

Controlled formation of nanoparticles utilizing laser irradiation in a flame and their characteristics

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Controlled synthesis of nanoparticles has been carried out using laser beam irradiation on aggregates forming in a flame. This coalescence enhanced method transforms titania aggregates into much smaller unagglomerate spherical anatase nanoparticles by reducing the characteristic time of coalescence of nanoparticles. These transformed nanoparticles exhibit not only better thermal stability, but also unusually small grain growth during a simple pressureless sintering, which ultimately lead to a full dense bulk ceramic with 60 nm grains. Such small grain size in full dense ceramics has not been achieved before without employing special sintering techniques. This would be attributed not only to the successful control of size and morphology of nanoparticles, but also to the synthesis of oxygen vacancy free particles, which was confirmed from Raman spectroscopy.

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Nanocrystalline materials have attracted much interest in recent years due to their unusual properties and excellent sinterability compared to conventional coarse-grained materials.^{1,2} However, the prospects for practical production of nanocrystalline materials have been seriously hampered by difficulties in controlling the rapid grain growth of nanoparticles during a sintering process which is ultimately needed to produce bulk nanocrystalline materials^{3,4} as well as synthesizing nanoparticles with controlled size, morphology, and phase at high concentrations.^{5,6} The rapid grain growth on the final stage sintering has been considered as almost inevitable, therefore, many researchers resort to high pressure consolidation at elevated temperatures,^{3,7,8} which has limitations in practical applications. Since nonagglomerated and smallest possible nanocrystals are usually needed to satisfy a necessary condition suppressing rapid grain growth,⁹ the controlled synthesis of nanoparticles should be very important. Internal defects such as oxygen vacancy are known to accelerate the rate of grain growth,¹⁰ therefore, synthesizing defect-free pure nanocrystals should be also important. Gas phase methods generally produce purer nanoparticles than liquid based processes since even the purest water contains traces of minerals.¹¹ Meanwhile, the most prominent problem of gas phase methods is poor controllability in growth of nanoparticles especially when particles are generated at high concentrations which are needed for practical applications.¹² If a vacuum based gas condensation method is utilized, the control of size and morphology would be relatively easy, however, concentrations of nanoparticles become too low.

Here, we report that the coalescence enhanced method using laser beam irradiation on small aggregates forming in a flame transforms titania aggregates into much smaller unagglomerate spherical anatase nanoparticles by reducing the characteristic time of coalescence of nanoparticles. These transformed nanoparticles exhibit not only better thermal sta-

bility than the original ones without laser irradiation, but also unusually small grain growth during a simple pressureless sintering, which ultimately lead to a full dense bulk rutile (density > 98% of theoretical value) with 60 nm grains. Such small grain size in full dense ceramics has not been achieved so far without employing special sintering techniques such as high pressure consolidation. The possible mechanisms which indicate how such a small grain size in a full dense ceramic has been realized in a simple pressureless sintering will also be discussed.

The morphology and size of particles are determined by the competition between the collision and coalescence of particles.^{12,13} The formation of aggregates is due to the faster collision of particles than coalescence. Recently, we investigated that CO₂ laser irradiation during the flame synthesis of amorphous silica particles could affect the growth of silica differently depending on the irradiation location.¹⁴ The present method relies on controlling the characteristic time for coalescence of nanoparticles by irradiation of laser beam on the early stage aggregates forming in a flame. The coalescence characteristic time decreases exponentially with particle temperature ($\propto \exp(E/RT_p)$, T_p : particle temperature, R : gas constant, and E : activation energy for coalescence)¹⁵ while the collision characteristic time^{12,16} decays according to $T_p^{-1/2}$. Therefore, the coalescence can be controlled nearly independent of Brownian collision by heating aggregates rapidly. As shown in Fig. 1, early stage aggregates forming in a flame are irradiated by a high power CW CO₂ laser beam ($\lambda = 10.6 \mu\text{m}$) to rapidly coalesce and become spherical particles. Since spherical particles have much smaller collision cross sections than volume equivalent aggregates^{12,16} much slower growth can be achieved. Therefore, much smaller, at the same time, spherical nanoparticles can be produced. Transmission electron microscopy (TEM) image analysis with localized thermophoretic sampling¹⁷ has been utilized for the estimation of the changes of size and morphology of titania nanoparticles generated in an oxy-hydrogen diffusion flame.¹⁸ Particles in a flame have been captured using a water-cooled cylinder at different flame

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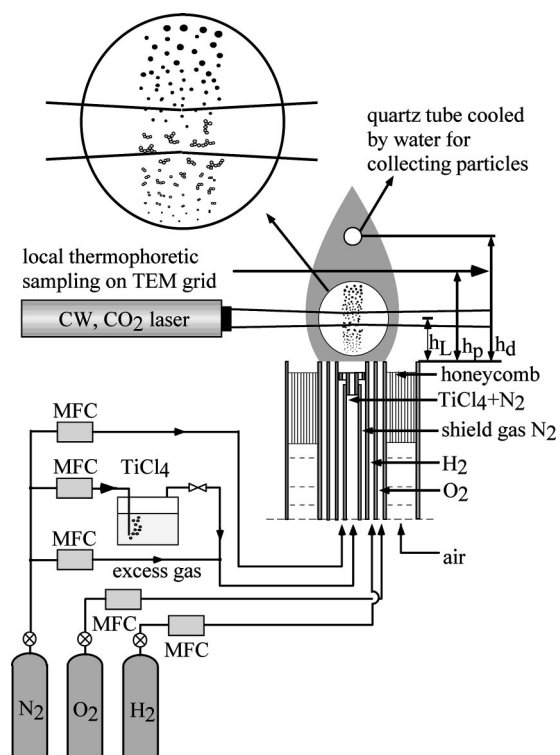


FIG. 1. Schematic for coalescence enhanced principle to synthesize unagglomerate and smaller nanoparticles utilizing laser irradiation in a flame; mass flow controller is shown.

heights (h_d in Fig. 1) and then rutile contents have been measured via x-ray diffraction (XRD) study. Raman spectroscopy has been used to investigate the degree of oxygen vacancy defect. A simple pressureless sintering has also been done to investigate the grain growth of our laser-controlled nanocrystalline particles using XRD and field emission-scanning electron microscopy (FE-SEM).

Figure 2 shows the changes of size and morphology of titania particles captured at 16 mm without or with CO_2 laser beam irradiated at 13 mm in a flame. As CO_2 laser powers increase, coalescence is clearly shown to be enhanced [see Figs. 2(b) and 2(c)] and original aggregates finally become fully sintered unagglomerate spherical particles [Fig. 2(d)]. The magnified TEM image indicates that the seemingly agglomerate particles in Fig. 2(d) are just multiple depositions of isolated sphere particles on TEM grid. As laser power increases, the projected area equivalent diameters significantly decrease (projected area equivalent diameters: 144 ± 3 nm for $P=0$ W and 28 ± 1 nm for $P=1665$ W). Furthermore, it is estimated from TEM image analysis^{17,19} that the volume equivalent diameters of particles also decrease substantially; 82 ± 3 nm for aggregates in Fig. 2(a) and 28 ± 1 nm for spheres in Fig. 2(d). It is noted that the sizes of primary particles consisting of aggregates obviously increase when the coalescence is enhanced. CO_2 laser beam irradiation near 13 mm rapidly enhances the coalescence of early stage aggregates formed near 13 mm and transforms them into spherical particles that have much smaller collision cross sections than the original (volume equivalent) aggregates. Therefore, the growth due to the Brownian collision of particles is retarded to finally produce much smaller sizes at 16 mm.

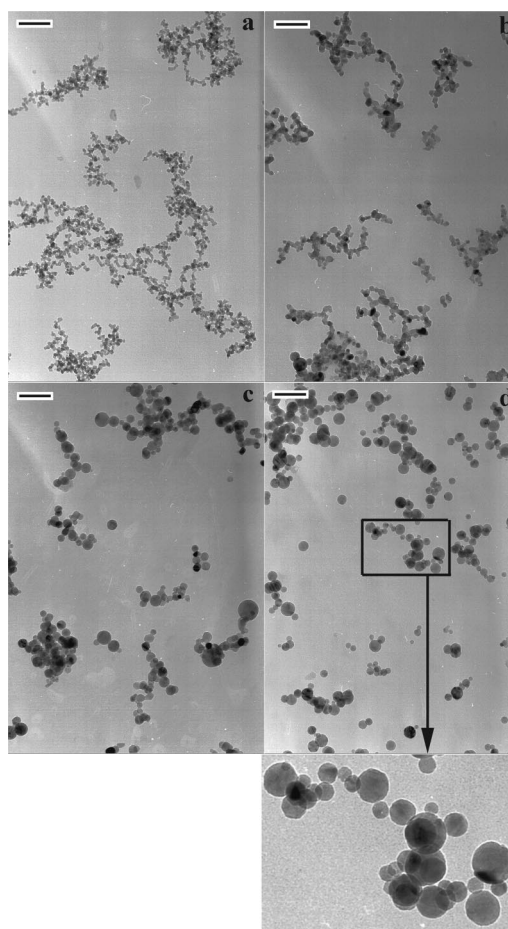


FIG. 2. TEM photographs showing the change of size and morphology of TiO_2 particles with or without CO_2 laser irradiation are shown. These reveal that the original aggregates are transformed into much smaller spheres; $h_L = 13$ mm, $h_P = 16$ mm, flowrates of gases (carrier gas N_2 : 300 cc/min, no excess gas N_2 , TiCl_4 vapor 26.3 cc/min, shield gas N_2 : 700 cc/min, H_2 : 2.5 l/min, O_2 : 5.0 lpm). Bar represents 100 nm. a: 0 W, b: 1031 W, c: 1440 W, d: 1665 W.

It is interesting to investigate how the crystalline phase of particles is varied along the flame in order to know their thermal stability. As shown in Table I, rutile weight percent of particles captured in a flame without laser irradiation increases gradually up to 17% at 60 mm. However, the particles irradiated by a CO_2 laser beam maintain anatase phase at all flame heights. The reason why laser controlled particles have better thermal stability would be attributed to the decrease of nucleation sites. Laser irradiation enhances the coalescence of particles and, therefore, reduces the neck area of the original aggregates, which decreases the surface free energy (this has been known as a driving force to transform anatase to rutile).^{20,21} Therefore, more stabilized anatase particles could be produced. The degree of oxygen vacancies in anatase particles can be also one factor to affect the anatase to rutile transformation.²² Therefore, we estimated the degree

TABLE I. Variations of crystalline phase of titania particles at different flame heights for the cases without or with laser irradiation at 15 mm are shown.

h_d (mm)	15	20	40	60	
Rutile content(%)	0 W	2	10	15	17
	1000 W	...	0	0	0

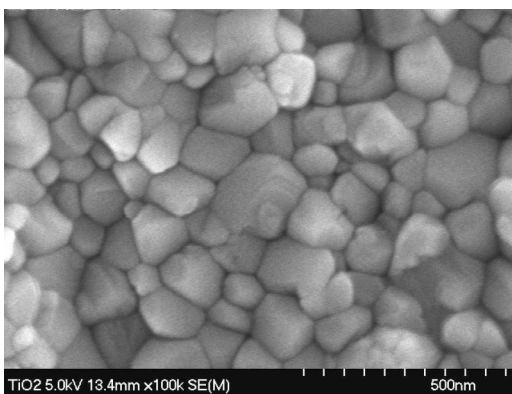


FIG. 3. Nanostructure of fully dense titania is shown: green compact pellet was pressurelessly heated up to 800 °C at the rate of 10 °C/min in air and held at 800 °C for 30 min, which yielded a full dense bulk titania with density >98% of theoretical density. There are no apparent pores. From FE-SEM micrographs, average grain size is estimated as about 75 nm while XRD data and the Scherrer equation gives 60 nm grains. Such small grain size in full dense ceramics has not been achieved before without employing special sintering techniques.

of oxygen vacancy²³ by measuring the position and width of 144 cm⁻¹ E_g peak of Raman spectra. Raman spectra for our sample show the peak position is very close to the theoretical value of 144 cm⁻¹ with a narrow width [for example, the peak position and the peak width full width at half maximum were equal to 145.9 cm⁻¹ and 14.9 cm⁻¹, respectively]. These data indicate that our nanoparticles have nearly perfect oxygen stoichiometry, i.e., TiO_{2.0} from the correlation curve suggested by Parker and Siegel²³ while their as-compacted samples obtained by gas condensation had a significantly high degree of oxygen vacancy, i.e., TiO_{1.89} (peak position of 154 cm⁻¹ and peak width of 34 cm⁻¹).

We finally examined the grain growth of 20 nm spherical titania particles captured at 18 mm with irradiating CO₂ laser beam in a flame at 15 mm. As noted in Fig. 3, green compact pellet made by applying an isostatic pressure of 10 MPa was heated pressurelessly in air up to 800 °C at the rate of 10 °C/min and held at 800 °C for 30 min, which yielded a full dense bulk of 100% rutile having nearly theoretical density (>98%). XRD study and Scherrer equation reveal this fully dense rutile has 60 nm grain size which is only 3 times the starting powder size. Such small grain sizes in fully dense ceramics have not been achieved so far without employing any special sintering techniques such as hot pressing^{3,7} or the addition of dopants⁹ or liquid phase processing including peptization and drying without calcination step^{24,25} or recent two step sintering method.⁴ Nanograins in fully dense TiO₂ can be clearly seen from FE-SEM micrograph without showing any apparent pores (Fig. 4). From FE-SEM micrographs, average grain size is estimated as about 75 nm while XRD data and Scherrer equation gives 60 nm grains. In contrast, the case without laser irradiation gives not only larger grain sizes but also lower density as shown in Table II. Other commercially available nanopowders also resulted in much lower density or much larger grain sizes. Generally, in the final stage of sintering, the densification process depends strongly on the size and the distribution of pores in grain boundaries.^{4,9,10,26} The unusually small grain growth of our laser controlled anatase powder would be partially attributed to completely nonagglomerated mor-

TABLE II. Comparison of sintering results between the present and other nanoparticles. A: our laser-controlled 20 nm particles, B: original aggregates without laser irradiation, C: commercial powder from Degussa (flame method, ~30 nm), D: commercial powder from Nanophase Tech. (gas phase condensation, 34 nm) is shown.

	A	B	C	D
Relative density (%)	98	95	91	88
Grain size (nm)	60	119	63	122

phology that would yield small pore size and also more homogeneous pore distribution when compacted than the original aggregates.^{4,9,10,25} Defects such as oxygen vacancies can act as one of diffusion paths that can cause additional grain growth.¹⁰ Our coalescence enhanced method using laser irradiation in a flame produced almost oxygen vacancy free particles as already mentioned and possibly might have cured other defects through laser annealing, which could also be a reason for the suppression of rapid grain growth. The present principle does not have limitations on the selection of materials and processes, therefore, could be applied to the controlled formation of various different nanoparticles and possibly their full dense nanocrystalline bulk materials. The present coalescence enhancement concept could also be extended to different gas phase methods such as gas condensation method.

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