitation of nano-anatase at pH = 7.0 from a highly transparent sol obtained by acidic peptization of hydrous titania precipitates, hydrolysed product of titanium isopropoxide. The weakly agglomerated nano-anatase precursor has been used for preparing well crystalline nano-TiO_2 sols by hydrothermal treatment at pH = 9.5 using a weak base, NH_4OH. The crystallite size gradually grew with increasing temperature and reached 7.6 nm (X-ray) at 175 °C after 4 h of hydrothermal treatment. The sizes of particles were mostly in the range 5–15 nm. The hydroxyl content in the nano-TiO_2 decreased with increasing hydrothermal temperature of treatment and supported a gradual growth of nano-TiO_2 as evident from the X-ray and TEM.

Key words: *nano-TiO_2 sol; peptization; hydrothermal treatment*

1. Introduction

Crystalline TiO_2 nanopowders find various photocatalytic applications [1–3]. Synthesis of TiO_2 powder via hydrothermal treatment of amorphous hydrous titania or its peptized sol (poorly crystalline) is a common approach. The literature mainly covers the formation of crystalline polymorphs under various experimental conditions [4–10]. On the contrary, very little attention has been paid to the *in situ* fabrication of aqueous nano-TiO_2 sol via a hydrothermal process [6] although it is known that handling of aqueous nano-TiO_2 sol will be much easier compared to dry nanopowder. An aqueous TiO_2 dispersion showed a maximum stability at pH = 10–11 where a maximum negative zeta potential was found indicating the maximum stability of the dispersion due to electrostatic repulsion [11]. *In situ* fabrication of nano-TiO_2 dispersion has been reported in basic solutions via hydrothermal treatment of poorly crystalline nano-TiO_2 sol obtained by peptization of amorphous hydrous titania by tetrabutylammonium hydroxide (TBNOH) [6].

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It has been shown that amorphous hydrous titania obtained by hydrolysis of titanium alkoxide in aqueous solution during peptization with either acids (HCl and HNO_3) or strong bases like tetraalkylammonium hydroxide (TANOH) transformed into titania sol containing poorly crystalline nano-TiO_2 particles [5]. Nano-TiO_2 obtained by acid peptization showed a relatively high degree of crystallinity compared to that obtained in the base petization process [5, 6]. The hydrothermal treatment of the peptized sols generates well crystalline nano-TiO_2 powders and the particle sizes of the hydrothermally treated nano-TiO_2 obtained from acid peptized sols were smaller than that obtained from base peptized ones [5]. Moreover, the application of the TBNOH peptized and hydrothermal sol for deposition of coatings may occlude TBN^+ which needs higher decomposition temperature for its removal as observed for the coprecipitation synthesis of $CoFe_2O_4$ [12]. In view of this, we report a hydrothermal synthesis of the *in situ* fabrication of aqueous nano-TiO_2 sol by separating poorly crystalline nano-TiO_2 from acid peptized sol and its subsequent hydrothermal treatment in basic solution using NH_4OH.

2. Experimental

Titanium isopropoxide (TTIP) technical grade (Sigma, Aldrich), 1-propanol (Qualigens, 99%), HNO_3 (69%, GR, Merck, India), ammonia solution (25%, GR, Merck, India) and distilled water were used for the preparation of nano-TiO_2 by the hydrothermal method. TTIP (0.5 M) solution in 1-propanol was prepared and to this solution distilled water was added under stirring keeping very high H_2O:TTIP mole ratio of 450. Hydrous titania precipitates were kept under stirring for 30 min and then filtered. The precipitate thus obtained was either directly treated hydrothermally in water or peptized with HNO_3 keeping the H^+/Ti mole ratio of 1.75 and wt. % TiO_2 of 0.5. The peptization of the resulted precipitate under stirring at room temperature generated a slightly bluish coloured transparent sol. pH of the sol was adjusted to 7.0 by adding 1 M NH_4OH under stirring and then the sol was filtered. The precipitate was then thoroughly washed with distilled water till the presence of NO_3^- ions in the filtrate was detected. The precipitate was then redispersed under stirring in aqueous solution of NH_4OH having the pH of 9.5 maintaining the wt. % equivalent TiO_2 of 0.5 and 2.0. The dispersion was kept overnight and finally pH was readjusted to 9.5 prior to hydrothermal treatment. All the hydrothermal treatment was carried out with ca. 420 g of suspension under stirring condition (400 rpm) in a 2 dm^3 Teflon lined autoclave under autogenic pressure. The heating rate of ca. 2 °C/min was used for achieving the final temperature of hydrothermal treatment and a natural cooling of the autoclave was maintained for all the experiments. Translucent titania sols were centrifuged at 8000 rpm. However, very little was found at the bottom. The sol was then kept at 50 °C in a Petri dish for drying. A thick paste was formed during drying and acetone was added to it followed by drying at 50 °C. It was then ground mildly in acetone and again dried at 50 °C. The process was repeated for 2–3 times and finally the dried powder was obtained.

X-ray diffraction (XRD) patterns of the powders were recorded with a Philips make diffractometer (Model: PW-1730). DTA and TGA of the powders were carried out using Shimadzu thermal analyzer (Models: DA-50 and TA-50). Transmission electron microscopic (TEM) measurements were carried out with a Jeol 2010 TEM. The samples for TEM study were prepared by adding a drop of diluted sols on carbon coated grids placed on tissue paper followed by drying at 50 °C.

3. Results and discussion

Hydrolysis rate of titanium alkoxide resulting in an amorphous powdery precipitate is very fast. However, the deliberate addition of water into alcoholic solution of titanium alkoxide generated various products depending on the amount of water, concentration of alkoxide and nature of alkyl group [13] indicating the extent of polymerization is different. The powdery precipitate obtained after hydrolysis of TTIP in the present study was X-ray amorphous. The hydrothermal treatment of the amorphous powder in distilled water showed the formation of mainly anatase with the presence of little amount of brookite (Fig. 1).

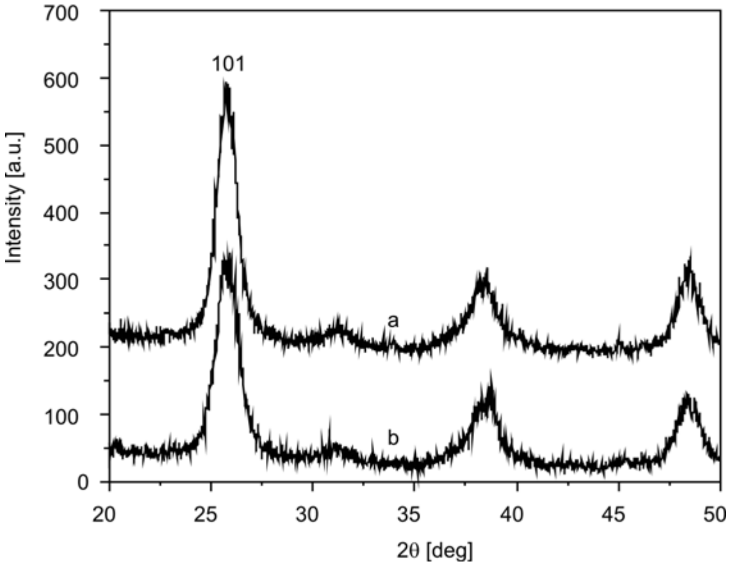

Fig. 1. X-ray diffraction patterns of the powders obtained after hydrothermal treatment of 0.5 wt. % slurry for 4 h at 175 °C (a) and 150 °C (b)

The particles were separated out from the mother liquid. As expected, higher temperature of hydrothermal treatment favours better crystallization. On the other hand, the amorphous precipitate under acid peptization at room temperature gradually converted to a slightly bluish coloured highly transparent sol indicating the formation of very small particles.

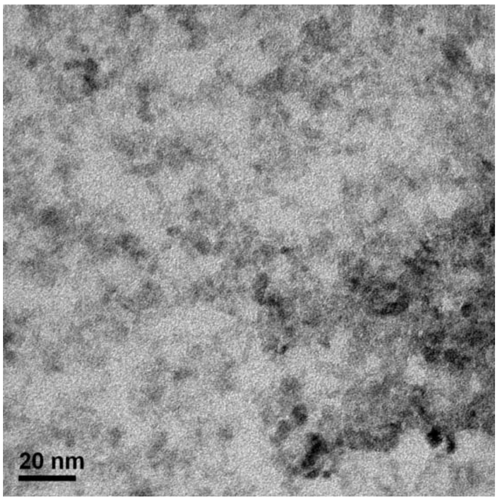

Fig. 2. TEM photograph of nano-TiO_2 present in a peptized sol

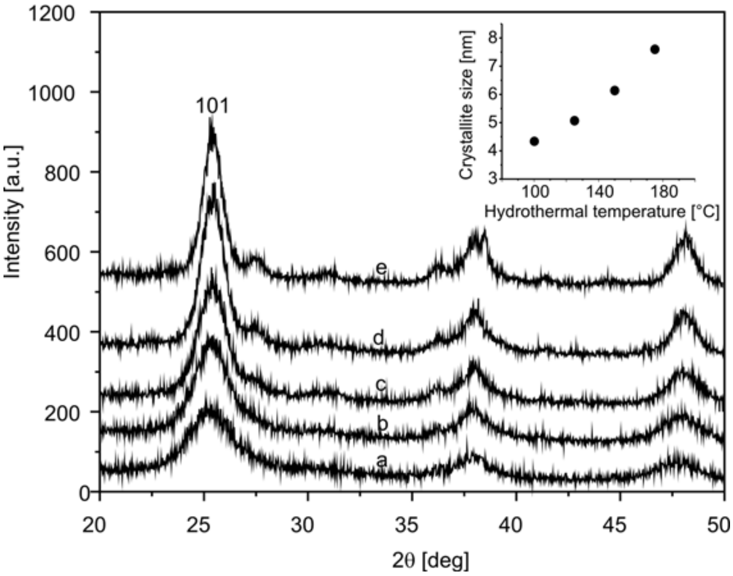

Fig. 3. X-ray diffraction patterns of the powders obtained from the 0.5 wt. % equivalent TiO_2 containing peptized sol (a) and after hydrothermal treatment of 0.5 wt. % equivalent TiO_2 containing suspension using reprecipitated anatase precursor at pH = 9.5 for 4 h at 100 °C (b), 125 °C (c), 150 °C (d) and 175 °C (e). Inset shows the corresponding crystallite size of hydrothermally treated samples

TEM photograph (Fig. 2) shows the formation of very small TiO_2 particles in the peptized sol. X-ray diffraction pattern of the powder obtained from the sol shows the formation of poorly crystalline nano-anatase (Fig. 3) with the particle size of about 3.5 nm as determined from Scherrer's equation. The formation of anatase and rutile during peptization of amorphous hydrous titania precipitate with H^+/Ti ratio of 1.0 and 4.0, respectively has been reported [4,14]. It is believed that during the peptization process the aggregated TiO_6 octahedra in the amorphous phase gradually break down via protonation of the –Ti–O–Ti– bonds. The protonated surface Ti–OH recombine with –OH groups of other TiO_6 octahedra to form –Ti–O–Ti– bridge bonds and the structural rearrangement causes transformation of amorphous to crystalline state. The structural rearrangement of the TiO_6 octahedra through edge sharing leads to formation of anatase from an amorphous phase under peptization with H^+/Ti mole ratio of 1.75. It is known that basic solution favours the formation of anatase through edge sharing of TiO_6 octahedra both in peptization as well as in hydrothermal processes [5]. It has been shown that the crystallization of TiO_2 from an amorphous precipitate during peptization was very poor in the case of basic peptization process (TBNOH and TENOH) compared to acid (HNO_3) peptization [5, 6]. Thus a relatively fine crystalline nano-anatase obtained by acid peptization is expected to produce fine crystalline nano-anatase at a relatively lower hydrothermal temperature under basic condition. The reprecipitation is expected to generate weakly agglomerated nano-anatase particles which were subsequently used as an intermediate precursor for hydrothermal treatment in basic aqueous medium for *in situ* fabrication of nano-TiO_2 sol.

Figure 3 shows the X-ray diffraction pattern of powders obtained after hydrothermal treatment at various temperatures. The increase of temperature is expected to increase crystallization. This is clearly evident from the diffraction patterns. Moreover, it is evident that increasing temperature favours the formation of small amounts of rutile along with major anatase phase. TiO_2 obtained at 100 °C was purely anatase. The rutile formation was started at 125 °C and the amount of rutile gradually increased with the increase of temperature of hydrothermal treatment. The formation of pure anatase at 200 °C under hydrothermal condition of the sol under basic solution (using TBNOH) has been reported [5]. However, the appearance of very slight amount of rutile along with the major anatase phase at 240 °C indicates that the higher temperature favours the formation of rutile [5]. The calculated crystallite size using Scherrer's equation gradually increases with increasing hydrothermal temperature as shown in the inset of Fig. 3. The crystallite size of nano-anatase obtained after hydrothermal treatment at 175 °C was about 7.6 nm whereas that of the nano-anatase present in the peptized sol was about 3.5 nm.

Figure 4 shows particle morphology of the nano-TiO_2 after hydrothermal treatment. It is clear from the TEM picture that well crystalline particles of the sizes mostly in the range of 5–15 nm have been formed and remained dispersed in the mother liquid as a translucent sol. Figure 5 shows the TGA of the samples hydrothermally treated at 100 °C and 175 °C for 4 h. The TG curves show a sharp weight loss up to about 130 °C and subsequent gradual weight loss up to 800 °C. The initial weight loss is due to the dehydration of adsorbed water. An endothermic peak observed at about

63 °C in the DTA supports the weight loss. The weight loss after about 450 °C is negligible. A similar result was observed for hydrothermally synthesized TiO_2 nanopowders from the amorphous hydrated titania obtained by hydrolysis of TTIP [7]. It has been observed that a higher weight loss in the temperature range 130°–450 °C for 100 °C sample (5.06%) compared to 175 °C sample (3.7%) indicates the presence of high amounts of Ti–OH in 100 °C hydrothermally treated sample. The better crystallization at higher temperature as evident from X-ray results supports the decreased weight loss due to Ti–OH.

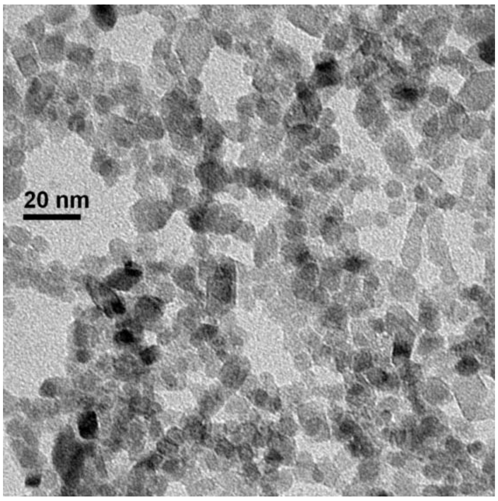

Fig. 4. TEM photograph of nano-TiO_2 present in the sol obtained after hydrothermal treatment of 0.5 wt. % equivalent TiO_2 containing slurry using reprecipitated anatase precursor at pH = 9.5 for 4 h at 175 °C

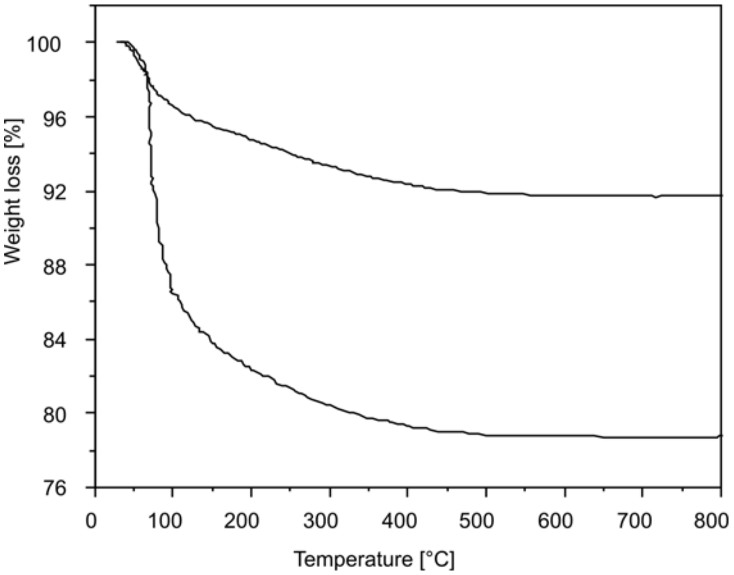

Fig. 5. TGA of TiO_2 powders obtained after hydrothermal treatment at 175 °C (top) and 100 °C (bottom) for 4 h

It has been shown by Chen et al. that the optical absorbance of TiO_2 dispersion in aqueous solution showed a maximum value in the pH range of 10–11 while a maximum negative zeta potential was found in this pH range [11]. This clearly suggests the maximum stability of the dispersion in this pH range due to a very strong electrostatic repulsive force. The optical absorbance in the acidic solution (pH from 2 to 6) was very low, indicating the instability of the TiO_2 dispersion though the zeta potential was negative ($pH > 4$) and positive ($pH < 4$). A similar hydrothermal result of TBNOH peptized titania sol was reported by Yung et al. [6] and explained based on a strong electrostatic repulsive force due to large negative zeta potential ($pH = 10$). Weakly agglomerated nanoanatase as a precursor and the development of a strong electrostatic repulsive force among the nano-TiO_2 particles were probably responsible for the *in situ* fabrication of nano-TiO_2 sol via hydrothermal treatment of the suspension at $pH = 9.5$ in the present study.

The increase of wt. % equivalent TiO_2 from 0.5 wt. % to 2 wt. % in the suspension for hydrothermal treatment also produces nano-TiO_2 sol. The calculated crystallite size was about 7.4 nm which is almost the same as observed in case 0.5 wt. % TiO_2 containing sol indicating that growth is almost independent of the concentration of TiO_2 at least in the present investigation. Thus weakly agglomerated nano-anatase precursor obtained by reprecipitation of the acidic peptized sol and subsequent hydrothermal treatment at $pH = 9.5$ using NH_4OH was found to be suitable for the fabrication of nano-TiO_2 sol. These sols may be suitable for the deposition of crystalline TiO_2 coatings at low temperatures as ammonia can be removed easily.

4. Summary

Aqueous poorly crystalline nano-anatase sols have been prepared via peptization in acidic medium of the amorphous hydrous titania precipitate obtained by hydrolysis of titanium isopropoxide. The nano-anatase thus produced has been reprecipitated at $pH = 7$ and used as intermediate precursor for *in situ* fabrication of well crystalline nano-TiO_2 sols in the basic solution (9.5) using a weak base, NH_4OH under hydrothermal. The hydrothermal treatment of the basic aqueous suspension of weakly agglomerated nano-anatase showed the formation of nano-TiO_2 sol. A gradual growth of nano-anatase with increasing hydrothermal temperature has been observed. The sol contains well crystalline nano-TiO_2 particles having the size mostly in the range 5-15 nm after hydrothermal treatment at 175 °C for 4 h. The weakly agglomerated nanoanatase as precursor and the development of strong electrostatic repulsive force among the nano-TiO_2 powders were responsible for the *in situ* fabrication of nano-TiO_2 sol via hydrothermal treatment. The reprecipitation of the poorly crystalline nano-TiO_2 sol generates an intermediate precursor which is suitable for the hydrothermal preparation of well crystalline aqueous nano-TiO_2 sol at $pH = 9.5$ using NH_4OH.

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