Letter

Flash synthesis of titanium dioxide nanoparticles by strong exothermic reaction between solids without external energy

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Abstract

This paper describes the innovative flash synthesis of metal oxide nanoparticles by using only a strong exothermic reaction between solids without any external energy, such as that from an electric furnace, and its implementation for the synthesis of titanium dioxide. Flash synthesis is regarded as a type of combustion synthesis, in which the adiabatic flame temperature of the solid phase reaction is greater than the boiling point of the product. In the experiments, raw materials of different-sized titanium particles and sodium perchlorate were intensively mixed and ignited by an electrical heating foil to produce titanium dioxide through the following reaction: $Ti + NaClO_4 \rightarrow TiO_2 + NaCl$. The product was obtained by removing NaCl by washing with distilled water. Evidently, all the products obtained through gasification in the heating process and nucleation and crystal growth in the cooling sublimation process were nanoparticles; the shape and crystal structure of the titanium dioxide product significantly depended on the particle size of titanium used as the raw material. That is, the smaller titanium particles (average size (AS) of 10 μm) resulted in rutile with an irregular shape, and the larger particles (AS of 25 μm) resulted in spheres of anatase with a size of 100–1000 nm. This method can be easily applied to produce other metallic oxides, thus offering many benefits such as easy mass production, energy saving, and short processing time.
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Keywords: Nanofabrications; Oxide materials; Self-propagating high-temperature synthesis (SHS)

1. Introduction

After years of evolutionary research on nanoparticle production, many technologies based on building-up processes such as the gas phase process, liquid phase process, and solid phase process have been practically developed to synthesize various nanoparticles of metal and oxide because of the easy preparation of 10–1000 nm particles with a narrow size distribution. However, the current building-up process still has crucial problems such as high energy requirement in the gas phase process, long operation time due to the many steps required, and water pollution in the liquid phase process. Thus, a new production method of nanoparticles is strongly required for the major industries.

To overcome the drawbacks of each process, the so-called combustion synthesis (CS) process seems attractive as an alternative process [1]. In general, CS offers many benefits for minimizing the energy requirement, simplifying the equipment, and shortening the operation time through the use of a sustainable exothermic solid–solid reaction among the raw materials. Theoretically, when the adiabatic flame temperature due to the exothermic heat exceeds the boiling point of the products in CS, a product of nanoparticles can be instantaneously obtained through both gasification in the heating process and nucleation and crystal growth in the cooling sublimation process.

We term this process as "Flash Synthesis" (FS) and compare it with the conventional CS, as shown in Fig. 1. Therefore, the purpose of this study is to produce nanoparticles of titanium dioxide by using FS for the first time; in this study, the effect of the raw material size on the product morphology was mainly examined. The results will appeal the new attractive process for producing nanoparticles in a very short time and with a cost

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Nomenclature

a, c	lattice parameter of tetragonal crystal (m)
C_p	molar specific heat of constant pressure (kJ/mol K)
d	plane distance (m)
h, k, l	miller index
ΔH_b	evaporation heat of fusion (kJ/mol)
ΔH_m	latent heat of fusion (kJ/mol)
ΔH_r	enthalpy of formation (kJ)
I_A	intensity of maximum interference line of anatase
I_R	intensity of maximum interference line of rutile
T_b	boiling point (K)
T_m	melting point (K)

Table 1
Experimental conditions for the preparation using titanium powders with different average particle sizes

Case	Raw material	Average particle size (μm)	Purity (%)
1	Ti	10	99.9
2	Ti	25	99.9

benefit, in which the size of the raw material can be an important operating parameter to control the product morphology.

2. Experimental

In the experiments, the samples were prepared from commercially available powders of titanium (Kojundo Chemical, 99.9% purity) and sodium perchlorate (Aldrich, 98% purity). In particular, different average-sized (AS) titanium powders were used for examining the effect of the particle size on the product morphology, as listed in Table 1. Eq. (1) gives the overall reaction equation in cases 1 and 2. Further, Table 2 indicates the molar specific heat of the products in Eq. (1) [2–5] for evaluating the adiabatic flame temperature (T_{ad}) from the heat balance of FS due to the titanium oxidation, as given by Eq. (2). T_{ad} evaluated for this reaction was 3019 K exceeding the boiling point of TiO_2 (3000 K) and

Table 2
Molar specific heat of the product materials given in Eq. (1)

Product	Specific heat, C_p ($J mol^{-1} K^{-1}$) $C_p = A + B \times 10^{-3}T + C \times 10^5 T^{-2} + D \times 10^{-6}T^2$				Temperature (Range (K))
	A	B	C	D	
TiO_2	70.195	7.573	−15.439	−1.523	298 ∼ 2143
TiO_2	100.416	0	0	0	2143 ∼ 3000
TiO_2	59.4	−1.272	−27.02	0.331	3000∼
NaCl	56.2970.	−13.015	−3.423	21.862	298 ∼ 1073.8
NaCl	66.944	0	0	0	1073.8 ∼ 1738
NaCl	37.56	0.383	−1.715	0.217	1738∼

NaCl (1738 K), which are the products.

$$Ti + 0.5NaClO_4 = TiO_2(s) + 0.5NaCl(s) + 958.93\,kJ \tag{1}$$
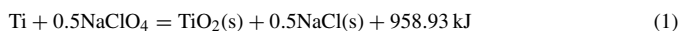
$$\Delta H_r + \int_{298}^{T_m} \sum n C_p dT + \Delta H_m + \int_{T_m}^{T_b} \sum n C_p dT + \Delta H_b$$
$$+ \int_{T_b}^{T_{ad}} \sum n C_p dT = 0 \tag{2}$$

The preparation procedure was as follows: titanium and sodium perchlorate powders were first well mixed by ball milling at a rotating rate of 60 rpm for 3 h in air, in which an alumina milling pot ($140\phi \times 95$ mm) containing alumina balls with a diameter of 10 mm and a ball-to-sample mass ratio of 6:1 was used. The powder mixture obtained was next placed in a graphite crucible (110 mm × 30 mm × 20 mm) without any compressive treatment. Before the experiments, the reactor was evacuated by a rotary pump and pure argon was supplied to maintain the atmospheric pressure.

Fig. 2 shows the top and side views of the reactor for the FS; the reactor comprised three parts: a stainless steel reactor, a gas supply system, and a vacuum system. In the experiments, a disposable carbon foil was placed in contact with one end of the reactant and was electrically ignited by a voltage of 50 V and a current of 100 A at room temperature. The phenomena of ignition, gasification, and sublimation were observed though a quartz window. Most of the products in the form of powder were first recovered using a filter attached to the equipment and were then dissolved with distilled water in a beaker and finally filtrated to remove sodium chloride.

After the experiments, the phase of the product obtained was identified by XRD diffraction (JDX-3500, JOEL). The morphology of the products was also observed by SEM (FE-SEM JSM-7000F, JOEL).
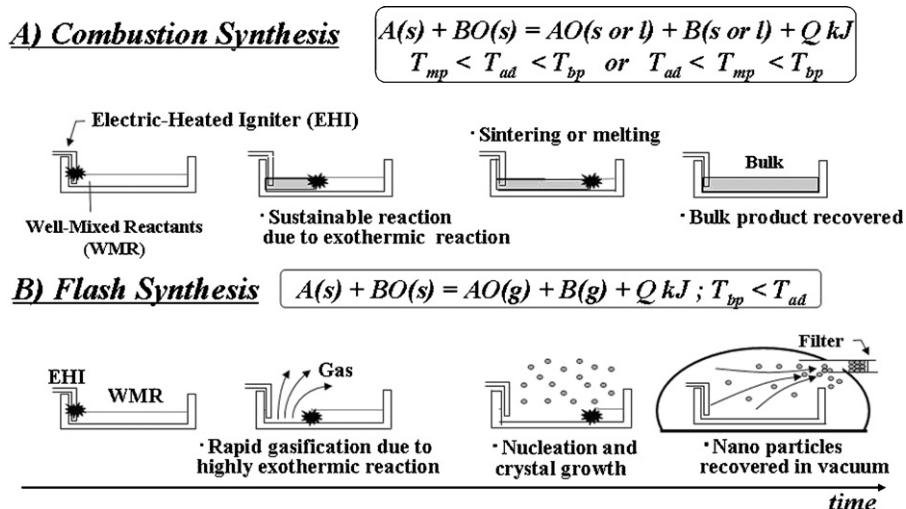

Fig. 1. Two methods of *flash synthesis* and the conventional combustion synthesis for producing oxide (AO), in which the theoretical estimated temperature, the so-called adiabatic flame temperature (T_{ad}), is compared with the boiling point (T_{bp}) of the product (AO) for the classification. T_{mp}: melting point.
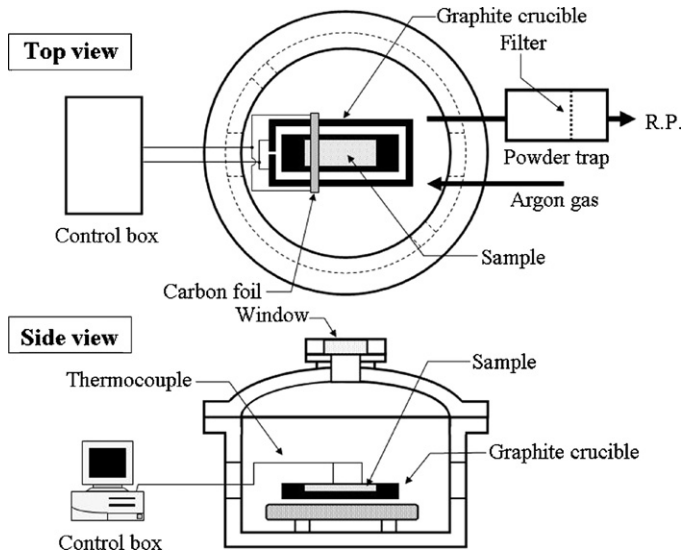
Fig. 2. Schematic diagram of the experimental apparatus for flash synthesis, in which one end of the well-mixed raw materials is ignited by an electrically heated carbon foil, and the generated nanoparticles are chiefly recovered by the filter in vacuum.

Fig. 3. XRD patterns of two flash-synthesized products using titanium as the raw material with average particle sizes of: (a) 10 (m and (b) 25 (m; the products were both titanium dioxide without any impure substance, but the crystal structure was not identical due to the different reaction temperatures caused by flash synthesis. The results suggest that the rutile-rich sample (a) experienced a higher temperature than sample (b) because mixing of the smaller particles cause a wider contacting surface among the particles, resulting in a higher temperature due to the strong exothermic reaction.

3. Results and discussion

In cases 1 and 2, the samples were successfully ignited, and the process was instantaneously completed with the emission of flashlight. The nanoparticles generated exhibited smoke-like behavior for sometime, and some products were deposited on the inner wall of the reactor. However, most of the products were finally recovered by a powder trap in the equipment.

Fig. 3 shows the XRD patterns of the products synthesized by FS; in this figure, the peaks of both products agreed well with the phase data of titanium dioxide-rutile or anatase. No peaks of Ti and $NaClO_4$ as un-reacted raw materials were observed. However, it is very interesting to note that the ratio of the rutile phase to the anatase phase in titanium dioxide varied with the particle size of titanium used as the raw material. In case 1, the main peaks were the rutile phase; we confirmed that this is similar to the commercially available titanium dioxide with high-purity rutile. Meanwhile, in case 2, the peaks of the anatase phase were relatively strong in comparison to the rutile phase.

Eqs. (3) and (4) indicate how to roughly estimate the content ratio of the anatase phase and rutile phase contents in titanium dioxide [6–8]. Table 3 shows the result of the quantitative estimation and the lattice constant of titanium dioxide synthesized by FS [9]. The lattice constant of the tetragonal crystal of titanium
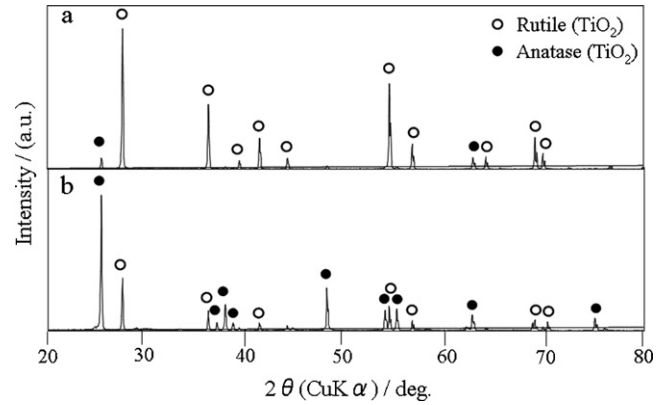
dioxide was also calculated from Eq. (5). The results showed that the products from the fine and coarse powders were 96% rutile-5% anatase and 33% rutile-67% anatase, respectively.

$$\text{content ratio of anatase (\%)} = \frac{100}{(1 + 1.265 I_A/I_R)} \tag{3}$$

$$\text{content ratio of rutile (\%)} = \frac{1 - 100}{(1 + 1.265 I_A/I_R)} \tag{4}$$

$$\frac{1}{d^2} = \frac{(h^2 + k^2)}{(a^2 + l)/c^2} \tag{5}$$

A time-temperature-transformation (TTT) diagram was effective for discussing the relationship between the particle size of the raw materials and the phase of the products from the viewpoint of the cooling rate. Fig. 4 shows the TTT diagram of titanium dioxide production along with the three typical cooling curves. In general, the higher maximum temperature (T_{MAX}) of the gaseous product causes a higher cooling rate due to a large temperature difference between T_{MAX} and the room temperature, which acts as a driving force of heat transfer. In Fig. 4, the temperature curve of the product in case A does not intersect the stable anatase phase for the generation of the pure rutile phase. In contrast to case A, the curve in case C intersects the 100% stable anatase phase for the generation of the pure anatase phase. We can easily predict that the T_{MAX} value of the products in case

Table 3
Quantitative estimation of the product from XRD patterns, in which Lattice constant of flash synthesized TiO_2 were very similar to values in literature [9]

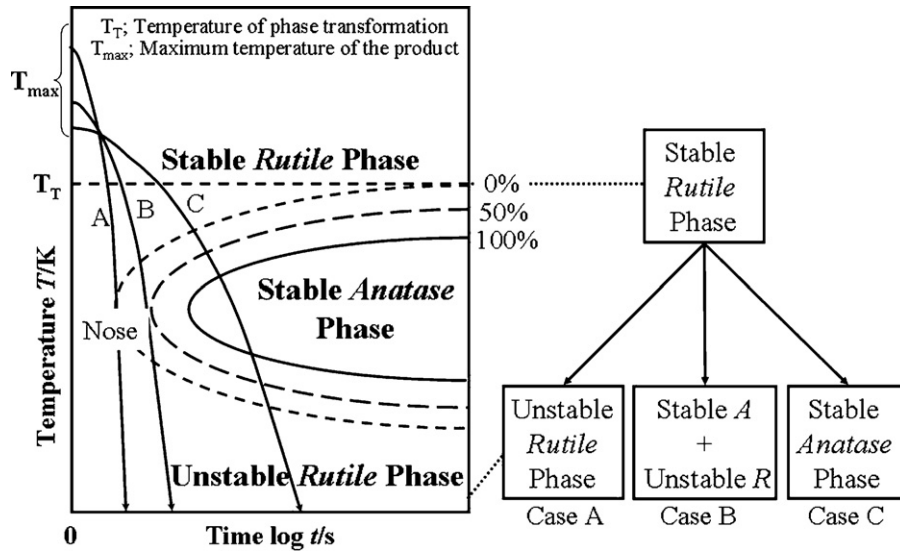| Case	Rutile content of TiO_2 (%)	Anatase content of TiO_2 (%)	Lattice constant of rutile phase (Å)		Lattice constant of anatase phase (Å)	
			a	c	a	c
1	95.2	4.8	4.574	2.947	4.035	9.783
2	33	67	4.588	2.951	3.778	9.372
Reported value [9]	100	–	4.593	2.959	–	–
	–	100	–	–	3.785	9.514

Fig. 4. Relationship between the cooling rate and TTT (time-temperature-transformation) diagram for TiO_2 production, in which the 0% curve implies the start of the transformation and the 100% curve implies the end of the transformation. The smaller size of the raw materials causes a higher T_{max} because the contacting area between the raw materials is considerably larger when the particle size is smaller: accelerating the reaction rate with less heat loss, such as in case A, and vice versa in case C.
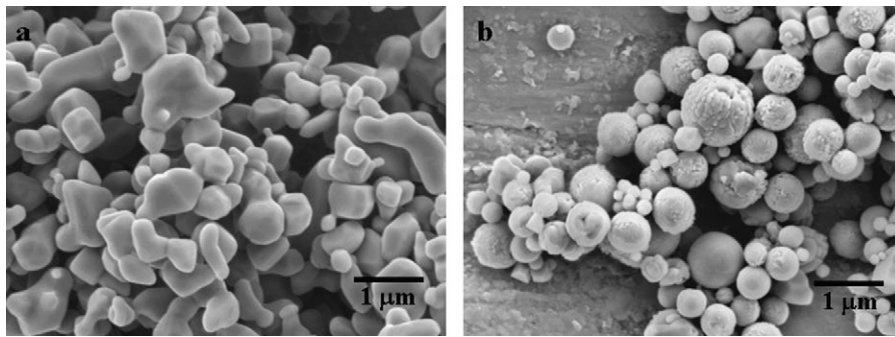

Fig. 5. SEM image of two flash-synthesized products from titanium of a raw material with different average particle sizes of: (a) 10 (m and (b) 25 (m; here, the products had a different shape. The former was irregular, and the latter, spherical.
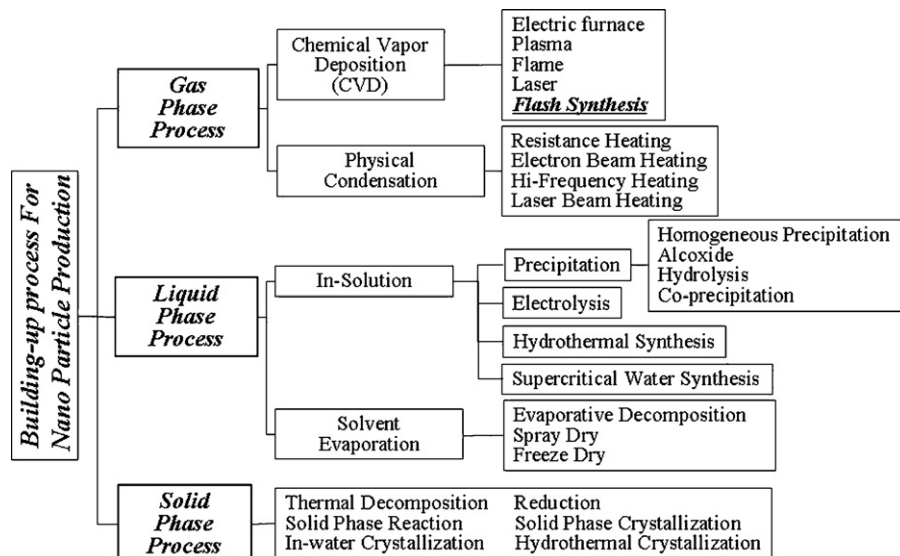

Fig. 6. Classification of building-up processes for producing nanoparticles, in which flash synthesis is newly categorized as a kind of CVD in gas phase process. Original classification is based on K. Okuda, J. Tsubaki, Production of fine particle, Nikkan kougyou sinnbunnsya, Japan, (2005) 67–68.

1 was higher than that of the products in case 2, because case 1 had a larger contacting area between the raw materials due to a fine particle size to accelerate the reaction rate with a low heat loss. Therefore, we can conclude that the quenching situation of the product in case 1 is similar to case A in Fig. 4 and that in case 2 is similar to case B.

Fig. 5 shows a comparison of the SEM images of titanium dioxides synthesized using titanium with an average size of 10 and 25 μm as the raw material. Apparently, both the products were in the form of nanoparticles. This fact revealed that FS definitely occurred because the size of the products 100–1000 nm, was much smaller than that of the raw material. The shape of the products depended on the particle size of the raw material. Here, the shape of the products in case 1 was irregular, whereas it was almost spherical in case 2. This was probably caused by the different cooling rates, as shown in Fig. 4.

The results obtained can be summarized as follows:

(1) In FS of titanium dioxide, nanoparticles with a size of 100–1000 nm were very quickly obtained through gasification, nucleation, and crystal growth from the following reaction: $Ti + 0.5NaClO_4 \rightarrow TiO_2(g) + 0.5NaCl(g)$.
(2) The shape and crystal structure of the nanoparticles obtained depended significantly on the particle size of titanium as a raw material—the smaller titanium particles (average size (AS) of 10 μm) resulted in rutile with an irregular shape; the larger particles (AS of 25 μm) resulted in spheres of anatase phase.

FS is a type of combustion synthesis with strong exothermic heat, in which the adiabatic flame temperature is higher than the boiling point of the product. This should be newly categorized as a type of CVD in the conventional classification of building-up nanoparticle production, as shown in Fig. 6 [10]. The results also suggested that FS can be easily applied to produce other metal oxide nanoparticles, in which the product phase might be controllable by changing only the size of the raw material.

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