Review

Synthesis of functional nanocrystallites through reactive thermal plasma processing

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Abstract

A method of synthesizing functional nanostructured powders through reactive thermal plasma processing has been developed. The synthesis of nanosized titanium oxide powders was performed by the oxidation of solid and liquid precursors. Quench gases, either injected from the shoulder of the reactor or injected counter to the plasma plume from the bottom of the reactor, were used to vary the quench rate, and therefore the particle size, of the resultant powders. The experimental results are well supported by numerical analysis on the effects of the quench gas on the flow pattern and temperature field of the thermal plasma as well as on the trajectory and temperature history of the particles. The plasma-synthesized TiO₂ nanoparticles showed phase preferences different from those synthesized by conventional wet-chemical processes. Nanosized particles of high crystallinity and nonequilibrium chemical composition were formed in one step via reactive thermal plasma processing.

Keywords: Nanosized particles; Thermal plasma processing; Nonequilibrium chemical composition; Particle size control; Phase formation; Reactor design

1. Introduction

Nanoparticles offer one possibility for the breakthrough needed to advance the conversion of substances into useful materials [1]. When considering the utilization of nanoparticles, their advantages may be described from two viewpoints. One is the so-called “nanosize effect” expected in physical properties such as luminescence or chemical properties such as catalytic activity. The other is the resource effect, which reduces the volume of materials required for functionalization. In both cases, the fundamental aim of nanoparticle production is to homogeneously produce highly functional substances in large volumes, and, if this could be achieved, the realization of nanoparticle technologies would be possible.

The present situation, however, is that the properties of nanoparticles have not yet been fully applied. To apply...
the properties of nanoparticles effectively, it will be important to control the crystallinity and surface properties as well as the homogeneity of crystallite size and chemical composition.

Powder synthesis should be used to precisely control the particle size, morphology and chemical composition. A monodispersed powder is defined as a powder with a standard deviation of particle size of below 10%. Conventionally synthesized nanopowders, however, generally do not satisfy this requirement. The morphology and chemical composition of particles are closely related to particles assembling and their functionalization. The control of surface properties is essential for the application of nanoparticles in functional ordered arrays and dispersed structures.

The nanoparticle synthesis of ceramic materials has conventionally been achieved by solution processes. Taking the example of luminescence properties, major factors that have hindered the functionalization of solution-synthesized oxide nanoparticles have included low crystallinity, quenching by surface hydroxyl groups and incomplete composition control (doping concentration, surface segregation). Moreover, the existence of surface hydroxyls is known to have a big impact on the dispersion of nanoparticles in a solvent.

The Plasma Processing Group of the Nano Ceramics Center, NIMS, has addressed itself to the synthesis of nanocrystalline powders by effectively utilizing thermal plasma with high temperatures exceeding 10,000 K. In this review paper, the authors will first describe thermal plasma processing and its characteristics, and then give its advantages in nanoparticle synthesis. Then, our research achievements based on our aim of finding a scenario of utilizing the highly functional nanoparticles synthesized using plasma will be presented.

2. Synthesis of ceramic nanoparticles in reactive thermal plasmas

Thermal plasmas possess many advantages and provide unique reaction fields for material processing. The improved controllability of the reaction fields, in which chemical reactions produce materials, should lead to the synthesis of unique materials with respect to morphology, crystal structure and chemical composition [2–8]. Arc discharge, which is often called as a thermal plasma, has proven to be a useful tool in the synthesis and surface modification of a wide range of metals and inorganic materials. Its advantages as a reaction field are as follows. (1) Thermal plasmas have high temperatures (up to 10,000 K). Because the plasmas are generated at relatively high pressures (close to atmospheric pressure), they have high densities and are considered to be at equilibrium (local thermal equilibrium). That is, the temperatures of heavy particles (such as atoms, molecules and ions) are almost equal to those of light species (electrons); (2) high concentrations of chemically reactive radicals enhance the reactivity of thermal plasmas; (3) superfine quenching (<10 K/s) takes place in the plasma tail flame region.

Thermal plasmas are mainly generated in DC arc torches and RF induction torches. DC arc discharges with a high energy density have been widely used for various industrial applications, such as plasma spraying and plasma metalurgy [2], as well as for powder synthesis [9]. Compared with DC arc discharge, RF induction plasma has a number of advantages. The plasma is inductively heated by an RF electrical power over 10 kW and a frequency of MHz order. The diameter of the plasma is 30–40 mm; thus, the plasma volume is relatively large. The axial plasma velocity is as low as 10–30 m/s and the residence time in the high-temperature plasma flame is as long as 10–20 ms, which is sufficiently long for chemical reactions to proceed. The generation of RF induction plasma does not use electrodes, and any type of gas can be used to generate the plasma, regardless of its oxidative, reductive or reactive properties. The above-mentioned characteristics of thermal plasma provide unique reaction fields for material processing.

A representative industrial use of thermal plasma processing is the spheroidization of materials with high melting temperatures and large particle sizes (such as 50–100 μm) (Fig. 1) [10]. For example, 30 kg of refractory tungsten metal particles can be treated per hour, which corresponds to 1 ton per week [11]. Because thermal plasma processing has its inherent characteristics, that is, processing at an industrially acceptable production rate, the results of ongoing studies on the nanostructure control of materials using thermal plasma technology are expected to be realized soon for practical use.

Nanosized particles are formed by a process of rapid quenching and condensation after precursors are added to the thermal plasma and are instantaneously evaporated. The rapid temperature decrease in the tail flame gives rise to supersaturation in the vapor phase, and then nucleation...
takes place. In the same way, rapid cooling suppresses grain growth, and therefore nanoparticles below 100 nm in size can be produced without difficulty. Advanced technologies should be pursued to control the plasma reaction fields to yield (a) high production rates, (b) a reduction of particle size and a narrowing of size distribution and (c) high crystallinity and phase control. Practical applications of nanosized particles will be possible once such technologies have been developed.

Nanoparticle production utilizing the advantages of thermal plasmas, i.e., a high-temperature heat source with an extremely large enthalpy, started with the use of solid-state precursors. Relatively coarse particles were introduced into thermal plasmas to synthesize nanosized particles through evaporation and subsequent coagulation. In this production method, problems arise from the residual coarse particles. When precursor powders are injected into a thermal plasma in which temperature and flow distributions exist both radially and axially, some of the precursor particles are not evaporated completely. The nonevaporated part, although small, necessitates an additional postseparation process [12,13].

To solve this problem and to produce uniform nanosized particles, liquid precursors have been used [14]. When a mist with a droplet size in the order of 10 \( \mu \)m is fed into a plasma having a high temperature exceeding 10,000 K, the mist vaporizes instantaneously, enabling the mass production of nanoparticles. Oxides with the prescribed cation ratio of the liquid precursor itself can be synthesized by this technique, and it is also possible to control the chemical composition, which is linked to the appearance of functions. A nonequilibrium composition and nonequilibrium structure have been observed in nanoparticles as a result of rapid cooling at the plasma tail flame, which are extremely interesting phenomena from a scientific viewpoint.

3. Size control of nanoparticles in thermal plasma processing

The effects of processing parameters are investigated in the synthesis of TiO\(_2\) nanoparticles via Ar/O\(_2\) RF thermal plasma oxidation of liquid precursor mists.

The nanoscale size control of particles is crucial to the control of their functions, in view of the quantum-size effects on catalytic, electric, magnetic and optical properties. Also, narrowing the size distribution should contribute to the extension of the application area. The easiest and most effective method of fabricating uniform nanosized particles is to allow chemical reactions to proceed under dilute conditions. In contrast, practical process control should be performed under high precursor loading conditions.

Nucleation from the gas phase and the subsequent grain growth take place in the plasma tail. Therefore, the size should be controlled by modifying the temperature and flow distribution in the downstream of the plasma. We have demonstrated the particle-size-controlled synthesis of well-dispersed TiO\(_2\) nanopowders via Ar/O\(_2\) thermal plasma oxidation of a liquid precursor mist, during which we manipulated the cooling rate by injecting quench gases (Ar, He) [15]. In this case, the TiO\(_2\) nanoparticles were synthesized via Ar/O\(_2\) thermal plasma oxidation of atomized liquid precursors containing titanium tetrabutoxide (TTBO, as the titanium source) and diethanolamine (a chelate preventing the hydrolysis of TTBO). RF power of 25 kW at a frequency of 2 MHz was introduced to generate the plasma at a pressure of 53.3 kPa. The precursor was atomized into a mist at the tip of the atomization probe by Ar carrier gas flowing through the probe.

Quench gas was injected in two different ways: transverse injection (Fig. 2(a)) and counterinjection (Fig. 2(b)). Fig. 3 shows a comparison of the morphologies of the TiO\(_2\) powders synthesized with and without the injection of Ar
quench gas. X-ray diffraction analysis showed that the synthesized powders consisted of rutile and anatase phases of TiO$_2$. The majority of particles assume spherical shapes, with sizes ranging from 5–10 to about 200 nm. The plasma-generated particles show weak agglomeration, which is in sharp contrast to those synthesized via most wet-chemical techniques.

The overall morphology of the powder does not alter significantly upon injecting 100 l/min of Ar in the transverse mode (Fig. 3(b)), but the powder becomes appreciably finer by injecting the same amount of Ar in the counterflow mode (Fig. 3(c)), revealing the significance of the quenching method in determining powder properties. The size distributions of the powders were evaluated by the analysis of SEM images. It was found that the powders synthesized without quench gas and with an Ar transverse flow have similar $d_{50}$ values of ~55 and 53 nm, respectively, while that synthesized with an Ar counterflow has a considerably smaller $d_{50}$ of ~35 nm. In addition, the size distribution of the powder becomes substantially narrower upon applying the counterflow Ar quench gas. The standard deviation, $\sigma$, for the powder synthesized without quench gas was evaluated to be 22 nm. The Ar transverse flow resulted in an increase in $\sigma$ to 30 nm, while the Ar counterflow decreased the value of $\sigma$ to 12 nm.

Modeling was performed to obtain a better understanding of the effects of quench gases and to optimize the process parameters and reactor design [15]. The plasma flow and temperature fields were simulated using a two-dimensional turbulence fluid model. Since the particles are synthesized from the vapor phase of the precursors, their trajectories should follow the streamlines of the fluid due to their small masses. As a simplified approach, we traced the motion of a test particle with negligible mass and infinite melting point in the plasma flow. Fig. 4 shows the calculated streamlines and temperature fields in the reactor. The dots in Fig. 4 indicate the predicted trajectories of a test particle released at the tip of the central probe. Comparing Figs. 4(a) and (b), we find that the transverse injection of Ar does not significantly alter the temperature fields of the plasma and the trajectories of the test particle. When Ar is injected counter to the plasma plume, on the other hand, the temperature field and also the trajectories of the particle are profoundly affected (Fig. 4(c)). The greatly decreased size of the plasma plume results in a shorter duration of the particle in the high-temperature zone, and hence favors the formation of finer particles. The above results of numerical analysis agree well with the experimental data given in Fig. 3.

4. Synthesis of titanium oxide nanoparticles: phase selection and formation of nonequilibrium chemical composition

TiO$_2$, which has often been used as a white pigment, exhibits interesting properties, such as high transparency in the visible wavelength region, a high refractive index, and remarkable chemical and thermal stability, allowing its new application in photocatalysis, solar cells, semiconducting gas sensors and biosensors, and as building blocks for photonic crystals. For its use as a photocatalyst, doping

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Fig. 3. SEM images showing morphologies of the TiO$_2$ powders synthesized (a) without the use of quench gas, (b) with a transverse swirl-flow injection of 100 l/min of Ar and (c) with a counterflow injection of 100 l/min of Ar.
TiO₂ with nitrogen and transition-metal ions has been shown to be an effective method of enhancing the photocatalytic activity under visible light irradiation, which extends its application to indoor use. Recently, transition-metal-doped TiO₂ has been extensively studied for its potential application as a ferromagnetic semiconductor, since room-temperature ferromagnetic properties have been reported in Co-doped TiO₂ thin films [16].

In high-temperature thermal plasma, highly crystalline nanosized particles modified by doping are formed by one-step processing, without further heat treatment. The present authors have reported the synthesis of TiO₂ particles through the plasma oxidation of TiC [12,13] and TiN [17] powder precursors. In the powder oxidation method, a high degree of supersaturation is attained in the vapor phase compared with vapor-phase precursor processing. Then, TiO₂ particles of micron–submicron–nanosize were formed depending on the degree of supersaturation in the vapor phase [12,13,18]. TiO₂ is known to have two common polymorphs: anatase and rutile. Interestingly, thermodynamically metastable anatase predominated the undoped TiO₂ nanopowders, which can be explained from a kinetic point of view based on classical homogeneous nucleation theory [18,19], while decreasing the oxygen partial pressure in the vapor phase produced pure rutile nanoparticles [20].

Also, liquid mixtures in which some metal elements exist as ions in aqueous solutions or as constituent atoms of metallorganic compounds have been used as precursors. The use of liquid precursors enables uniform nanoparticles to be formed and has the advantage of a high production rate. Precise control of the chemical composition also allows the formation of particles with nonequilibrium doping, in which the doping quantity is greater than the solubility limit under an equilibrium condition.

TiO₂ nanoparticles have been synthesized via Ar/O₂ thermal plasma oxidation of atomized liquid precursors. In the case of iron doping, mixtures of TTBO and ferrocene dissolved in ethanol were used as precursors [19]. The liquid precursor used for Eu doping was made by the following procedure [20]. Diethanolamine was added to TTBO to stabilize it against hydrolysis. Separately, europium nitrate and citric acid were dissolved in water, and the pH of the solution was adjusted to 9.0 using ammonia solution. Mixing the above two solutions yielded a stable clear solution that could be used as a liquid precursor. Also, the stabilization of alkoxides against water enables the use of a simple procedure for the fabrication of TiO₂ nanoparticles in ambient air [21], while a watersensitive alkoxide requires handling in a glove box filled with Ar gas [22].

In iron-doped TiO₂ nanoparticles, no phases apart from anatase and rutile TiO₂ were identified for a wide range of iron-to-titanium atomic ratios (R_{Fe/Ti}) ranging from 0 to 0.2, although the solubility of iron in TiO₂ was reported to be approximately 5 at% in conventional wet-chemical processes. Upon iron doping, the formation of rutile was strongly promoted, because rutile is more tolerant than anatase to defects such as oxygen vacancies resulting from the substitution of Fe³⁺ for Ti⁴⁺ in TiO₂. The concentration of oxygen vacancies reached its maximum at R_{Fe/Ti} = 2%, above which the excess oxygen vacancies tended to concentrate. As a result of this clustering, an extended defect-like crystallographic shear structure developed (Fig. 5) [19]. The highly iron-doped TiO₂ nanocrystals showed paramagnetic properties. Fe³⁺ substitutes for Ti⁴⁺ and is uniformly distributed in the TiO₂ lattice [23]. Photocatalytic activity appeared under both UV and visible-light irradiation, and the activity depended on the iron dopant concentration [24].

Fig. 4. Streamlines and temperature distribution for (a) no quench gas, (b) transverse swirl-flow injection of Ar at 100 slpm and (c) counterflow injection of Ar at 100 slpm.
The amount of Eu$^{3+}$ that can be doped into the TiO$_2$ lattice was limited to 0.5 at%, above which Eu$_2$Ti$_2$O$_7$ pyrochlore was formed. Such a phenomenon is conceivable from the large size discrepancy between Ti$^{4+}$ (0.0605 nm for 6-fold coordination) and Eu$^{3+}$ (0.0947 nm for 6-fold coordination) ions. Fig. 6 shows typical emission spectra of TiO$_2$:Eu$^{3+}$ nanoparticles as well as those of pure Eu$_2$O$_3$ and Eu$_2$Ti$_2$O$_7$ under 325 nm He–Cd laser excitation [25]. The $^5D_0$–$^7F_j$ transitions give a bright red color. The Eu$^{3+}$-doped samples exhibited clearly different emissions from those of Eu$_2$O$_3$ and Eu$_2$Ti$_2$O$_7$ in terms of peak positions and peak shapes, implying different local environments. Efficient nonradiative energy transfer from the TiO$_2$ host to Eu$^{3+}$ ions, which has seldom been reported in nanoparticles or thin films of the same system derived by wet-chemical processes, was confirmed by combined studies of excitation, UV–vis absorption, and photoluminescence spectroscopy.

5. Summary

When aiming at the application of highly functional nanoparticles, it is considered necessary to structure nanoparticles in the form of (1) dispersoids, (2) fillers and (3) patterns. For example, in the case of red, green and blue fluorescent particles used in plasma displays, fluorescent particles of several micrometers in diameter produced via a solid-phase method by comminution are currently used. However, when using even smaller fluorescent nanoparticles of several tens of nanometers with excellent dispersion, the resolution markedly improves and light scattering decreases, and as a result, high energy efficiency can be expected. Similarly, the absorption properties of GHz and electromagnetic wave absorbers used in mobile devices are significantly improved with the use of magnetic nanoparticles completely dispersed in plastic matrices.

Consequently, whether using the liquid phase or the vapor method for synthesis, the most important tasks at present are to improve the crystallinity of the nanoparticles, create additional functions through composition control, prevent aggregation through surface property control and prepare complete dispersoids. In situ dispersion is expected to become a key word, regardless of the synthesis method used.

In thermal plasma processing, nanoparticles are formed through coagulation from the vapor phase. The thermal plasma method, although similar to the spray pyrolysis method and the flame spray method, can produce highly crystalline nanoparticles with little surface residue, since the synthesis temperature is far higher. Because high crystallinity is related to functionalization and the surface control is indispensable to dispersion, thermal plasma
processing is expected to make a significant contribution to nanoparticle applications. Also, the SEM images in Fig. 3 show that the plasma-synthesized nanoparticles are spherical and hardly agglomerated. We are now conducting research into the fabrication of functional structures composed of well-dispersed nanoparticles.

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