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Critical Nuclei Size, Initial Particle Size and Packing Effect on the Phase Stability of Sol-Peptization-Gel-Derived Nanostructured Titania

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The influence of the initial particle size and packing of anatase crystallites on the phase stability of nanostructured titania was investigated. Dried anatase gels with different degrees of particle packing were prepared through the peptization-induced electrostatic stabilization of primary particles in the sol. The initial size of anatase primary particles was varied by precalcination prior to the anatase–rutile phase transformation that occurred during final calcination. In the case of well-packed titania, the initial size of anatase primary particles does not influence the phase-transformation behavior whereas loosely packed titania shows a strong initial anatase primary particle size dependence on the phase-transformation behavior.

Titania is one of the most studied ceramic oxides because of its interesting photovoltaic,¹ photocatalytic,^{2,3} photo-/electrochromic,^{4,5} and sensing⁶ properties. Titania exists in a number of polymorphic forms with anatase and rutile being the most common ones. Both anatase and rutile crystallize in the same tetragonal structure, but their symmetry and properties are considerably different. Anatase is usually considered to be photocatalytically more active than rutile and a good photocatalyst for the degradation of organic pollutants.^{7–9} However, there are other studies showing the effectiveness of the rutile phase^{10–14} and the synergistic effects for anatase–rutile mixed phases^{15–17} in these applications.

Almost all chemical methods of preparation of nanostructured titania yield anatase, which is a metastable phase and upon heat

treatment transforms irreversibly to the stable rutile phase.¹⁸ The exact temperature and rate of transformation depend on many factors, such as the primary particle size, solution pH,¹⁹ washing²⁰ and drying temperature,²¹ cation content, packing of primary particles,²² physical nature of the precursor, and hydrolysis and reaction conditions.^{19,23–25} Even though there are several papers published in the area of anatase-to-rutile phase transformation, no clear picture describing the influence of these factors either on the phase transformation or phase stability has emerged.^{22,26–33}

There have been several reports in the past 20 years indicating the existence of a critical primary particle size below which anatase becomes stable and does not transform to rutile.^{23,26} Kumar and co-workers also suggested that this critical particle size effect may very well explain the formation of anatase in the as-precipitated state.³⁴ Whatever may be the exact value of critical nuclei size for the anatase-to-rutile transformation, the ability of anatase primary particles to grow and reach the critical nuclei size

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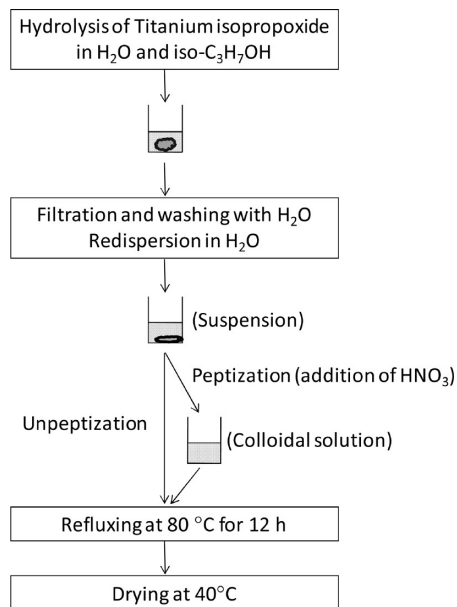


Figure 1. Sol-peptization-gel process for making nanostructured titania.

will ultimately determine the phase stability of the anatase phase.²⁴ For chemically pure anatase, the growth of primary particles should depend mainly on its initial size, the packing within the aggregates, and the particle morphology. In this letter, we report the influence of the initial size and packing of anatase primary particles on the phase stability of sol–gel-derived nanostructured titania.

To study the influence of the initial size and packing of primary particles on the anatase-to-rutile transformation, gels with two different degrees of packing were prepared through a sol-peptization-gel technique elaborated on by Kumar et al.^{22,26} A detailed flowchart showing the various steps such as hydrolysis, filtration and washing, redispersion, peptization, and drying is given in Figure 1. A particulate hydrosol of anatase was prepared by hydrolyzing the 0.55 M alcohol solution containing 12 g of titanium isopropoxide with 130 g of isopropyl alcohol containing 14 mL of water at room temperature under vigorous stirring. The precipitates were then filtered and washed with water multiple times to remove the excess alcohol. After washing, the precipitate was redispersed in 183 mL of water to form an unpeptized sol. The peptized sol was prepared by adding nitric acid with a H^+/Ti^{4+} ratio of 0.5 at RT to the unpeptized sol. Subsequently, this acidic sol was heated to 80 °C under reflux with vigorous stirring for 12 h to form a peptized (PP) sol. The unpeptized (UP) sol (without the addition of nitric acid) was also heated under similar conditions to that of peptized sol. After being refluxed, the unpeptized sol appeared to be a milky white slurry whereas the peptized sol had a light-blue color. Both sol samples were dried via evaporation at 40 °C. For the TEM, X-ray diffraction (XRD), and selected area electron diffraction (SAED), dried gels were powdered before being subjected to these measurements (Figures S1 and S2, see Supporting Information). For all other measurements such as field-emission scanning electron microscopy (FE-SEM) and N_2 adsorption–desorption isotherm measurements, dried, thin, flaky samples were used. Crystallite sizes of both anatase and rutile were calculated on the basis of XRD line broadening using Scherrer's equation

$$D_{hkl} = \frac{K\lambda}{B_{hkl} \cos \theta} \quad (1)$$

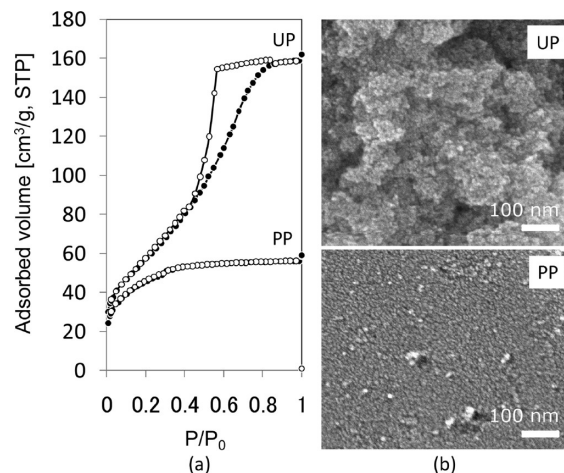


Figure 2. (a) N_2 adsorption–desorption isotherm and (b) FE-SEM image of as-synthesized PP and UP titania.

where D_{hkl} is the average nanocrystalline size and K is a constant (in the present case, a value of 1.38 was assumed).¹⁸ λ is the wavelength of the Cu $K\alpha$ line, B_{hkl} is the fwhm, and θ is the peak angle. The relative amount of rutile present in the sample has been calculated using the following equation³⁵ and references therein

$$W_R = \frac{1}{1 + 0.8 \left(\frac{I_A}{I_R} \right)} \quad (2)$$

and

$$W_A = 1 - W_R \quad (3)$$

where W_R and W_A are the fractions of rutile and anatase (in percentage), respectively. I_A and I_R are the integrated areas calculated using the trapezoidal rule from the absolute value of the regions between the baseline and the curves of anatase (101) and rutile (110), respectively.

Figure 2 shows the N_2 adsorption–desorption isotherm and FE-SEM micrographs of the as-dried gels of both PP and UP titania. It can be clearly seen from the isotherms that UP samples adsorbed more than 3 times the volume of N_2 compared to PP samples. This is a clear indication of the fact that primary particles in PP are much more tightly packed than the particles in UP. This is in agreement with what has been reported by Kumar et al.²² This difference can be explained by understanding particle rearrangement, packing, and shrinkage during drying. In the beginning of the first stage of drying, very little difference between PP and UP is expected because during this period only evaporation of the liquid medium of the sol, that is, water, takes place. However, the first stage of drying ends when the volume fraction of the liquid in the sol drops below 40 to 60%. Mechanistically, this happens when the volume percentage of solid particles in the sol reaches the percolation threshold. Towards the end of the first stage of drying, sol particles rearrange differently in PP than in UP. In the case of the PP sol, particles are positively charged through the peptization treatment. During the peptization treatment, H^+ ions from nitric acid get adsorbed onto the surface of sol particles and they repel each other to form a stable colloidal sol. This electrostatic repulsion also prevents particles from sticking together and forming aggregates. Toward the end of the first stage

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Table 1. Sorption Properties of Nanostructured Titania

titania	S_{BET} (m ² /g)	V_{total} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{micro} (cm ³ /g) ^a
peptized	156	0.09	0.03	0.06
unpeptized	215	0.25	0.17	0.08

^a Calculated using the Saito–Foley method.

of drying, titania particles in the sol begin to experience drying stresses that are directly proportional to the surface tension of the pore fluid, in this case, water, and inversely proportional to the size of the pore in the hydrogel.³⁶

Even though both PP and UP experience more or less similar levels of drying stress, the rearrangement and packing of primary sol particles will be different in PP than in UP. Although drying stress tries to pull sol particles closer, electrostatic repulsion prevents them from coming closer. These opposing forces will help particles to rearrange and pack well without forming aggregates. In other words, the PP particles can flow freely, resulting in dense packing under the influence of drying stress. During the second stage of drying, marked by the appearance of a pore fluid meniscus, the particulate gel network will continuously experience increasing levels of compressive stress, which will further consolidate the PP sample. Even though primary particles in UP experience the same level of compressive stress, there is very little opposing force to prevent particles from forming hard aggregates. In the absence of electrostatic repulsion, the strong bonds between neighboring UP particles may hinder their movement during drying processes and lead to a larger pore formation and loose packing. Moreover, as can be seen from Figure 2, total porosity and the average pore size of PP are slightly smaller than those of UP, which will in turn increase the compressive stress experienced by PP during drying. Also, because of the fact that UP is not a stabilized sol, particles in UP will aggregate even before the start of drying. Suspensions with aggregates of particles will produce gels with relatively larger pores. This can be clearly seen from the difference between the adsorption isotherms of UP and PP in Figure 2. UP gave a representative type IV isotherm indicating that a majority of the pores are in the mesoporous range with size larger than 2 nm whereas PP gave a typical type I isotherm corresponding to an average micropore size of less than 2 nm.³⁷ The total porosity of UP is almost 3 times higher than that of PP as indicated by the amount of N₂ adsorbed as shown in Figure 2 and Table 1. This is in total agreement with the drying-stress-assisted rearrangement and packing described previously.

Both UP and PP samples with initial anatase crystallite sizes ranging from 4 to 8 nm were prepared by precalcination at 300 °C for 1 and 100 h in a muffle furnace exposed to atmospheric air. After precalcination, all samples were held at 600 °C for 8 h. Characterization by TEM reveals that the particle size increases after precalcination for both PP and UP titania (Figure 3), and the SAED (Figure S2, see Supporting Information) study shows that all as-synthesized and precalcined samples correspond to crystalline anatase. TEM images indicate the presence of crystalline lattice fringes, and a high amount of porosity was also observed within the aggregates.

As can be seen from the SEM image (Figure 4), irrespective of the initial size of the anatase particles, PP samples transformed to more than 99% rutile after calcination at 600 °C for 8 h, hence giving a negligible fraction of anatase (Figure 5). In the case of UP, the anatase-to-rutile transformation was effectively retarded and showed an increase in the fraction of anatase with increasing

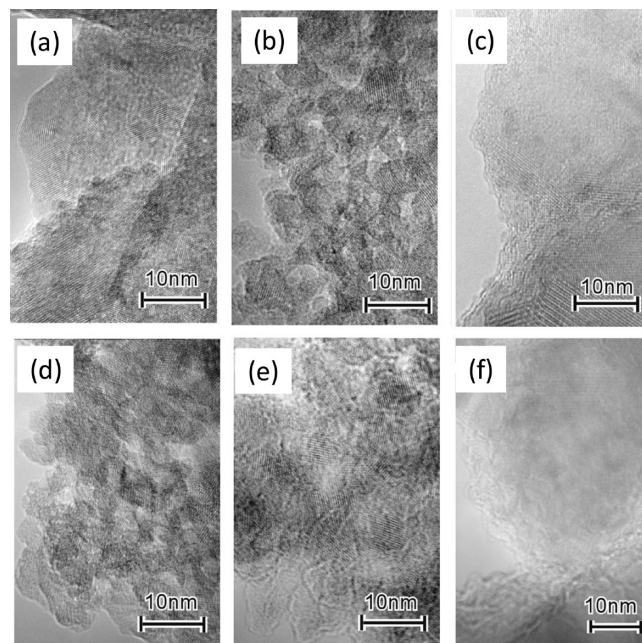


Figure 3. HRTEM micrographs of (a–c) PP and (d–f) UP titania (a, d) as prepared and (b, e) precalcined at 300 °C for 1 h and (c, f) 100 h.

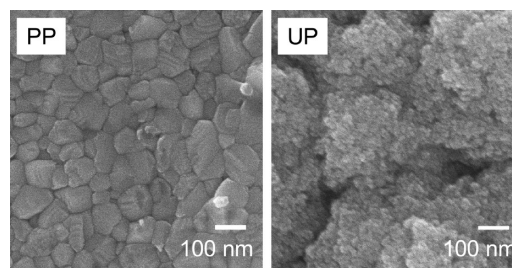


Figure 4. FE-SEM images of as synthesized PP and UP titania calcined at 600 °C for 8 h.

initial anatase particle size. When anatase titania is heat treated, it will convert to rutile only after growing to a certain size called the critical nuclei size, which can be determined as follows.^{27,35}

The total free-energy change, G_{total} , for the anatase-to-rutile transformation can be written as

$$G_{\text{total}} = \frac{4}{3}\pi r^3 G_{\text{chem}} + 4\alpha\pi r^2 \gamma_{\text{GR}} + 4\beta\pi r^2 \gamma_{\text{AR}} + 4\delta\pi r^2 \gamma_{\text{RR}} \quad (4)$$

Differentiating eq 4 with respect to the radius of the embryo, r , and equating it to zero at the maxima of the function will yield the critical nuclei size, r_c

$$r_c = -2 \left[\frac{\alpha\gamma_{\text{GR}} + \beta\gamma_{\text{AR}} + \delta\gamma_{\text{RR}}}{G_{\text{chem}}} \right] \quad (5)$$

where G_{chem} , γ_{GR} , γ_{AR} , and γ_{RR} are the Gibbs free energy and the gas (air)–rutile, anatase–rutile, and rutile–rutile interfacial energies, respectively. α , β , and δ are the fractions of interfacial area contributed by gas (air)–rutile, anatase–rutile, and rutile–rutile interfaces, respectively, such that $\alpha + \beta + \delta$ always equals 1. Please note that even though several researchers have hypothesized the importance of strain energy in the metastable to stable transformation of zirconia systems, here we have assumed the

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contribution of strain energy to be negligible.^{38,39} This is because Kumar and co-workers have shown that, in the case of titania, the contribution of strain energy is relatively higher in the supported and constrained systems compared to that in the unconstrained systems.¹⁸ Such quantitative estimates of the relative difference in the critical nuclei size of these systems would be more meaningful to obtained; however, we are faced with several difficulties at this point, and this in fact becomes our

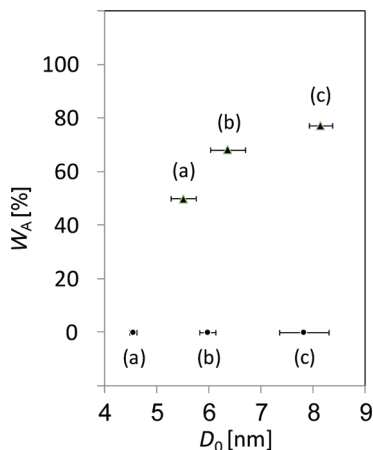


Figure 5. Fraction of anatase as a function of several initial anatase particle sizes after calcining the precalcined (●) PP and (▲) UP titania at 600 °C for 8 h with (a) an as-synthesized sample and samples precalcined at 300 °C for (b) 1 and (c) 100 h.

current research topic at the moment. A proper justification is indeed required for better correlation between the proposed theory and experimental data.

On the basis of eq 5, the critical nuclei size, r_c , for PP should be smaller than that for UP because in PP the fraction of the rutile–rutile interface is much higher than that of the air–rutile interface and the rutile–rutile interfacial energy is much lower than the air–rutile interfacial energy. From Table 2 it can be seen that PP samples indeed have a smaller rutile crystallite size compared to that of UP samples. It is also interesting that for both UP and PP there is an inverse relationship between the starting particle size and the final size of anatase (only for UP and PP that have completely transformed to rutile) and rutile crystallites. This may be due to the fact that smaller particles have a larger driving force for growth.⁴⁰ In the case of UP, as noted before, a similar inverse relationship is seen between the initial particle size and the fraction of rutile after heat treatment. For example, an average starting anatase particle size of 5.5 nm resulted in 50% rutile whereas an average starting particle size of 8 nm resulted in only 23% rutile. Conventional wisdom would point to the fact that a larger initial size should lead to a higher rutile content because of the fact that the larger initial size is relatively close to the critical nuclei size of rutile. This opposite effect can be explained by looking at the particle growth and sintering mechanism of porous systems. The driving force for particle growth can be expressed as⁴¹

$$\Delta\mu_s = \frac{3V_m\gamma}{r} \quad (6)$$

Table 2. Influence of Primary Particle Size on the Anatase-to-Rutile Phase Transformation

precalcination condition	D_0 (nm) ^a		W_A (%) ^b		D_A (nm) ^c	D_R (nm) ^d	
	PP ^e	UP ^e	PP	UP	UP ^e	PP ^e	UP ^e
as prepared	4.53 ± 0.07	5.50 ± 0.24	0.10	50.0	31.00 ± 0.66	85.51 ± 3.69	101.42 ± 11.37
300 °C, 1 h	5.96 ± 0.16	6.35 ± 0.33	0.10	68.4	29.17 ± 0.63	84.30 ± 2.87	100.88 ± 7.11
300 °C, 100 h	7.82 ± 0.47	8.14 ± 0.22	0.10	77.3	28.21 ± 1.71	78.21 ± 8.10	94.43 ± 19.61

^a Initial anatase particle size. ^b Fraction of anatase after calcination at 600 °C for 8 h. ^c Anatase crystallite size after calcination at 600 °C for 8 h. ^d Rutile crystallite size after calcination at 600 °C for 8 h. ^e Absolute error estimation from three experimental points.

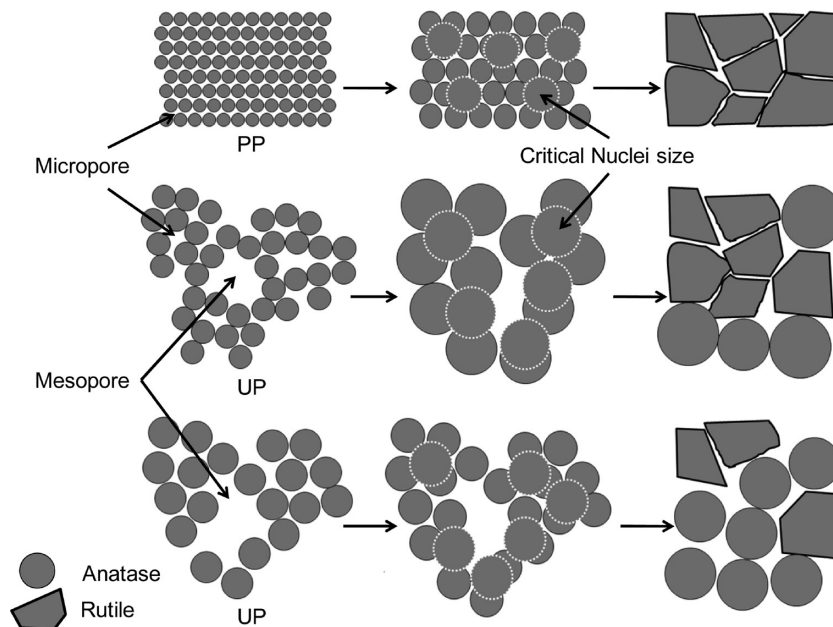


Figure 6. Schematic representation of the influence of the initial primary particle size and the packing and critical nuclei size for the anatase-to-rutile transformation of sol-peptization-gel-derived titania.

where $\Delta\mu_s$ is the change in the surface free energy when one mole of anatase particles with an average radius of r grows to a dense system without any grain boundaries. V_m and γ are the molar volume and surface energy of rutile particles, respectively. According to eq 6, smaller starting particles clearly have a higher driving force for growth. This is in line with what has been observed. In the case of UP, there is an inverse relationship between the initial size of anatase particles and the size after calcination at 600 °C (Table 2), and it is schematically represented in Figure 6. A faster growth rate leads to a higher rutile content because the probability of reaching critical nuclei size for the anatase-to-rutile phase transformation increases with decreasing initial anatase particle size. At the same time, the situation is slightly different for PP because of the higher packing density (Figure 2). In the case of well-packed systems, according to eq 5, the critical nuclei size itself will be smaller because of the presence of a higher fraction of the solid–solid interface that has a lower interfacial energy than the solid–gas (air) interface, which results in a complete anatase-to-rutile phase transforma-

tion. As a result, in the case of PP, the amount of anatase-to-rutile phase transformation is independent of the particle growth rate.

In summary, it has been shown that the initial particle size of anatase is an important parameter that influences anatase-to-rutile transformation kinetics in loosely packed nanostructures (Figure 6). The initial particle size effect was explained on the basis of the size dependence, the driving force for particle growth, and the importance of critical nuclei size in nucleation-growth-type transformations.

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Supporting Information Available: XRD, TEM, and SAED patterns of PP and UP nanostructured titania. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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