Nanoscale engineering of TiO₂ nanoparticles: Evolution of the shape, phase, morphology, and facet orientation

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The solvothermal synthesis of nanostructured TiO₂ has been studied to examine the processing parameters that control crystallite size, phase, morphology, and facet orientation. Control over the characteristics of these materials makes them useful for a wide range of applications in photocatalysis, environmental pollution remediation, and solar energy conversion. Moreover, this simple, low cost, and low toxicity synthesis process could be extendable to the controlled synthesis of other functional oxide crystals with well-defined morphologies and tunable sizes with active facet orientation.

Keywords: Nanoparticles, Facets, Synthesis, Solvothermal method

1. Introduction:

Due to its well documented properties, TiO₂ nanoparticles (NPs) have been employed in diverse applications, such as optoelectronics, photovoltaics, thermally activated catalysis, ambient detoxification, sensing, fuel cells, lithium-ion batteries, and hydrogen storage/production, enhancing each of these to a higher level of performance. These applications originate from the unique physical and chemical properties of TiO₂, which depend on the particle size, morphology, phase and crystallinity [[1-6]]. Many synthesis methods, including microemulsion mediated hydrothermal method, combustion synthesis, sol-hydrothermal approach, reverse micelle method, low-temperature process, ultrasonic approach, hydrothermal method, and gas-phase hydrolysis, have been used to synthesize nanostructured TiO₂ with different morphologies [[7-14]].

The majority of those studies involved hazardous or toxic chemicals (like HF, HCl, and HNO₃), complicated precursors (like ionic liquids), and/or extended, high temperature heating processes (~12-24 h) to tune the morphology and facet orientation of the final products. Most importantly, the sizes of the final products, associated with the aforementioned studies, were approximately 50-500 nm, which are still too large for a number of applications that demand high specific surface areas. **For instance, Li *et al.* used linoleic acid as a capping agent for the synthesis of TiO₂ NPs [8]; however, these particles were discernably larger and longer than our target sizes. Wu *et al.* prepared TiO₂ nanocrystals (NCs) by using trace amounts of water and oleylamine as the hydrolysis agent and the capping surfactant, respectively [9]. Jun *et al.* reported the synthesis of bullet-, diamond-, and rod-shaped TiO₂ *via* a nonhydrolytic process, which employed both lauric acid as a selective surfactant and trioctylphosphine oxide as a nonselective surfactant [10]. Truncated tetragonal bipyramids and square sheets of TiO₂ crystals were synthesized using ionic liquids (particularly, 1-butyl-3-methylimidazolium tetrafluoroborate) [11].**

Feng and co-workers reported the solvothermal synthesis of mesoporous TiO₂ microspheres using a mixed reaction solution of sodium hydroxide and ethanol [12]. Yu et al. reported that surface-fluorinated TiO₂ hollow microspheres were prepared by a one-step hydrothermal strategy that employed ammonium bifluoride as a morphology controlling agent [13]. Yang et al. used hydrofluoric acid—a very toxic chemical—as a shape-controlling agent to synthesize TiO₂ crystals [14]. Matijević and co-workers prepared stable aqueous colloidal dispersion of titania spheres through the elevated temperature hydrolysis of TiCl₄ in the presence of sulfate ions [15]. Barringer and Bowen prepared titania spheres by controlling the hydrolysis of titanium tetraethoxide within dilute alcohol solutions [16], while Jiang et al. produced spherical titania particles through the slow hydrolysis of titanium glycolate precursors [17]. Given the assortment of synthesis approaches to produce faceted TiO₂ nanostructures, this Letter reports a solvothermal technique for the tailored synthesis of crystalline TiO₂ NPs with dimensions smaller than the above studies (< 50 nm) and with controlled morphologies by simply varying the solvothermal synthesis condition and parameters with less hazardous precursors at shorter heating process (6h). Thus, the reported synthesis method is more environment-friendly and cost effective.

2. Experimental Section

2.1 Nanoparticle Synthesis. All of the chemicals were used as received without further purification. We employed a modified version of a Schlenk technique, under a nitrogen atmosphere [15] in the solvothermal process. In a typical procedure, either 1 mL of titanium tetrachloride (TiCl_4 , Fluka, $\geq 98.0\%$) or 1 mL of tetrabutyl titanate (TBT, Fluka, $\geq 97.0\%$) was slowly added into a solution comprised of a mixture of 5 mL oleic acid (OAC, Aldrich, technical grade 90%), 15 mL oleylamine (OAM, Aldrich, technical grade 70%), and 20 mL cyclohexane, under stirring in a conical flask. The solution was transferred into a 100 mL Teflon-lined stainless steel autoclave after stirring for 30 min; the autoclave sat in an oven at 250 °C for 6 hours. After the reaction, the autoclave was cooled to room temperature (20 °C), and a white precipitate was collected by centrifugation and washed several times with butanol, propanol and ethanol. For each washing step and subsequent centrifugation, an ultra-sonication bath was used to disperse the precipitate completely into the corresponding solvent and to remove physically adsorbed molecules from the particles' surfaces.

2.2 Characterization. TEM samples were prepared by casting one drop of suspension containing the NPs on a Cu-TEM grid coated with an amorphous carbon thin film and then dried in air. The TEM characterization was conducted on a Philips CM20 microscope operating at 120 kV. For XRD measurements, a commercial θ -2 θ X-ray diffractometer (Philips, PW1730) was used, equipped with a horizontal goniometer, a Cu anode X-ray tube, and a graphite monochromator. The measurements were performed at room temperature with the characteristic Cu K_α X-ray lines.

The evolution of the shape and morphology of the TiO_2 NPs, optimized under various synthesis conditions, is summarized in Table 1.

Table 1. Synthesis conditions, morphologies, and size determinations of the optimized, final products.

<u>Sample</u>	<u>Ti</u> <u>Precursor</u>	<u>Acid/base</u>	<u>Extra</u> <u>Solvent(s)</u>	<u>Temperature</u>	<u>Resultant</u> <u>Morphology</u>	<u>Size</u> <u>(nm)</u> <u>XRD</u>	<u>Size</u> <u>(nm)</u> <u>TEM</u>
1	TiCl_4	OAC	Cyclohexane	250 °C	No NP	—	—

	1 mL	5 mL, OAM 15 mL	20 mL			—	—
2	TBT 1 mL	OAC 5 mL, OAM 15 mL	Cyclohexane 20 mL	250 °C	disordered/ irregular	5.5	5.8
3	TBT 1 mL	OAC 15 mL	Cyclohexane 25 mL	250 °C	asparagus	2.9	3.3
4	TBT 1 mL	OAC 15 mL	Cyclohexane 25 mL	150 °C	wire	2.2	2.3
5	TBT 1 mL	OAC 15 mL	Cyclohexane 23 mL, water 2 mL	250 °C	cubes	6.5	6.7
6	TBT 1 mL	OAC 15 mL	Cyclohexane 23 mL, water 2 mL, Na- oleate 1 gr	250 °C	eggplant	4.8	5.2
7	TBT 1 mL	None	Acetic acid 40 mL	250 °C	cubes	21.2	22.4
8	TBT 1 mL	None	Acetic acid 35 mL, Ethanol 5 mL	250 °C	tetragons	9.0	9.8

3. Result and Discussion

Initially, a Schlenk line-based synthesis process (performed under a nitrogen environment) was adopted, motivated by the work reported by Gordon *et al.* [19]. Unfortunately, this approach yielded no NPs, as TiCl_4 appears to have had reaction kinetics that were too rapid for the nucleation and growth of NPs (sample# 1). TBT was selected as the new titanium source because of its low hydrolysis rate (due to the presence of longer alkyl groups that retard diffusion and growth processes compared with TiCl_4). Changing the TiCl_4 precursor to TBT resulted in disordered and irregularly shaped nanoparticles whose average diameter was approximately 10 nm. The associated XRD spectrum confirmed that all of the observed diffraction peaks are in good agreement with the anatase TiO_2 with good crystallinity.

The elimination of amines as precursors led to the formation of asparagus-like TiO_2 NPs (sample # 3, Fig. 1). The results indicated that the absence of the amine had a marked effect on the morphology of the produced nanoparticles. By using surfactants that possess different functional groups with distinct binding strengths, the morphology of resulting particles were controlled [16-21]. In the absence of amines, growth along a preferred crystallographic direction was predominant in the system. Subsequently, the formation of NPs with an elongated morphology, such as that observed with an asparagus-like morphology, was favored (Fig.1). The associated XRD pattern that was obtained from the nanoparticles (Fig. 1d) shows reflections

Fig. 1. a)-c) TEM micrographs of different magnifications and **d)** a XRD spectrum of TiO_2 NPs in sample# 3 (R stands for rutile in the XRD spectrum).

characteristic of anatase TiO_2 with few impurities (originated from the rutile) in the phase. **The XRD patterns of samples #3 suggested that its sharp, (004) diffraction peak indicated an evolution of growth along the [001] direction of TiO_2 NPs toward an elongated structure, which was observed in its rod-like structure.** The intensity ratio of the (004) peak relative to the (200) peak represented a meaningful parameter for the anisotropic growth along the [001] direction, since the intensities of two peaks are always independent.

To examine the effect that the reaction temperature had on the morphology of our nanoparticles, another sample was synthesized under the typical conditions (detailed in the Experimental Section) but at a lower reaction temperature (150 °C, sample# 4). The resultant nanomaterial consisted of wire-shaped nanoparticles with uniform length of ~15 nm and width of ~2 nm. These NPs also possessed a small amount of rutile phase impurity. The lower temperature suppressed the formation of the *asparagus*-like tip on the nanostructure. At higher temperatures, the crystals grew rapidly on the faces with high surface energy (which are the [001] faces, corresponding to (004) in XRD pattern). To confirm this point, the intensity ratios of the (004) peak relative to the (200) peak for samples #3, 2.38, and #4, 2.01, were calculated.

Another ordered structure was observed during the solvothermal synthesis with the addition of deionized water (sample# 5). The addition of the water considerably accelerated the hydrolysis and condensation processes of TBT, as well as the nucleation and growth of the TiO₂ nanocrystals. This led to the rapid formation of a larger amount of TiO₂ nuclei than previous synthesis conditions, which resulted in the final TiO₂ NPs possessing a smaller net diameter. Fig. 2 depicts typical TEM images of the TiO₂ NPs synthesized in the presence of water. The TiO₂ NPs were cubic and possessed a narrow size distribution. As confirmed by the XRD pattern, these shape-controlled particles possessed uniform morphology and size with a pure TiO₂ anatase phase, absent of any secondary phases.

Fig. 2. a)-c) TEM micrograph of different magnifications and d) XRD spectrum of TiO₂ NPs in sample# 5.

When sodium oleate was added into the solvothermal solution (sample #6), while the other composition parameters were kept unchanged (compared to sample #5), the resultant TiO₂ NPs were characteristically elongated structures, but with a wider, eggplant-like morphology (Fig. 3) with an aspect ratio of ~3.5-4.0. Here, sodium oleate played a prominent role in the formation of this morphology. Selective adsorption of sodium oleate led to a decrease in the growth rate of the adsorbed crystal plane, which facilitated the

formation of the eggplant structure. Apparently, the sodium oleate molecules were bound more facilely to the anatase [001] facets of the TiO_2 nucleus. When sodium oleate selectively and strongly bound to [001] facets, the growth rate in this direction kinetically decreased. The difference in the growth rates in the two directions of the facets resulted in the suppression of (004) peak, as observed in the XRD spectrum (Fig. 3d).

The chemical modification of TBT by carboxylic acids was the rational strategy to tune the reactivity of the precursors;

acetic acid adjusted the reactivity of TBT through the coordination with titanium centers, thereby influencing the nucleation and growth of the TiO_2 NPs (sample# 7). The TEM results (Fig. 4) implied that acetic acid influenced the properties of TiO_2 NPs significantly, yielding cubic morphology with an average diameter of approximately 20 nm. The XRD pattern of these TiO_2 NPs (Fig. 4d) exhibited well-defined peaks that were assigned to the pure anatase phase, indicative of the high crystallinity of this sample. The intensity of the (004) peak in the XRD pattern, in combination with the TEM results in Fig. 4, confirmed that acetic acid acted like a surface-selective surfactant, binding to the anatase [001] facet and affecting the resultant crystal shape. **Note that acetic acid played important role as surfactant and dispersant (solvent) in this reaction, which significantly simplified the synthesis process.**

Fig. 3. a)-c) TEM micrographs of different magnifications and d) XRD spectrum of TiO_2 NPs in sample# 6.

Fig. 4. a)-c) TEM micrograph of different magnifications and d) XRD spectrum of TiO_2 NPs in sample# 7.

ethanol, used to synthesize the NPs, suggested that the solution composition played a key role in this TiO_2 nanoparticle synthesis. Further, the primary XRD peaks, as seen in Fig. 5d, corresponded to anatase TiO_2 . These findings were supported by the previous work of Liao *et al.* work on the synthesis of anatase TiO_2 nanocrystal colloids [24]. Their solvothermal reaction investigation found that ethanol-based syntheses suppressed the growth rate along the [001] direction and transformed the shape of the nanoparticles from rod-like to rectangular.

4. Conclusions

In summary, a facile solvothermal process was demonstrated to prepare TiO_2 NPs with different morphology, shape, phase, and facet orientation via a chemistry approach for which no highly toxic/corrosive reagents (like HF or HNO_3)

To study the effect of solvent choice on the morphology of the TiO_2 nanomaterials, synthesis experiments were performed using TBT as the reaction agent within an ethanol solution that contained acetic acid (sample# 8). Fig. 5 illustrates the resultant, synthesized nanocrystals that possess truncated, octahedral crystal geometry. This crystallinity was the most thermodynamically stable geometry for the anatase crystal phase, and was comprised of two [001] facets and eight [101] facets (Fig. 5c- inset). The aspect ratio of edge lengths labelled by A and B was 1:3.5. The TBT in

Fig. 5. a)-c) TEM micrographs of different magnifications and d) a XRD spectrum of TiO_2 NPs in sample# 8.

were involved. The size and morphology of the nanoparticles varied with the preparative conditions. **Most importantly, in all cases studied in this investigation, all synthesized nanoparticles were monodispersed and were smaller than 50 nm.** Such nanocrystals with controlled shape, size, and facet orientation will be valuable for further investigation of shape-dependent properties of TiO₂ with active facets. Overall, the results presented here represent a notable step forward in the engineering of low-dimensional TiO₂ nanostructures.

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