Ceramic Nanomaterials and Nanotechnology III

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Technical Resources

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This volume of Ceramic Transactions consists of papers presented at Symposium 6 on Nanostructured Materials and Nanotechnology, which was held during the 106th Annual Meeting of the American Ceramic Society (ACerS) in Indianapolis, Indiana, April 18-21, 2004. A total of twenty-nine papers are included in this volume plus a summary of a nanotechnology panel discussion. It divides into five chapters: Chapter I: Synthesis and Functionalization of Nanoparticles; Chapter II: Nanostructured Membranes, Films, Coatings, and Self-assembly; Chapter III: Processing and Characterization of Nanomaterials; Chapter IV: Nanotubes and Nanorods; and Chapter V: Environmental and Health Applications and the Future of Nanotechnology. This book is the third symposium proceedings titled "Ceramic Nanomaterials and Nanotechnology" from the unique nanotechnology symposium series during the annual meetings of the American Ceramic Society.

The symposium 6 followed three successful symposia on "Nanostructured Materials and Nanotechnology" during ACerS annual meetings in 2001, 2002, and 2003. The 2004 symposium consisted of eight sessions on ceramic nanomaterials, including Synthesis and Functionalization of Nanoparticles; Nanostructured Membranes, Films, Coatings, and Self-assembly; Dispersion and Sintering of Nanomaterials; Characterization Techniques for Nanomaterials; Nanotubes, Nanorods, Nanowires I: Carbon Nanotubes; Nanotubes, Nanorods, Nanowires II: Alternatives; Nanotechnology for the Future: Environment, Health, and National Security; and a panel discussion on nanotechnology: past, current, and future.

A total of 104 papers were presented in the symposium: 75 oral papers including 15 invited papers, and 28 poster papers, reflecting a significant increase of forty percentage from the same symposium a year ago. This well-organized and well-attended symposium was the largest symposium during the three-day conference. Authors came from seventeen countries and regions around the world, and from academia, national laboratories, industries, and government agencies, truly indicating the international impacts of this symposium and the broadening research activities of nanostructured materials and nanotechnology. Extensive collaborations between authors from different countries, different disciplines, and from academia, national laboratories, and industries have been strongly evidenced.
The symposium was sponsored by PPG Industries, Inc., and the Basic Science Division of the American Ceramic Society. The organizers sincerely thank these sponsors for their kind supports to ensure a very successful symposium. The editors would like to thank Greg Geiger at ACerS Headquarters for invaluable assistance in organizing the review process and coordinating the production of this volume of Ceramic Transactions. Finally, the editors thank all of the authors who contributed manuscripts to the proceedings or who assisted with reviewing manuscripts for this volume.

Editors
Song Wei Lu
Michael Hu
Yury Gogotsi
Synthesis and Functionalization of Nanoparticles
ABSTRACT

Liquid-feed flame spray pyrolysis (LF-FSP) involves aerosolizing an alcohol solution containing alkoxyde or carboxylate metalloorganic precursors with oxygen, igniting the aerosol to combust the alcohol fuel and precursor molecules, followed by rapid quenching at rates exceeding 500°C/sec. The resulting soot, or nanopowders typically consist of single crystal particles that are relatively unagglomerated with a composition identical to that in the original solution phase. The rapid cooling rates result in the production of nanopowders that are typically kinetic phase products. For example, LF-FSP provides access to nano δ-Al_2O_3 not α-Al_2O_3. Efforts to produce nanopowders along the Al_2O_3-TiO_2 tie line result in doping of Al^{3+} for Ti^{4+} ions inducing a phase transformation to the rutile crystal structure. LF-FSP of Y_3Al_5O_{12} composition gives what appears to be a novel phase that is not YAG but does convert very easily to the YAG phase.

INTRODUCTION

Mixed metal-oxide (MMO) materials are used in areas ranging from photonics, to electronics, to catalysts, to health applications. Their widespread utility is based on their mechanical, electronic, photonic and catalytic properties. The potential of nanosized MMO powders ranges from the mundane (e.g. transparent sunblock cosmetics) to the highly sophisticated and novel (e.g. random, incoherent lasers). Unfortunately, there are currently no simple, general ways to make diverse MMO nanopowders with controlled chemical and phase composition. Thus, it is quite difficult to develop unified composition-structure-property relationships in such materials.

At the University of Michigan (UM), we have identified a new method of forming MMO nanopowders that combines simplicity with low-cost and exceptional generality. The process, called liquid-feed flame spray pyrolysis (LF-FSP), also represents a novel form of green manufacturing that could have considerable impact on traditional ceramics processing methods. The LF-FSP process appears to offer the means to make both single-phase MMOs and, in some instances, nanocomposite (mixed phase) materials in a single synthesis step.

In LF-FSP, alcohol solutions of low-cost chemical precursors are aerosolized with O_2, thereafter the aerosol is ignited and the resulting combustion process generates soot or oxide nanopowders with the exact composition of the precursor solution (to ppm), see Figure 1. The as-produced nanoparticles are predominantly high surface area, single crystal materials, often immediately ready for use. For example, LF-FSP has been used to produce nanocomposite powders of CeO_{0.7}Zr_{0.3}O_2 solid solution, phase segregated from and dispersed on α- or α-Al_2O_3. This MMO system, produced in one step, is identical to the system used commercially in three-way auto exhaust catalysts (TWCs). However, TWC washcoats are currently manufactured using 5-7 production steps. The catalytic activities of the LF-FSP materials are identical to those of commercial materials.
One of the primary difficulties facing those who wish to explore the potential of nanosized materials, e.g. metal oxides, is availability. Although there are numerous potential applications for nanopowders in areas ranging from luminescent materials,1-9 to catalysts,10 to nanocomposites,12-14 the availability of large quantities of well-defined, high quality nanopowders is limited and costs can be high ($/g). Furthermore, there appear to be very few viable routes to large quantities of dispersible, chemically and phase pure mixed-metal oxide nanopowders. LF-FSP provides this opportunity as illustrated below where we discuss the synthesis of several examples of mixed-metal oxide nanopowders and some of their novel properties. First we briefly review methods of generating nanopowders.

Typical methods of producing nanopowders

Current methods of producing nanopowders can be broadly classified as liquid or gas phase processing. Liquid phase approaches include: sol-gel, precipitation, hydrothermal, sonochemical, shear-cavitation,9 or electrochemical processing.15-19 Gas phase approaches include:11 spray pyrolysis, evaporative metal, flame spray pyrolysis, laser pyrolysis, or CVD methods.20-29

Of these methods, spray pyrolysis,11,19 metal evaporation,12,26 and flame spray pyrolysis10,27 are the primary commercial methods of making nanopowders with the latter two offering the best control of particle size, composition and morphology. Historically, FSP is the primary commercial method of making large quantities of ultrafine powders (100-250 nm) and nanopowders (1-100 nm). Ultrafine and nanotitania, and fumed (nano) silica are produced in thousand ton/yr quantities by combusting volatile TiCl₄ or SiCl₄, in a H₂/O₂ flow. Combustion (> 1000°C) generates nanopowders as a ceramic soot, and chlorine and HCl gases as byproducts.10,27 Although these byproduct gases are easily removed; they are toxic, corrosive pollutants as are the starting metal chlorides. The resulting nanopowders (e.g. titania) are not particularly different from those produced by metal evaporation or LF-FSP of metal alkoxides.30,31
Our interest in exploring LF-FSP derives from the discovery of methods of making very inexpensive single and mixed-metal metalloorganic precursors as illustrated in reactions (1)-(4):

\[
\text{SiO}_2 + N(\text{CH}_3\text{CH}_2\text{OH})_3 \xrightarrow{200{}^\circ\text{C}/-\text{H}_2\text{O}} \text{silatrane}
\]

(1)

\[
\text{Al(OH)}_3 + N(\text{CH}_3\text{CH}_2\text{OH})_3 \xrightarrow{200{}^\circ\text{C}/\text{EG}/-\text{H}_2\text{O}} \text{alumatrane}
\]

(2)

\[
\text{Mg(OH)}_2 + 2\text{Al(OH)}_3 + 3 \text{TEA} \xrightarrow{200{}^\circ\text{C}/-\text{H}_2\text{O}} \text{x's EG}
\]

(3)

\[
\text{SiO} + 2\text{ZrO}_2 + 2\text{Al(OH)}_3 + 6\text{TEA} \xrightarrow{200{}^\circ\text{C}/-\text{H}_2\text{O}} \text{x's EG}
\]

(4)

The precursors shown in reactions (1)-(4) are molecular species; but some precursors are simple homogeneous mixtures. The mullite precursor is a homogeneous 6:2 alumatrane: silatrane EtOH solution.

The Figure 1 FSP apparatus "Smaug" was constructed in our laboratories and is a tenth generation device. It combusts EtOH aerosols containing 1-20 wt. % ceramic (as precursor) with the optimum (for viscosity reasons) being 5-15 wt % depending on the precursor. CeO\textsubscript{2}/ZrO\textsubscript{2} precursor solutions at 20 wt.% oxide can be "shot" quite easily (>100 g/h). Flame temperatures are ≤ 2000 °C based on down-stream measurements and calculations. The temperature drops rapidly (∼ 1400°C) to 400-300°C about 1 m from the flame, just beyond the main chamber (20 cm dia.).

Here we briefly describe selected materials produced by LF-FSP beginning with Table 2.

**FSP of single metal n-oxides.**

\textbf{TiO}_2. In-depth studies of nano-TiO\textsubscript{2} made by LF-FSP compare favorably with Degussa P-25 nano-TiO\textsubscript{2} and metal evaporation derived nanoTiO\textsubscript{2} (Nanophase). These nanoTiO\textsubscript{2}s have similar specific surface areas (SSAs), particle sizes and are all approximately 90% anatase, 10 % rutile.

\textbf{Al}_2\text{O}_3. LF-FSP of various precursors including alumatrane, reaction (2), give the products such as shown in Figure 2. Note that the AICl\textsubscript{3} and Al(NO\textsubscript{3})\textsubscript{3} precursors provide both nanopowders and mixtures of micron sized particles with some nanosized powders.
Table 1. Typical powders produced by LF-FSP at the University of Michigan.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Density (g/cc)</th>
<th>F (nm)</th>
<th>Surface Area (m²/g)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>--</td>
<td>60-20</td>
<td>30-80</td>
<td>(90-10 anatase-rutile)</td>
</tr>
<tr>
<td>CeO₂</td>
<td>7.047-7.104</td>
<td>30-90</td>
<td>10-15</td>
<td>single &amp; twinned crystals</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>--</td>
<td>40-20</td>
<td>50-80</td>
<td>β-Al₂O₃</td>
</tr>
<tr>
<td>CaO</td>
<td>--</td>
<td>40-20</td>
<td>50-80</td>
<td>some CaCO₃ and Ca(OH)₂</td>
</tr>
<tr>
<td>MgO</td>
<td>--</td>
<td>40-20</td>
<td>50-80</td>
<td>trace MgCO₃ and Mg(OH)₂</td>
</tr>
<tr>
<td>CeO₂/ZrO₂</td>
<td>--</td>
<td>20-40</td>
<td>30-50</td>
<td>10/90 to 90/10 cubic</td>
</tr>
<tr>
<td>MgOAl₂O₃</td>
<td>--</td>
<td>50-30</td>
<td>40-60</td>
<td>spinel, faceted single xtsls</td>
</tr>
<tr>
<td>3Al₂O₃·2SiO₂</td>
<td>2.825</td>
<td>70-80</td>
<td>40-50</td>
<td>mullite @ 1000°C</td>
</tr>
<tr>
<td>β⁺-alumina</td>
<td>Nₐ1.00 Al₆.00 Li₉.00 O₁₈.0 (a)</td>
<td>30-50</td>
<td>partially crystalline</td>
<td></td>
</tr>
<tr>
<td>Sr₂Al₅O₁₈·2SiO₂</td>
<td>--</td>
<td>50-30</td>
<td>40-60</td>
<td>SAS, amorphous as shot</td>
</tr>
</tbody>
</table>

'BET, **Estimated from surface area/mass, "XRD Debye-Scherrer calculations. and/ TEM.

Although LF-FSP flame temperatures reach nearly 2000°C, the major phase observed for all conditions whether the particles are small or large or even hollow (Figure 2b), is the d-phase. We have proposed that this is a consequence of the high water contents in the flame; however, even the Nanophase alumina powders are also d phase. An alternative explanation is that the surface curvature for nanoalumina powders imparts such a high surface energy that the phase transformation from a density of 3.5 g/cc for d to 4.0 g/cc for a is not favorable.
These alumina precursors are the basis for a number of other materials. If we "shoot" alumatrane with the titanium analog of silatrane (titanatrane) both of which are mutually soluble in EtOH, then we can explore the (TiO₂)ₓ(Al₂O₃)₁₋ₓ phase space, which we have recently done with the idea of determining what could be used to provide optimal photocatalytic activity with good-to-excellent wetting. As seen in Figure 4, we can make many different compositions very easily.

Perhaps the most important observation here is that the addition of just 15 mol % alumina forces a transformation from primarily anatase phase to rutile. This transformation appears to be driven by replacement of Ti⁴⁺ ions with Al³⁺ ions and the creation of oxygen vacancies making this material equivalent to a highly defective titania phase. The important implication is that the band gap of this material is not the same as that of rutile and may offer different photocatalytic properties.

![Figure 4. LF-FSP produced nanopowders in the (TiO₂)ₓ(Al₂O₃)₁₋ₓ phase space. Average particle sizes are 2-40 nm with surface areas of 45-60 m²/g.](image)

**Y₃Al₅O₁₂** Efforts to develop yttrium aluminum garnet nanopowders led to materials that have the correct composition but are not YAG. Thus, the nano Y₃Al₅O₁₂ powders shown in Figure 5 were produced using an yttrium propionate/aluminum acetylacetonate precursor. The powders are uniform on a micron length scale showing no large particles. At the nanometer length scale, they are also quite uniform with average particle sizes of 20 nm as shown in Figure 6.

XRD powder patterns of samples of these powders reveal an apparently new phase with the Y₃Al₅O₁₂ composition that is an hexagonal perovskite. Sets of powders with the Y₃Al₅O₁₂ composition from different precursors were heated at 10°C/min and the transformation activation energy was determined as shown in Table 2. The activation energy for this process is very low compared with the crystallization of YAG from glass and reflects the fact that the new phase is 30% denser than YAG which drives the transformation process.
Table 2. YAG starting formation temperature and $E_a$. *

<table>
<thead>
<tr>
<th>Precursor</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>YAG formation (°C)</td>
<td>1280</td>
<td>1270</td>
<td>1060</td>
<td>1050</td>
<td>960</td>
<td>1100</td>
<td>1110</td>
<td>1100</td>
<td>1075</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>210</td>
<td>208</td>
<td>210</td>
<td>280</td>
<td>86</td>
<td>106</td>
<td>166</td>
<td>100</td>
<td>96</td>
</tr>
</tbody>
</table>

*The formation starting temperature was obtained at a heating rate of 10°C/min.

Figure 5. SEM micrograph of powders made from $Y(O_2CCH_2CH_3)_3/Al(O_2C_3H_6)_3$.

Figure 6. TEM micrograph of powders made from $Y(O_2CCH_2CH_3)_3/Al(O_2C_3H_6)_3$.

As we will report at a later date, these nanopowders sinter much better than micron size YAG powders and we can achieve complete densification at 1400 °C in 6-8 h with final grain sizes of <200 nm with minimal processing. Thus, these materials offer potential for both structural applications and for transparent polycrystalline lasers.

In summary, LF-FSP provides access to a wide variety of well known materials as well as materials that are kinetic phases rather than thermodynamic phases. Consequently, LF-FSP also
offers the opportunity to develop materials with very novel properties for many different applications.

ACKNOWLEDGEMENTS.

We would like to thank AFOSR (F49620-03-1-0389) and the DSO National Laboratories of Singapore, and Hyundai-Kia Motors Co. for support of this work.

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SIZE AND MORPHOLOGY CONTROL OF CERIUM-TITANIUM OXIDE NANOPARTICLES THROUGH HYDROTHERMAL SYNTHESIS

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ABSTRACT  
Cerium-titanium oxide nanoparticles were synthesized by a hydrothermal treatment. The particle size, morphology and crystal structure were characterized by laser scattering analyzer, transmission electron microscopy, and X-ray diffractometry (XRD) analyses. The control of secondary and primary particle size as well as particle shape is investigated. The effects of titanium and cerium concentrations, amount and types of bases, reaction temperature and duration on particle size and shape are presented and discussed.

INTRODUCTION  
Ceria (CeO$_2$), either in its pure form or doped with alien cations, has attracted considerable interest because of its wide range of applications including gas sensors, electrode materials for solid oxide fuel cells, oxygen pumps, amperometric oxygen monitors, catalytic supports for automobile exhaust system, and abrasives for chemical mechanical planarizations.\textsuperscript{1}

Ceria fine particles can be produced by thermal decomposition,\textsuperscript{2} flash combustion,\textsuperscript{3} sol-gel,\textsuperscript{4} precipitation\textsuperscript{5} and hydrothermal methods.\textsuperscript{6} In the case of sol-gel and precipitation, calcinations of gels or precursors at relatively high temperature are usually needed to produce cerium oxide, and additional treatment such as grinding and classification is necessary to obtain ultra-fine particles with narrow size distribution.\textsuperscript{7}

Hydrothermal synthesis, the method of precipitation from solution under hydrothermal conditions, is attractive for the direct synthesis of crystalline ceramic particles including ceria (doped or undoped) at relatively low temperatures, providing particles with excellent homogeneity and particle uniformity.\textsuperscript{8}

For its various applications, ceria particles with different characteristics are required. It is known that the unique chemical and physical properties of nanoparticles are determined not only by their large portion of surface atoms, but also by the crystalllographic structures of the
particle. The former is determined by the size of the particles, and the latter relies on the particle shape. In present work, the size and shape control for cerium-titanium composite particles (titanium-doped ceria particles) synthesized through hydrothermal treatment is investigated.

EXPERIMENTAL

Particle Synthesis

In a typical preparation, the required amount of cerium (IV) ammonium nitrate \((\text{NH}_4)_2[\text{Ce(NO}_3]_6\) (GFS Chemicals, 98.5%) was dissolved in water. The desired amount of titanium isopropoxide (Gelest #AKT872, 99%) was mixed with the above cerium (IV) solution under continuous stirring. The mixed cerium-titanium solution and \(\text{NH}_4\text{OH}\) (28%) were then added to another beaker. The resulting gelatinous pale yellow or brown suspension was heated at \(>150^\circ\text{C}\) for a few hours in a sealed stainless steel vessel. Thereafter, the vessel was taken out and cooled to room temperature. The reaction product was decanted, washed, filtered and pH adjusted for further measurements and applications.

Particle Characterization

The secondary particle size (aggregate size) was analyzed by laser scattering particle size distribution analyzer (Horiba LA-910). The slurry sample was diluted with deionized water and suspended with Darvan 821A (ammonium polyacrylate, R.T.Vanderbilt Company, 40%) and sonicated for 5 minutes before analysis. The volume-based distribution of particle size was demonstrated by \(D_{50}, D_{10}\) and \(D_{90}\) (diameter on 50%, 10%, and 90%).

The primary particle size and morphology were investigated by high-resolution transmission electron microscopy (HRTEM) using a JEOL 2010, and XRD (Philips PW 3020 Diffratometer) analysis. A holey Cu grid was dipped into the slurry just below the surface to collect some particles, and then the grid was allowed to dry before TEM analysis. Powder X-ray analysis was carried out using Cu-K\(\alpha\) radiation \((\lambda = 1.54056 \text{ Å})\) by backfilling samples into clean holders and collecting the diffractogram over a period from \(2\theta = 10\) to 70 degrees with 0.02 degrees as a step size. The crystallite size was calculated from line broadening of the 220 diffraction peak according to the Scherrer equation, and compared with primary particle size determined from HRTEM measurement (average among 10 to 100 particles). The two results agree well, and the crystal size from XRD was taken as the primary particle size in this work.

The crystallographic and surface structures of ceria particles were determined by HRTEM, performed using JEOL 4000EX transmission electron microscope operated at 400 KV, which is ideally suited for high-resolution structural imaging at a point-to-point Schertz image resolution better than 0.18nm.

RESULTS AND DISCUSSIONS

In a basic environment, cerium and titanium cations in their starting salts would hydrolyze to form hydroxide or hydrous oxide nuclei, which would convert to a composite oxide via a dissolution-reprecipitation mechanism\(^{10,11}\) of crystal growth during hydrothermal treatment. The change of synthesis conditions would affect this nuclei formation and growth mechanism, and as a result, the final particle properties would be changed.
Independent Control of Primary and Secondary Particle Size

A typical nanoparticle generally consists of several primary particles as shown in Figure 1. These primary particles tend to agglomerate into the "secondary" particle, due to their very high surface-to-volume ratio. The strength and size of agglomerates (secondary particles) depend on the surface properties of the nanocrystalline particles, and these properties are sensitively dependent on the powder synthesis conditions. A typical example of titania-doped ceria particle in our study is shown in Figure 2, which demonstrates the weak or loose aggregate of primary particles. In the following discussion, we show how the primary particle and secondary particle sizes of nano-sized cerium oxide can be independently controlled through changes in the starting cation concentrations, base amount (medium pH), reaction duration, and reaction temperature.

Starting cation (major metal and dopant metal ions) concentration effect: Cerium concentration has a dominant effect on the secondary particle size, as shown in Figure 3b, and a minor effect on the growth of the primary particle size (crystallite size), as shown in Figure 3a. The primary particle size slightly decreased and then increased with increasing cerium (IV) concentration. In concentrated cerium solutions, because the average diffusion distance for the diffusing solute was short and the concentration gradient was steep, more and more diffusing material passed per unit time through a unit area, favoring more and more crystal growth of ceria particles. When starting with highly concentrated solutions, a large number of particles are formed within the same liquid volume, the mean path of particle collisions is shortened and the high ionic strength also reduces the thickness of the particle double layers, all of which favor the agglomeration of particles. This is why we observed the dominant effects of secondary particle size increase with an increase in cerium concentration as shown in Figure 3b.
Figure 3. Computer Interpreted Data: The effect of cation (Ce⁴⁺ and Ti⁴⁺) concentration on primary (a) and secondary (b) particle size of titanium-doped ceria particle. X and Y axes are the concentration values (mole/l), and Z axis is the normalized value of particle size.

Figure 3 also clearly shows that the doping of Ti into the cerium oxide lattice has a dominant effect on the growth of primary particle size, while its effects on the growth of secondary particle size are minimal. With the incorporation of titanium (IV) into the ceria crystal lattice, the mismatch of cation size (ionic radius) and the possible cation valence (Ce⁴⁺ ↔ Ce³⁺) between dopant Ti⁴⁺ and host Ce⁴⁺ ion, together with the lattice strain and electrostatic interaction by a space charge mechanism, is expected, resulting in the increase of crystal size with more and more Ti⁴⁺ adding into cerium solution, as shown in Figure 3a. It is also interesting to notice that as the primary particle size is increased dramatically with increasing Ti content in the particles, the secondary particle size gradually decreases. This is probably due to the fact that the growth of the primary particle size is so rapid that the cerium ion in the solution is not enough to feed the crystal growth, and the agglomerated smaller primary particles are also consumed in the growth of the large primary particles.

The above discussion shows clearly that the main control on secondary particle size growth is the host cerium concentration, while the key control for primary particle size is through titanium dopant concentration. Understanding this fundamental growth mechanism enables us to independently control primary and secondary particle sizes.

**Effect of base amount (medium pH effect):** It is well known that the medium pH has a large effect on particle size growth for many oxides. To study this effect, different amounts of ammonia (in terms of 6x to 12x of the mole amount of cerium ions) were utilized in the synthesis of ceria oxide particles. The excess amounts of ammonium hydroxide were added into the solution to form yellow to brownish geletinous slurries. The effects of the amount of ammonia on primary particle size and secondary particle size are shown in Figure 4.
The influence of ammonia concentration on particle size was complicated, and the explanation for the decrease and then increase in crystallite size upon the addition of excessive base has not been clearly established yet. It was suggested that the initial increase in the amount of ammonia (from 6× to 10×) results in a higher concentration of hydroxides. This means that more nuclei are formed under higher pH conditions with the same starting cerium concentration. More nuclei compete for the same amount of cerium supply in the solution, resulting in the low concentration solute in the solution, and thus the rate of crystal growth must be low due to the insufficient supply of the solute by diffusion. Therefore, the final primary particle size decreased. As more ammonia is added (from 10× to 12×), the additional amount of ammonia does not contribute to more hydroxide in the solution due to the limited basicity of ammonia. On the other hand, the large amount of ammonia may enhance the formation of cerium-ammonia complexes on the surface, which retards the dissolution of the primary crystals. If the primary crystal dissolution is hindered while the dissolution-reprecipitation equilibrium established for the growth of the primary crystals still continues, it will result in an increase in primary particle size as the ammonia amount changes from 10× to 12×, as shown in Figure 4a.

An increase in the amount of ammonia decreases secondary particle size, as shown in Figure 4b. This is probably due to the fact that the insufficient supply of cerium in the solution as more ammonia is added also promotes the consumption of the agglomerated small primary crystals to sustain other primary crystallite growth (an effective de-agglomeration). The coating of cerium particles with ammonia through cerium-ammonia complex formation discussed previously also does not favor secondary particle size growth. Therefore, the addition of different amounts of ammonia provides us with another effective means of adjusting secondary and primary particle sizes.

Hydrothermal temperature and duration effect: It is obvious in Figure 5a that the primary particle size increases proportionately with an increase in hydrothermal treatment temperature (200°C to 300°C). This is probably due to the fact that high temperature provides a high driving force and energy for the growth of the crystals (hydrothermal conversion of cerium hydroxide to ceria is an endothermic process). It is also very interesting to see from Figure 5b...
that the secondary particle size decreases proportionately with temperature. With the limited amount of cerium in the reaction system, the growth of some of the primary particles has to be at the expenses of some other smaller primary crystals (smaller particles have higher solubility). This process effectively consumes part of the agglomerated primary particles, resulting in smaller secondary particle sizes.

Figure 5. Computer Interpreted Data: The hydrothermal temperature and duration effect on primary (a) and secondary (b) particle size of titanium-doped ceria particle. X and Y axes are time (hr) and temperature (°C) values, Z axis is the normalized value of particle size.

The reaction duration effects on particle size (both primary and secondary) are much less pronounced in comparison with the temperature effects as shown in Figure 5. The increases in reaction time always increase the primary particle size due to the time needed to build the crystals and the fact that the large crystals built do not re-dissolve as long as the reaction conditions do not change. The secondary particle size shows a more complicated behavior, which needs more understanding in terms of the initial primary and secondary particle size increase and the longer duration decrease in secondary particle size and how this feeds primary size growth.

The temperature of reaction offers us yet another useful control in manipulating primary and secondary particle size.

Particle Shape Control

It is known that nanoparticles usually have specific shape, especially when they are small, because a single crystal nanoparticle has to be enclosed by crystallographic facets that have lower energy. Surface energies associated with different crystallographic planes are usually unique, for face centered cubic structures. For a spherical single-crystalline particle, its surface must contain high-index crystallography planes, which could possibly result in a higher surface energy. Facets formation on the particle surface serves to increase the portion of the low-index planes to minimize the energy of the system. Therefore, small particles of less than 20nm are usually polyhedral.9
Taking $R$ as the ratio of growth rate in the $\{100\}$ to that of $\{111\}$, Wang et al. had reported\(^9\) that the longest direction in the octahedron ($R=1.73$) is the $\{100\}$ diagonal, the longest direction in the cube ($R=0.58$) is the $\{111\}$ diagonal, and the longest direction in the cubo-octahedron ($R=0.87$) is the $\{110\}$ direction. The particles with $0.87<R<1.73$ have the $\{100\}$ and $\{111\}$ facets, which are named “truncated octahedral”. An octahedron has eight $\{111\}$ facets (Figure 6-a and b), while the truncated octahedron has eight $\{111\}$ and six $\{100\}$ facets, and the $\{100\}$ planes are created by cutting the corners of the octahedron (Figure 6-c, d, e). A truncated octahedron looks like a spherical particle when the particle size is small as shown in f and g of Figure 6.
In our nanoparticle synthesis, we can produce particles with different shapes by utilizing different bases (urea, ammonia hydroxide and potassium hydroxide) for the hydrolysis of cerium and titanium salts, as shown in Figure 7. It should be noted that urea produces ammonium and cyanate ions ($\text{H}_2\text{N-CO-NH}_2 \leftrightarrow \text{NH}_4^+ + \text{OCN}^-$) when heated to certain temperature. In neutral and basic solutions, carbonate ions and ammonia are formed ($\text{OCN}^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_3^{2-}$). Among the three bases, with the same mole amount of base addition, the case with urea has the lowest concentration of hydroxide ions and therefore the fewest cerium nuclei before hydrothermal treatment, and potassium hydroxide provides the highest hydroxide concentration due to its complete dissociation of hydroxyl group and the most cerium nuclei. The ammonia system is in the middle.

Under the same hydrothermal conditions, the nuclei in a urea reaction system would have the most complete crystal growth, resulting in the formation of the biggest octahedral of any of our reaction systems due to the $\{111\}$ surface giving the system its lowest energy, as shown in Figures 6a, 6b and 7c. The high concentration of hydroxides in the potassium system favors higher energy surface $\{100\}$ formation, and the low concentration of cerium due to the high occurrence of cerium nuclei formation also limits the growth of $\{111\}$ facets.\textsuperscript{16} The end result is the formation of a truncated octahedral, as evidenced by the formation of the small round particles (Figures 6f, 6g and 7a). The ammonia system can promote the formation of high energy $\{100\}$ facets and also has a sufficient cerium concentration to grow $\{111\}$ facets, resulting in elongated faceted particles as shown in Figures 6c, 6d, 6e and 7b.

CONCLUSIONS

Understanding the particle formation mechanism and properly controlling the experimental conditions allow production of monodispersed CeO$_2$-TiO$_2$ nanoparticles through hydrothermal conditions. The primary and secondary particle sizes of these particles can be controlled independently. Precise control is achieved through manipulating the concentrations of starting cerium ions and dopant titanium ions, the amount of base used, the reaction temperature, and the reaction duration. The particle shape can be controlled by using different types of bases such as urea, ammonia, and potassium hydroxide, preferentially promoting low energy surface growth and formation of high-energy facets.