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Effect of precipitation conditions on crystallization of TiO_2 nanoparticles in acidic route

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ABSTRACT
Herein, the crystallization of anatase TiO_2 particles under the different precipitation conditions in acidic route is reported. The nanocrystalline TiO_2 particles are prepared by using simple precipitation route with titanium tetra isopropoxide (TTIP) and sodium hydroxide as precursor materials. The Ti-hydroxide precipitation at ice bath and hot conditions followed by annealing of as-dried precipitate in a temperature zone between 350 – 450 ^{0}C leads the formation of nanocrystalline TiO_2 particles. The OH/TTIP molar ratio for all preparations is kept nearly equal to 5.0. The as-annealed powders are characterized by using X-ray diffraction, field emission scanning electron microscopy, and UV-Visible spectroscopy. The structural characterization results revealed the crystallization of nanocrystalline TiO_2 particles. The morphological characterization results indicated nearly uniform size distribution of softly agglomerated spherical particles in as-prepared phase pure TiO_2 powders. The energy dispersive X-ray analysis confirmed the purity of material of resultant powders. It is noted that precipitation conditions play vital role on crystallanity, morphological nature and band gap energy of resultant TiO_2 particles.

Keywords: TTIP, Acidic route, X-ray diffraction, FESEM.

INTRODUCTION

Titanium oxide (TiO_2) is very useful material for large number of applications such as solar cells, sensors, ceramic membrane, catalyst for photocatalytic decom-position, textiles, pigments, cosmetics and optoelec-tronics [1-10] owing to its better biocompati-bility, non-toxicity, better thermal stability long term photo-stability and strong oxidized stability. The various methods like anodization, vapor deposition sol-gel, hydrothermal, emulsion, microwave, electrochemical, homogeneous precipitation at low temperatures, ionized cluster beam deposition, aerosol process, mechano-chemical, mechanical milling, combustion synthesis, chemical vapor deposition, glycothermal and precipitation are reported for the synthesis of TiO_2 [11-26] particles of different morphologies like nanoparticles, nanotubes, nanowires, nanorods, nanosheets, nanoribbons, nanoflakes, nanofibers, spheres, needles, cubes, star shapes etc. The experimental conditions and phase symmetry of material play an important role in deciding the properties of the material. The properties of the materials are also depending upon the materials purity and crystallanity.

In present work, the TiO_2 powders with anatase phase symmtery are generated by using simple method of precipitation-followed by annealing at elevated tempeartures. The titanium tetraisopropoxide is used as Ti-precursor. Herein, the TiO_2 nanoparticles (NPs) are prepared by using acidic route under both ice bath and hot conditions. The precipitation of Ti-hydroxide is carried out at ice bath temeparture as well as at 70 ^{0}C (hot condition). The effects of hot and ice bath conditions during the processing by acidic route on the crystallization of TiO_2 NPs are studied in present work. The data obtained pertaining to this is presented in this communication.

METHODOLOGY

Initially, 0.2 M solution of titanium tetra isopropoxide (TTIP) was prepared by adding 2.27 ml of TTIP in 40 ml isopropyl alcohol. Similarly, 1 M solution of NaOH was prepared by dissolving 1 gm of it in 40 ml double distilled water (DDW). In acidic route, the TTIP solution was added in NaOH solution drop by drop at a temperature of 70 ^oC and resultant mixture was stirred for 5 hr. The precipitation reaction was started within half an hour. The precipitate obtained was filtered and thoroughly washed with 0.1 N HCl. Finally, the precipitate was again washed for several times with DDW and then dried at room temperature. The as-dried precipitate was then annealed at 350 and 450 ^oC for 2 hr. to obtain TiO_2 nanoparticles (NPs). The powders prepared by using acidic route at temperature of 70 ^oC were identified as AH. The above mentioned precipitation reaction was also repeated in ice bath conditions. The precipitate obtained was filtered and thoroughly washed with 0.1 N HCl. Finally, the precipitate was again washed for several times with DDW and then dried at room temperature. The as-dried precipitate was then annealed at 350 and 450 ^oC for 2 hr. to obtain TiO_2 nanoparticles. The powders prepared by using acidic route at ice bath temperature were identified as AI. For both reactions the OH/TTIP ratio was kept nearly equal to 5.0. The resultant powders were characterized by using different physical techniques. The X-ray diffraction patterns of resultant powders were recorded by using Bruker D8 Advance (filtered CuK_α radiation, λ = 1.5406 Å) machine. The morphological analysis was done by using scanning electron microscope [JEOL JSM-6360-LA and Philips XL-30]. The optical spectra of powders were recorded by using the UV-Visible spectrophotometer [V-670, JASCO UV-VIS-NIR spectrometer].

RESULTS AND DISCUSSION

The figure -1 gives the X-ray diffraction (XRD) patterns of as-prepared powders obtained under different processing conditions in acidic route. The powders: AH350 and AI350 prepared by using the acidic route at hot as well as ice bath conditions and annealed at 350 ^oC for 2 hr. show clearly the amorphous nature. The XRD patterns of both the powders clearly show only a broad hump around the position of anatase TiO_2 reflection having 100 % relative intensity. However, the powders: AH350 prepared by using the acidic route under the hot conditions and annealed at 350 ^oC for 2 hr show much better crystallanity as compared to the powders: AI350 prepared by using the acidic route under the ice bath contditions and annealed at 350 °C for 2 hr. The powder: AH350 show the slight evolution of (101), (200) and (204) reflections of TiO_2 with anatase symmtery. Further, the powders: AI450 and AH450 prepared by using the acidic route under the ice bath and hot conditions respectively and annealed at 450 ^{0}C display much better crystalline nature. The different observed reflections are indexed to TiO_2 phase. The diffraction peaks: (101), (103), (004), (112), (200), (105), (211), (204), (116), (220) and (215) observed in both XRD patterns are found to be perfectly macthing with the the JCPDS data [JCPDS card no.: 71 – 1166] given for TiO_2 with anatase symmtery.

This clearly indicates the formation TiO_2 with anatase symmtery in resultant AI450 and AH450 powders. However, powder: AI450 prepared by using acidic route under ice bath condition and annealed at 450 ^{0}C shows very good crystallanity as compared to the powder: AH450 prepared at hot bath conditions.

The large difference in the relative intensities of various corresponding peaks is observed in XRD patterns of two powders: AI450 and AH450. The relative intensity ratio of peaks is found to be ~ 3.03 for two powders: AI450 and AH450.

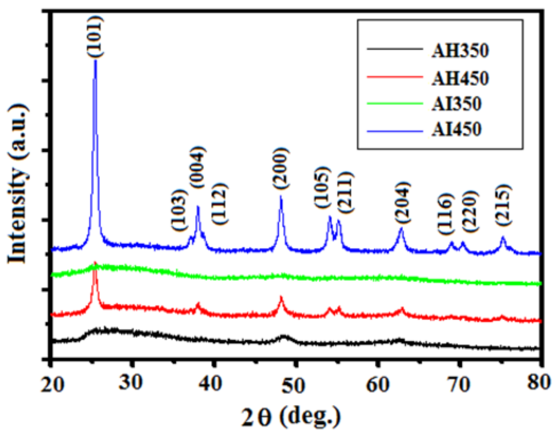

Fig. 1. The X-ray diffraction (XRD) patterns of pure TiO_2 prepared under different processing conditions

Thus, the powder AI450 is more crystalline as compared to the powder AH450. From all these observations, it is clear that the powders obtained by using the acidic route at the ice bath precipitation tempearture are highly crystalline as compared to the powders obtained at ~ 70 ^{0}C hot precipitation temperature. Thus, acidic route processing at ice bath precipitation temperature followed by annealing at 450 °C generates the well crystalline TiO_2 powders with anatase symmtery. The values for crystallite size (D) for the powders: AI450 and AH450 are obtained by using Scherrer's formula:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

where, λ = 1.54 A°, β = full width at half maximum and θ = Bragg's diffraction angle. The values for crystallite size for the powders: AI450 and AH450, are found to be 14.77 nm and 16.49 nm respectively. The higher value of crystallite size in case of AH450 powder might be due to the sintering effect in primary particles leading to bigger TiO_2 particles. The sintering of the of primary particles is due to the processing of precipitation reaction at 70 ^{0}C.

Thus, the crystallite size for powders processed at ice bath condition is smaller as compared to crystallite size for powders processed at hot condition. Thus the ice bath processing helps in keeping lower crystallite size and limits the particle growth. The field emission scanning electron microscopy (FESEM) and scanning electron microscopy (SEM) images for AI450, and AH450 powders are shown in figure - 2. both images show the following general observations. The primary particles are nearly spherical. The primary spherical particles are agglomareting to form the soft / hard agglomerates. The agglomeration nature in case of AI450 powder is soft. However, primary particles are fusing to form hard agglomerates in case of AH450 powders. The evolution of hard agglomerates in case of AH450 powder might be due to the processing of these powders under hot condition during the precipitation reaction. This observation is consistent with crystallite data obtained from X-ray diffraction studies. Further, figure-2 also gives the particle size distribution data in terms of histograms alongwith corresponding microscopy images. From histograms, the particle size for both powders are obtained. The particle size distribution for both powders: AI450 and AH450 is almost nearly uniform.

The average particle/agglomerate size for AI450 and AH450 powders are found to be ~ 34 nm and 69 nm respectively. From all above morphological observations, it is clear that the TiO_2 powders prepared in present work are nanocrystalline in nature. Further, the synthesis of TiO_2 powders: AI450 by using the acidic route at ice bath temperature leads the generation of spherical particles with lower average particle size. All these observations are consistent with results obtained during X-ray diffraction studies of these powders. Figure - 3 (left) gives the UV-Visible absorbance spectra for the resultant powders: AI450 and AH450. The absorbance spectra are used for finding the energy band gap (E_g) values in resultant powders : AI450 and AH450. The optical band gap value of resultant powder is estimated from Tauc plot. The Tauc's relation of photon energy ($h\nu$) with absorption coefficient (α) is given as:

$$\alpha = \frac{\alpha_0 \left(h\upsilon - E_g\right)^n}{h\upsilon} \qquad (2)$$

where, E_g = band gap energy, α = absorption coefficient, α_O = constant. Tauc's plots generated from the UV-visible spectra for resultant AI450 and AH450 powders are given in figure -3 (right). The value of band gap energy (E_g) is obtained by extrapolation of straight-line portion of the plot to zero absorption edge. The values for band gap energies for the AI450 and AH450 powders are found to be 3.38 and 3.31 eV respectively. The band gap values are found to be matching with the reported data. The higher band gap energy for powder AI450 as compared to band gap energy for AH450 powder is due to increase in average particle size in case of AH450 powder.

In present work, the TiO_2 powders are prepared by using the method consisting of two steps: precipitation of Ti-hydroxide and annealing of this hydroxide at elevated temperatures. In first step, the precipitation of Ti-hydroxide is carried out by using acidic route under two different conditions of temperatures: ice bath and 70 °C. In second step, the annealing of thoroughly washed as-dried Ti-hydroxide is done at two different temperatues: 350 and 450 °C for 2 hr.

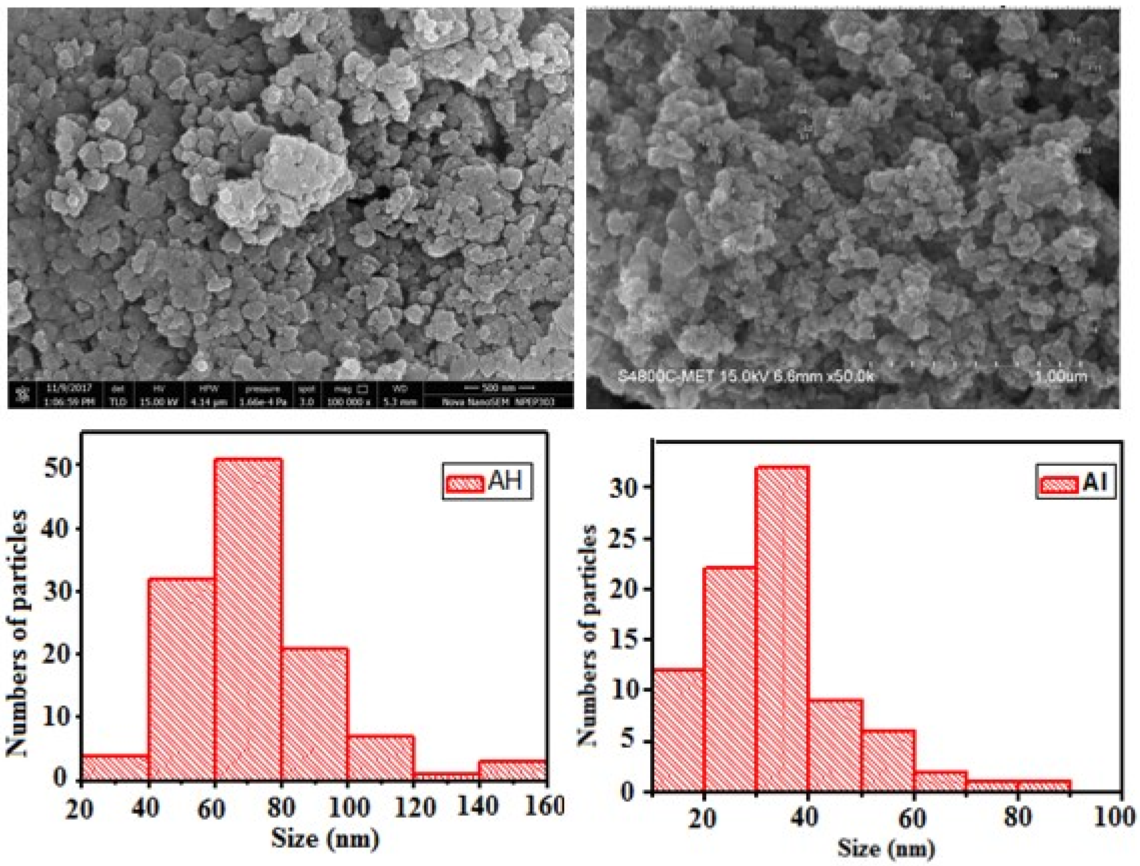

Fig. 2. The microphotographs and corresponding particle size distribution for AH450 (left) and AI450 (right) TiO_2 powders

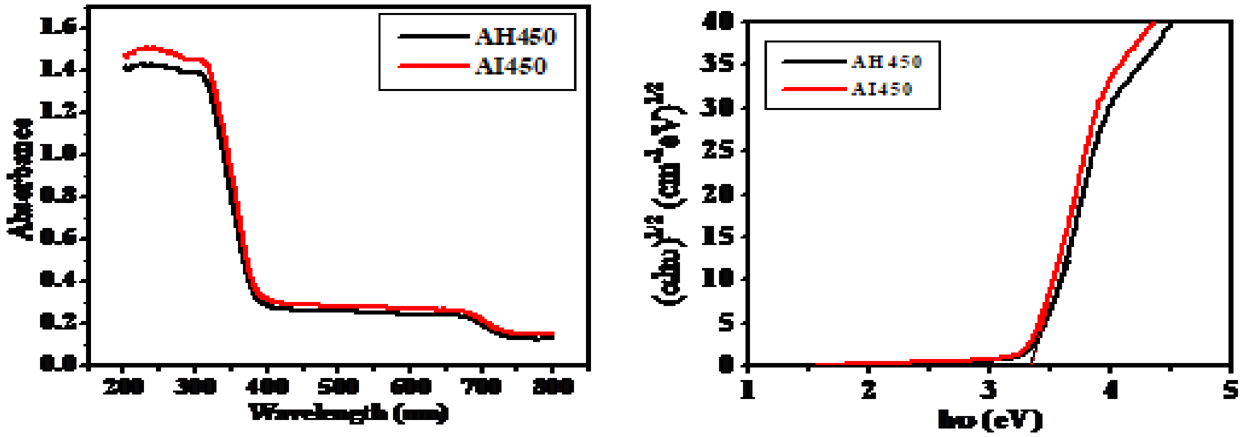

Fig 3. UV-Visible spectra and corresponding Tauc plots for AH450 and AI450 TiO_2 powders

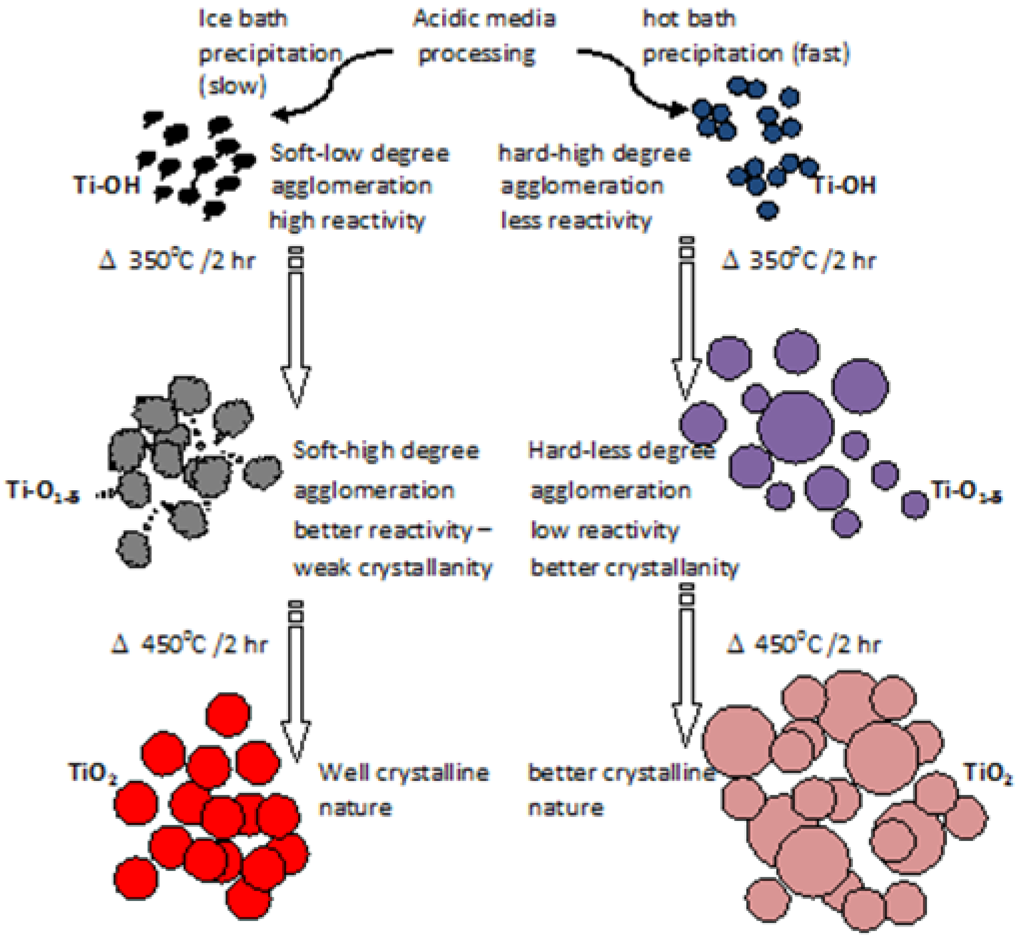

Fig. 4. The mechanism for processing of TiO_2 powder with anatase symmtery by using the acidic route

The results presented in this communication showed well crystalline nature of powders processed under ice bath temperature as compared to the powders generated by using precipitation at hot condition (at 70 °C). The mechanism for this could be as follows. The figure – 4 illustrates the said mechanism of processing of anatase TiO_2 powder by using the acidic route. In case of the Ti-hydroxide precipitation at ice bath temperature, the hydrolysis of Ti-precursor occurs slowly. The slow hydrolysis favours the precipitation of Ti-hydroxide particles with low degree of agglomeration.

Further, processing at low i.e. ice bath temperature gives rise soft agglomeartes with high degree of reactivity. The annealing of such as-prepared Ti-hydroxide particles having soft agglomeartion nature with low degree of agglomeration and high degree of reactivity at moderate tempearture i.e. 350 ^{0}C leads Ti-oxide powder with very weak crystallanity.

The weak crystallanity might be realized beacuse of lower rate of reaction and hence crystallization of soft agglomerates due to insufficent thermal energy gained at moderate tempearture of annealing (350 ^{0}C). On futher processing i.e. annealing at higher temperature of 450 ^{o}C, due to availability of sufficient thermal energy and higher degree of reactivity of soft agglomaretes leads the TiO_2 powder with very well crystallanity.

In another case, the Ti-hydroxide precipitation is carried out at higher temperature of 70 ^{0}C. This increases the rate of hydrolysis as compared to the hydrolysis at ice bath temperature. The hydrolysis at 70 ^{0}C leads the precipitation of Ti-hydroxide particles with increased level of agglomeration. Further, the agglomeration nature is hard. The hard agglomerates decreaes the reactivity of corresponding particles. On annealing of the such agglomerates at moderate temperature, 350 ^{0}C leads Ti-oxide powder with better crystallanity due to sintering effect as compared to the oxide powder obtained at 350 ^{0}C during ice bath processing. Furthermore, the annealing of this Ti-oxide powder at higher tempearture of 450 ^{0}C do not increases the crystallanity much further because of less reactivity of sintered hard agglomerates as compared to the crystallanity of oxide powder obtained at 450 ^{0}C during the ice bath processing. The above mentioned mechanism generates well crystalline TiO_2 powders with anatase symmetry in case of acidic route under ice bath temperature precipitation of Ti-hydroxide.

CONCLUSION

In present work, TiO_2 powders are prepared by using simple precipitation reaaction by using acidic route at hot and ice bath conditions. In a acidic route, ice bath conditions are found to be more effective for preparation of well nanocrystalline TiO_2 particles with nearly uniform size distribution. This might be due to the controlled hydrolysis-precipitation of Ti-hydroxide particles leading into soft - less agglomeration with high degree of reactivity. Further, annealing of such precipitate at high temperature generates well crystalline anatase TiO_2 nanoparticles due to soft agglomeration of intermidate product with high reactivity and smaller average particle size.

Conflicts of interest: The authors stated that no conflicts of interest.

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