

Development of nanostructure in ultra-fine anatase powders derived by the low temperature sol gel-solvothermal process

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Ultra-fine crystalline anatase nano-powders of less than 6 nm particle size have been obtained at the early stage of crystallization using the one step low temperature non-aqueous sol gel-solvothermal treatment of the $\text{Ti}(\text{OEt})_4$ precursor. The solvothermal treatment is held at 110 °C for 10, 20, 40, 60 hours in the presence of 2-etoethanol and ethanol as solvent. Nanostructural development is followed by TEM, HRTEM, electron and X Ray diffraction. Particle coarsening by oriented attachment is evidenced by HRTEM observations and by particle growth kinetics during the solvothermal treatment.

Key Words: Sol gel-solvothermal, Oriented attachment particle coarsening, Anatase nanostructural development.

Introduction

Solution-based synthesis is the most powerful and economic method to create nanostructured anatase TiO_2 with unique physical and chemical properties and has been applied successfully to various II-VI and III-V semiconductors. A vast amount of titania research has been done for a broad range of applications e.g. dye sensitized solar cells in which the need to tailor anatase nanostructure is of prime concern. The size of anatase nanoparticles affects the power output of dye-sensitized TiO_2 solar cells (DSSCs) by increasing the effective surface area of the diode and also the powder morphology can affect the power output of the DSSCs [1]. The porous structure of the anatase electrode allows it to reduce transparency and improve light scattering within, for a better photon capture by the dye molecules. Regarding the preparation of anatase TiO_2 nanoparticles a number of methods have been used such as microemulsion, chemical precipitation, hydrothermal or solvothermal crystallization, and sol-gel [2-4]. Common synthesis methods of titanium dioxide typically require an additional high temperature step to crystallize the amorphous material, thus resulting in larger particles and low surface area. On the other hand, one step low temperature processes such as aqueous acidic sol-gel, hydrothermal or solvothermal synthesis may give access to crystalline titania with high surface area [5]. Solvothermal treatment after sol-gel processing may allow for good control of shape, surface area and crystallinity of TiO_2 nanoparticles though the resulting nanocrystals are rather agglomerated.[6-8] The

Solvothermal synthesis can be carried out in hydrolytic or nonhydrolytic conditions and in the presence of an organic solvent. In this process it is possible to induce slight changes in hydrolytic reaction rates and use of additives which can lead to changes in size and shape of the crystalline nanoparticles [8]. In general solvothermal synthesis allows for the precise control over the shape, size distribution, crystallinity and crystal facets exposed by metaloxide nanoparticles.

Wahi *et al.* [9] produced anatase nanoparticles with large surface area at low temperature (140-300 °C), short reaction times (2 h) and near-neutral conditions. They used ethanol as solvent and a known amount of ultrapure water for the hydrolysis of titanium (IV) ethoxide inside the autoclave. At low temperature only spherical particles were observed, and at elevated temperature spherical and cubic shapes were found. Regardless of hydrolysis ratio (r), the crystallite size showed a minimum between r values of 5 and 15. The highest surface area of 250.6 m^2/g was found at 140 °C, using a $[\text{Ti}(\text{OEt})_4]$ of 0.02 mol L^{-1} and r of 20. However, the absence of a peptizing agent produced that some of the primary particles form hard aggregates that reduce their surface area. Further studies by Yang and Gao[10] on the solvothermal process at 110-220 °C for 22 h in an autoclave obtained different titania morphologies like spherical, nanorod and nanoflower. Bosc *et al.* [4] obtained nanocrystalline anatase and analyzed the effect of surfactants on the nanostructure. In the synthesis, they use titanium isopropoxide as titania precursor and HCl for peptization at 30 °C. Anatase phase was observed in 2 h of peptization and a mixture of anatase and rutile was formed later of 5 h. After calcination at 350 °C and without the use of surfactant the specific surface area of the anatase was 26 m^2/g . Using the surfactant triblock copolymer

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poly(ethylene oxide)-poly(propylene oxide)-poly-(ethylene oxide) the surface area was 190 m²/gr. In the peptization process it is possible to use an acid or a base, because electrostatic stability of the particles is ensured when the pH deviates from the isoelectric point of the titania nanoparticles (6.5-7) [5]. S. Hore, *et al.* [11] produced anatase from titanium isopropoxide and showed the influence of acid/base peptization step on particle nanostructure observing that in the acid peptization higher surface areas were obtained. In the stage of peptization, nitric acid, a mix of acetic and nitric acid and tetramethylammonium hydroxide were used at 80 °C. After hydrothermal treatment in the temperature range of 180-230 °C, the anatase nanoparticles showed particle sizes and specific surface areas between 15-40 nm and 39-145 m²/gr, respectively. The powders peptized with the mix of acetic acid and nitric acid showed the lower particle size and the higher surface area. Kumar *et al.* [12] analyzed the difference on peptized and unpeptized titania particles on sintering and phase transformation. 6 nm anatase crystallites were prepared from hydrolysis of titanium isopropoxide and peptized with nitric acid and heating at 80 °C for 12 h. In the peptization procedure, H⁺ ions from nitric acid formed a stable sol. These are adsorbed onto the surface of the titania and induce a high particle surface charge. On the other hand, unpeptized sols formed highly aggregated clusters of primary particles. Peptized sample was microporous showing a uniform distribution of pores with diameter size less than 2 nm and a specific surface area of 160 m²/g. Regarding the unpeptized titania, this showed bimodal pore size distribution because of the presence of aggregates and a specific surface area of 300 m²/g. Coarsening and aggregation can compete with nucleation and growth in modifying the particle size distribution in a system [13].

A good understanding of the process and parameters controlling the precipitation of particles during synthesis helps to improve the engineering of the growth of nanoparticles to the desired size and shape [14, 15]. Particle coarsening under liquid phase synthesis can take place by Ostwald ripening (OR) or oriented attachment mechanisms (OA). Particle growth based on OR involves the dissolution of small particles and growth of larger particles at a rate that is directly proportional to the solid's solubility and solid-liquid interfacial tension [14]. The kinetics of crystal coarsening growth by OR strongly depends on the structure of the material, the properties of the solution, and the nature of the interface between the crystals and the surrounding solution. OR coarsening of nanoparticles from homogeneous solution follows the rate law derived by Lifshitz, Slyozov, and Wagner (LSW)[16, 17] for micrometer-sized colloidal particles.

$$\bar{r}^3 - \bar{r}_0^3 = kt,$$

Where $\bar{r}$ is the average particle radius, $\bar{r}_0$ is the average initial particle size, t is the time, and k is the rate constant.

OA mechanism occur when nanocrystals get alignment and coalescence between them to form large crystals with irregular morphologies [18]. The oriented attachment (OA) mechanism has also been found to be a significant coarsening mechanism in the growth of several nanomaterials. It is significant that many of the materials that have been observed to grow by OA are relatively insoluble. Both mechanisms have been found to operate simultaneously, with the dominant pathway changing with solution chemistry, particle surface condition, and temperature.

The present work is an attempt to quantify the nanostructural development of ultra high surface area anatase titania ceramics at the very early stage of crystallization that has not been previously reported, while being subject to the non-aqueous sol gel-solvothermal treatment of the Ti(OBu)₄ precursor. In the present approach the use of carboxylic acid type capping agents that promotes the development of the low energy anatase facets was avoided in order to explore the possibility of having a high percentage of the more reactive high energy anatase facets. Ultra fine particle size distribution functions were determined by TEM, HRTEM and X Ray diffraction as a basis for assessing the coarsening kinetics and the relative importance of the OR and OA particle coarsening mechanisms. It is hoped that the present results will contribute to the preparation of ultrafine anatase nanostructure with tailored morphologies and thus tailored properties.

Materials and Methods

An 0.5 M solution of Ti(OBu)₄ in ethanol was prepared; 2-ethoxyethanol was added to ethanol in a one molar ratio (2-ethoxyethanol/Ti(OBu)₄). The use of ethanol as solvent in the presence of 2-ethoxyethanol was effective to produce TiO₂ nanoparticles. After stirring the solution during 2 hours, it was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated and maintained at 110 °C for 10, 20, 40 and 60 h, and then cooled to room temperature. After solvothermal treatment, the precipitate products were purified by three successive cycles of washing with ethanol, centrifugation, and drying at 80 °C. A stable colloidal suspension was prepared dispersing the particles in aqueous solution containing 0.1 M nitric acid. A schematic diagram of the synthesis process is shown in fig.1. Regarding powder characterization a Siemens apparatus (Model D5000) with CuK α radiation at 20 kV and a scanning range from 10° to 70° was used during X-ray diffraction (XRD) measurements. The Crystallite size was estimated according to the Scherrer formula. Surface area was determined from N₂ adsorption

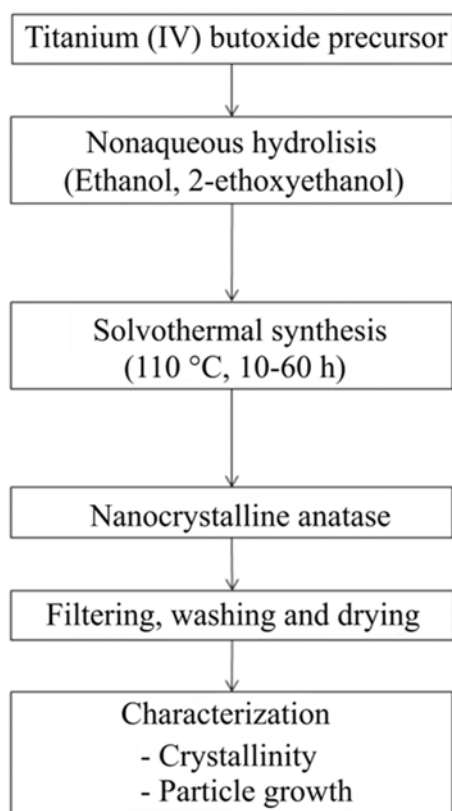


Fig. 1. Experimental scheme of non aqueous sol gel-solvothermal synthesis of high surface area anatase nano-powders.

onto the titania powders using a Quantasorb Jr equipment by the method of Brunauer-Emmett-Teller (BET); Samples were degassed at 150 °C prior to the measurements. The size, morphology and crystallinity of the nanoparticles were examined using a transmission electron microscope (TEM), Philips TECNAI 20 super Twin, at 200 kV on the modes of electron diffraction and HRTEM. TEM samples were prepared by placing a small drop of titania suspension on a copper/carbon grid. Particle size measurements were done on TEM dark field images containing 500 particles by using the “Image J” software [19].

Results and Discussion

Fig. 1 shows the scheme of the sol gel-solvothermal anatase processing starting out from the slow and partial hydrolysis of the $\text{Ti}(\text{OBU})_4$ precursor in 2-ethoxyethanol/ethanol, that presumably acts as a chelating agent to promote crystallization [20] according to the overall reaction, $\text{Ti}(\text{OBU})_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{BuOH}$. Subsequently, slow steps of hydrolysis and condensation occur during the solvothermal synthesis that may give rise to the formation of high energy planes as suggested elsewhere [21]. The next step involves the thermal treatment in autoclave at low temperature to increase anatase crystallization while maintaining a small particle size.

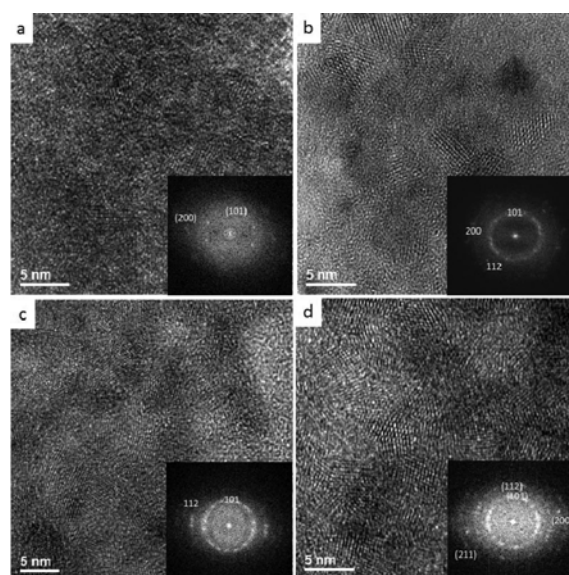


Fig. 2. Development of nanostructure in samples solvothermally treated at 10(a), 20(b), 40(c) and 60 hrs(d). by means of HRTEM and fit insets for the (200) high energy plane. Note the increase of crystallinity at higher treatment time.

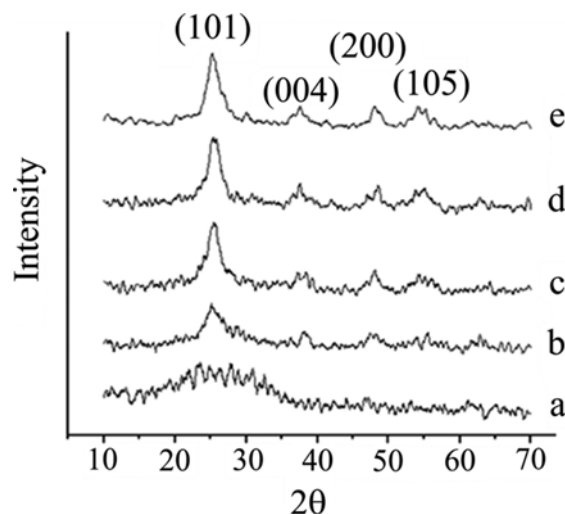


Fig. 3. XRD patterns of specimens subject to a) sol-gel, and sol gel-solvothermal treatment at 110 °C for b) 10, c) 20, d) 40, and e) 60 h.

Development of nanostructure

Fig. 2 shows the development of nanostructure in samples solvothermally treated at 10, 20, 40 and 60 hrs. by means of HRTEM fit for the (200) high energy plane. The shortest treatment time shows basically the (101) plane during the early stage of crystallization, while at 60 hrs. treatment various planes start appearing and several plane orientations form rings at the fit that demonstrates a well crystallized sample. The appearance of the (200) high energy plane at 60 hrs. is typical of non-aqueous processing [8].

Fig. 3 provides X-ray diffraction data for specimens subject to sol gel-solvothermal treatment at 110 °C for various times, showing that only the anatase phase is present (JCPDS file 70-8501). Fig. 3a shows amorphous

anatase subject to hydrolysis without solvothermal treatment. Figs. 3b-3e demonstrates the crystallinity development as time increases from 10 to 60 h. This finding agrees with the latter ffit results in fig. 2.

Anatase full crystallization

Fig. 4a is a HRTEM for anatase full crystallization after 60 h treatment showing the roughly rounded crystals at high resolution. Fig. 4b SAED shows a high proportion of well crystallized high energy planes i.e. (200), (103), (112), (211). Fig. 4c HRTEM shows the arrangement of the high energy planes i.e. (200), (103), (112), (211) etc. as worked out from diffraction and fringe measurements. Anatase pyramidal shapes are also seen by the well dispersed crystallites in fig. 4d by TEM dark field; Such dispersity of intermediate nanocrystals formed by self-assembling processes may lead to higher periodicity of the crystalline arrangement as shown in 4c and 5c. Fig. 4e is a plot of the measured particle size distribution function, showing a 5.9 nm average particle size. It is clear from this results, that crystallization of anatase is strongly dependent on solvothermal treatment time; It is also apparent that the

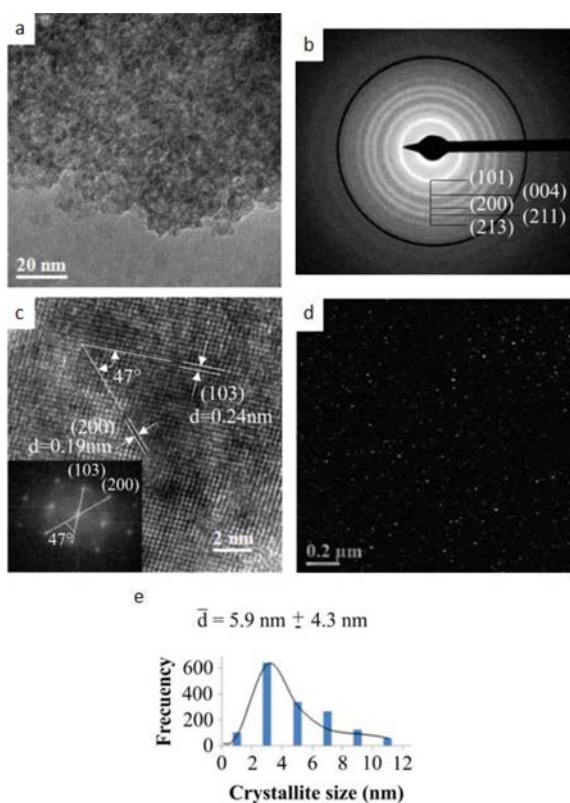


Fig. 4. Anatase Nanostructure developed after non-aqueous solvothermal treatment. a) HRTEM of anatase full crystallization after 60 h treatment showing the roughly rounded crystals at high resolution. b) SAED of 60 h specimen pointing to the high proportion of high energy planes i.e. (200), (103), (112), (211). c) Detail of the high energy planes as worked out from the diffraction pattern and fringe measurements. d) TEM dark field of well dispersed individual extremely fine nano-crystals. e) Particle size distribution of 5.9 nm average crystal size.

particles remain highly dispersed and that readily grow into two dimensional structures.

Anatase particle coarsening mechanism

Fig. 5a is a TEM micrograph illustrating one dimensional primary nanoparticles self assembled by the OA, that is a crystal growth mechanism that relies on the minimization of the surface energy of the system and allows to form larger particles and two dimensional structures. Fig. 5b is a HRTEM of the individual particles attached through the (004) plane growing in the [001] direction and whose growth velocity may be expected to influence the final shape of the crystal. It will also be seen that such crystallites do not have straight continuity, besides they present varying contrast along the formed secondary crystal. These features are characteristic of OA [22, 23]. Fig. 5c points to the OA of particles through the (103) planes into a contrastingly planar nanostructure while the ffit inset illustrates the translational symmetry for the (103) plane. The driving force for the auto assembly is the elimination of the pairs of (103) high energy planes that may lead to a substantial reduction in surface free energy.

Common descriptions of particle growth are based on the concept of Ostwald ripening (OR), which involves dissolution of small particles and growth of larger particles at a rate that is directly proportional to the solid's solubility: In the present case the solubility during the solvothermal treatment was rather low and

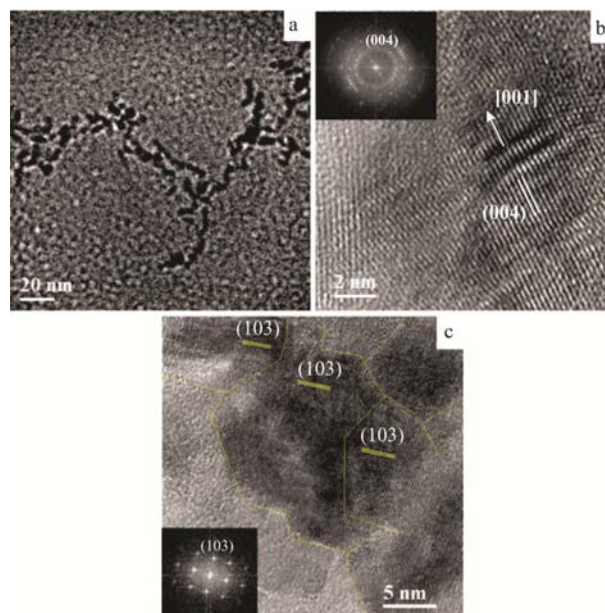


Fig. 5. HRTEM of self organization of nanostructures. a) Large field of view of single nanoparticles attached to each other and growing in one direction. b) Detail of adjacent particles grown through OA of primary particles showing the characteristic varying contrast of oriented attachment. c) Showing various particles attached alongside the (103) plane forming a two dimensional, planar nanostructure.

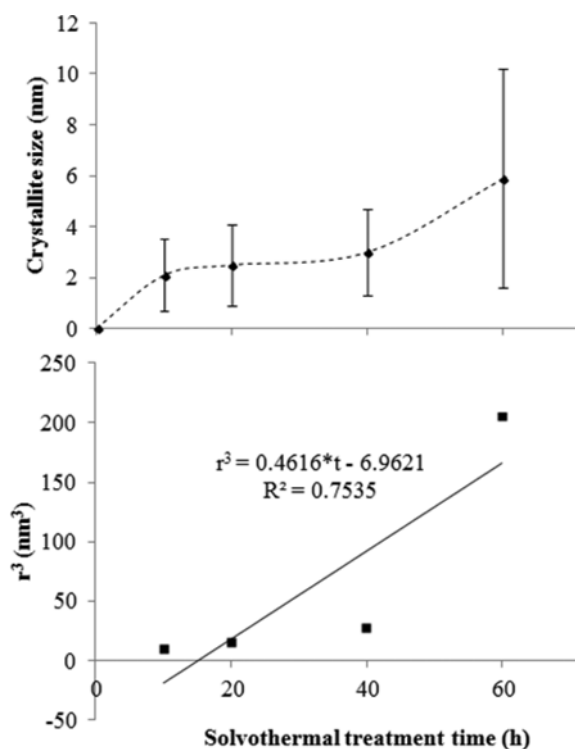


Fig. 6. Anatase coarsening mechanism a) Coarsening kinetics during solvothermal treatment at 110 °C and b) Particle radius cubed vs time. Note the lack of fit, meaning the Ostwald ripening mechanism does not apply.

also during the peptizing stage since it involved very low PH, 1. Therefore the OR coarsening mechanism may not be expected to play a fundamental role in particle growth. On the other hand Oriented attachment (OA) as an alternative growth pathway in which larger crystals form by crystallographically controlled assembly of primary nanocrystals and particles that approach each other and attach on crystallographic matching terminating surfaces was extensively observed by HRTEM.

Fig. 6 shows the kinetics of particle growth for 10, 20, 40 and 60 h. treatment. The average diameter of anatase particles measured from dark field TEM images is plotted as a function of solvothermal treatment time, at 110 °C in fig. 6a. At low treatment time the slope of the curve changes slightly, however at 60 hrs treatment the slope abruptly changes, this may reflect the predominance of the OR mechanism over the OA, which has also been reported by Huang *et al.* [24] The OR coarsening model [16, 17] is based on the equation $r^3 = r_0^3 + kt$: where r_0 is the initial average diameter, k is a temperature dependent constant, t is time, whose kinetics is a linear plot. It will be seen that the present data however, did not produce a linear behavior, as shown by the fig. 6b meaning that the OR coarsening mechanism do not apply substantially in the present conditions, and thus favours the OA coarsening mechanism.

In summary, the solvothermal processing allowed to get ultrafine well crystallized anatase nanoparticles that

were strongly influenced by the time of treatment and produced nano-structures with a high proportion of high energy planes. HRTEM provided evidence on self-assembled anatase to form close packed ordered two dimensional structures of faceted nano-particles. The 2-ethoxyethanol presumably prevents the anatase nanoparticles dissolution and its intrinsic negative charge may be attracted by the positive titania particles to self-assemble into a two dimensional close packed structure.

Concluding Remarks

The formation of well dispersed, ultra-fine anatase powders from the $\text{Ti}(\text{OBU})_4$ precursor was achieved through the non-aqueous sol gel-solvothermal low temperature one step process at a reaction temperature of 110 °C, that is lower than those currently reported in the literature. The solvothermal approach rendered a fully crystalline material with a high proportion of exposed high energy facets, {200}. Crystallite size ranged from 3.9 to 6.4 nm from X-ray measurements. Solvothermal processing up to 60 h showed increased crystallinity and coarsening was due mainly to oriented attachment as extensively seen by HRTEM and also deduced from coarsening kinetics. Peptization with nitric acid presumably played a major role on the attainment of well dispersed fine particles. HRTEM showed self-assembled anatase into close packed ordered two dimensional nano-structures. The fine and fully crystalline material attained may be used for photocatalysis and for DSSC solar devices.

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