

Chapter 2

Synthesis of TiO₂ Nanoparticles by Stagnation Swirl Flame

2.1 Experimental Methods

Figure 2.1 shows the experimental system for the synthesis of TiO₂ nanoparticles by stagnation swirl flame (SSF). The system is composed of three main parts, i.e., a delivery system for reactant gases and precursor, a downward stainless steel tube of 18 mm i.d with a vane swirler inside, and a temperature-controlled substrate. Mass flow controllers meter the delivery of CH₄, O₂, and N₂. Nitrogen also serves as the carrier gas for the liquid precursor (titanium tetraisopropoxide, TTIP, Aldrich, 97%), which is heated to 80 ± 2 °C by an electrical mantle to achieve a high vapor pressure. The precursor concentration is calculated based on the assumption that the loading rate is proportional to the carrier nitrogen flow rate. Downstream lines are heated to 130 °C to avoid precursor condensation prior to delivery to the burner. The vane swirler, which is 14-mm long with eight 45° blades, is situated inside the burner tube at a position of 73 mm above the burner exit. It introduces swirling flow to the main gas stream, greatly stabilizing the flame impinging on the substrate. The outer diameter of the vanes is 18 mm, while that of the central bypass channel is 8.0 mm, filled with metal meshes. This design of the vane swirler with an open center-channel allows a portion of reactants to remain unswirled, which inhibits vortex breakdown and promotes flow divergence—the key aerodynamic feature for the low-swirl flame stabilization method (Cheng et al. 2009). The ratio of the swirled and unswirled gas determines swirl number S ,

$$S = \frac{G_{\phi}}{G_x R} \quad (2.1)$$

where G_{ϕ} is axial flux of angular momentum, G_x is axial flux of momentum, and R is tube inner diameter. Similar swirlers have been used for low NO_x combustors

researchers in Lawrence Berkeley National Lab (Johnson et al. 2005; Cheng et al. 2009). It has been proposed that the swirl number of such type of swirler can be calculated as,

$$S = \frac{2}{3} \tan \gamma \frac{1 - R^3}{1 - R^2 + K^2 \left(\frac{1}{R^2} - 1 \right)^2 R^2} \quad (2.2)$$

where γ is the angle between swirler and main flow, R is tube inner diameter, and K is the ratio of the swirled and unswirled gas, measured by experiments. Therefore, the swirl number can be adjusted by altering the resistance of central meshes and, in this work, is fixed to be 0.248, meeting the low-swirl limit value of 0.6. Generally, strong swirled flames show recirculation zones, which is absent in low-swirl flame (Gupta et al. 1984). This is consistent with our observation. The low-swirl flame is formed between combustor tube and substrate, as shown in the photograph in Fig. 2.1. The typical distance between burner exit and substrate is 19 mm. The silicon substrate on which the TiO₂ nanoparticles deposit is placed on a temperature-controlling device, which consists of an aluminum sheet (embedding a K-type thermocouple), quartz glass blocks, and a heat sink with cooling water. The substrate temperature can be precisely set by adjusting the thickness of the quartz glass blocks which serve as thermal resistance, as well as the flow rate of cooling water. The substrate temperatures examined in this work range from 100 to 550 °C, with a controlling accuracy of ± 10 °C.

A typical case is 2.25 L/min methane, 6.6 L/min oxygen, and 24.9 L/min nitrogen, corresponding to an equivalence ratio of 0.68. The measurement of precursor container mass loss shows that per 1 L/min carrier gas carries 0.0249 g

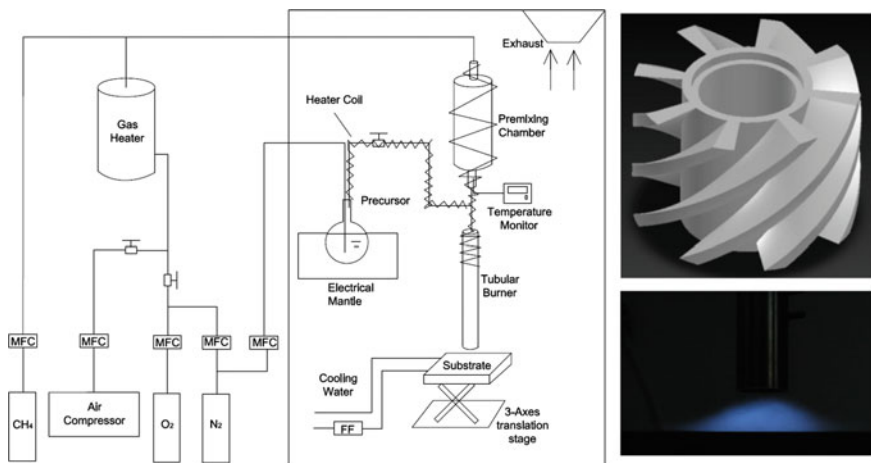


Fig. 2.1 Schematic of experimental system for synthesis of TiO₂ nanoparticles by stagnation swirl flame

TTIP, adding a precursor concentration of 58.2 ppm to the total premixed gas. The gas velocity at nozzle exit is about 3 m/s, resulting in a residence time of 0.04 s for particles.

Precursor TTIP reacts with H_2O or O_2 in the flame and produces TiO_2 monomers. After nucleation, TiO_2 particles keep growing by collision-coalescence mechanism until depositing to the substrate, as illustrated in Fig. 2.2. By introducing a water-cooling substrate, the particle residence time in high temperature regime is well controlled. Figure 2.3 shows TEM photographs of TiO_2 nanoparticles collected on the substrate. The average diameter is 6 nm after counting over

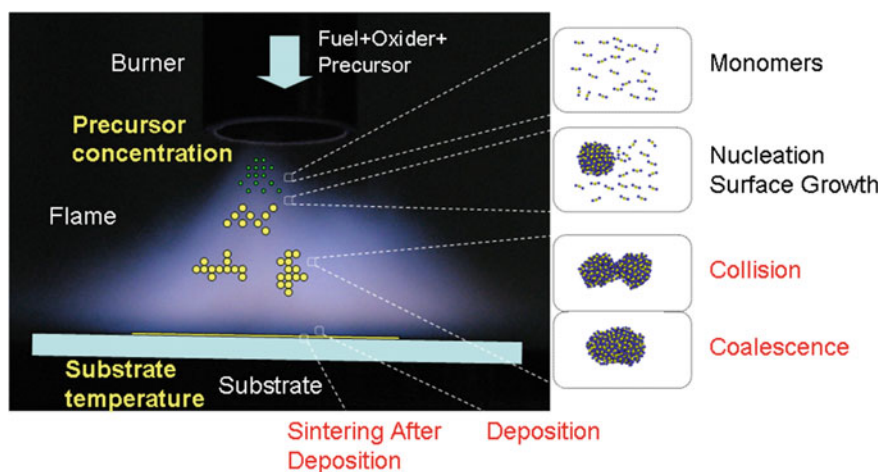


Fig. 2.2 An illustration of steps from precursor to nanoparticle products

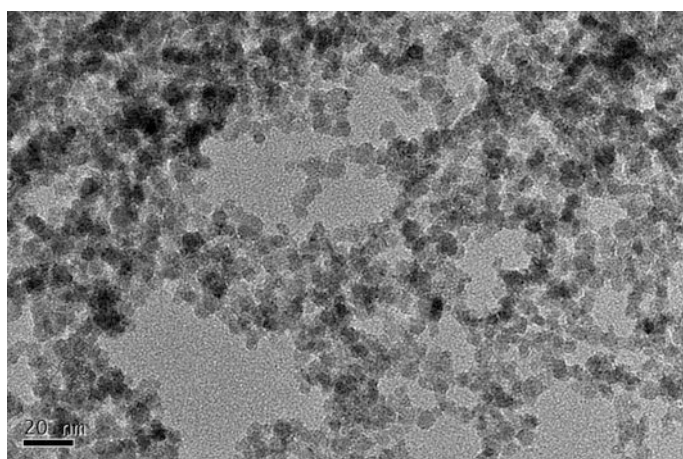
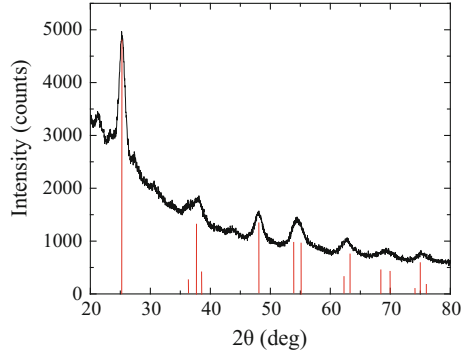


Fig. 2.3 TEM photograph of TiO_2 nanoparticles synthesized with 1 L/min carrier gas

Fig. 2.4 XRD results of TiO₂ nanoparticles synthesized under 3 L/min carrier gas



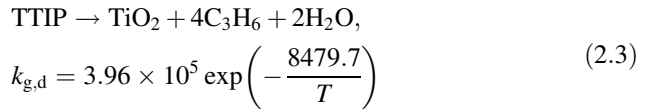
100 particles. BET absorption results indicate a specific surface area (SSA) of 230 m²/g, corresponding to a diameter of 6.7 nm. Figure 2.4 shows XRD measurement of collected particles, indicating that the main phase is anatase (red line from ICDD database, PDF#97-015-4602). The small peak around 30° shows a minor portion of rutile phase also exists.

2.2 Population Balance Modeling of Nanoparticle Coagulation in Stagnation Swirl Flame

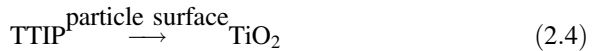
2.2.1 Comparison of Characteristic Times for Different Steps

A comparison of characteristic times is very helpful for better understanding of different steps from precursors to nanoparticles, which include chemical reaction, nucleation, collision, coalescence, deposition, and sintering after deposition. There are three pathways for precursor TTIP to transform to TiO₂ monomers:

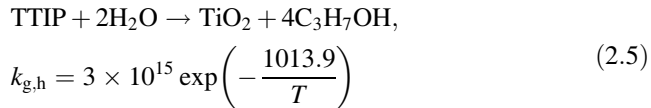
Self-dissociation in high temperatures (Okuyama et al. 1990),



heterogeneous reaction on TiO₂ particle surface (Okuyama et al. 1990)



and hydrolysis with H₂O in flames (Tsantilis et al. 2002),



The calculation of reaction rates shows that hydrolysis is faster than self-dissociation by nine orders of magnitude in the temperature range 400–2000 K. The reaction rate of heterogeneous reaction is associated with surface area and thus difficult to quantify. Anyway, the characteristic time for precursor chemical reaction is already as short as 0.1 ps even we neglect heterogeneous reaction. Hence, comparing with flow time and coagulation time, chemical transition of TTIP to TiO_2 monomers can be regarded as instantaneous in post-flame gas.

The next step could be nucleation, which represents the transition from gas phase monomers to particle phase. Classical homogeneous nucleation theory considers that only those clusters exceeding critical nucleation radius can keep on growing. The critical nucleation radius is expressed as (Mullin 1993),

$$r_c = -\frac{2\sigma}{\Delta G_v} \quad (2.6)$$

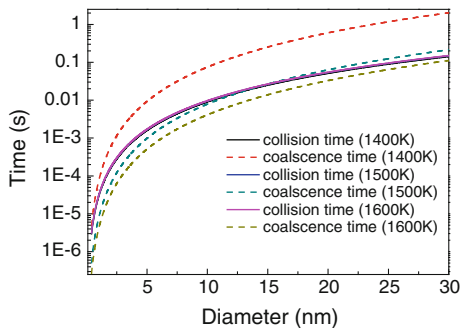
where r_c is the surface tension of particle phase and σ is Gibbs free energy per unit volume. The calculation of TiO_2 system shows that the critical nucleation radius is even smaller than the radius of a TiO_2 monomer (Ulrich 1971; Pratsinis 1998), which indicates that every TiO_2 monomer is already a stable nucleus and the nucleation becomes an instantaneous process.

After nucleation, nanoparticles grow larger by collision-coalescence process. Particles collide due to Brownian motion in high temperature flows and sinter with each other afterward driven by the tendency of reduction of surface energy. The collision-coalescence process is the key stage that controls the morphology and structure of final products. Chapter 4 will look into this process in a microscopic view. Here, in this chapter, we describe the process from the view of classical aerosol theory. The characteristic time of Brownian collision is expressed as,

$$\tau_{\text{collision}} = \frac{2}{\beta n} \quad (2.7)$$

where β is the collision kernel function and n is number density. The collision kernel function of free-molecular regime is expressed in Eq. (1.3). Since the chemical reaction time and nucleation time are ultrashort compared to collision-coalescence process, there is no overlap for these different time scales. It should be noted that the situation could be quite different for other cases where significant overlaps can be found, for instance the formation of ultrafine particles in coal combustion. For a ‘pure’ collision-coalescence process, the total particle volume fraction is conserved. The solid line in Fig. 2.5 shows the characteristic collision times for several different temperatures. As for the coalescence time,

Fig. 2.5 Variation of collision and coalescence times with particle size for different temperatures



currently there is no universal theory. Most formulas are empirical or semi-empirical ones fitted from experiments. Here, we adopt the empirical expression from Ehrman et al. 1998,

$$\tau_{\text{coalescence}} = 1.87 \times 10^9 T d_p^3 \exp\left(\frac{34,372}{T}\right), d_p \text{ in m}; \quad (2.8)$$

The dotted line in Fig. 2.5 shows the characteristic coalescence time for different sizes and temperatures. Both collision and coalescence times exhibit strong dependence on particle size. The collision time increases from 10^{-7} to 10^{-1} s as particle diameter increases from 0.4 to 30 nm. The effect of temperature on collision time is less profound because Brownian motion velocity only scales with square root of temperature. As for the coalescence time, the temperature dependence is much stronger since the solid state diffusion coefficient scales exponentially with temperature. The competition between collision and coalescence time determines the morphology of growing particles. For instance, at 1600 K, the coalescence time is always shorter than collision time for the size range discussed. This means that the two collided particles will coalesce into a new sphere before next collision occurs. As long as that the flow time is long enough, the particles will keep on growing in spherical shape up to at least 30 nm. At 1500 K, there is an intersection of collision and coalescence time at about 15 nm. Hence, for particles below 15 nm, the coalescence process can finish before next collision. But as particles grow larger than 15 nm, the time between two collisions is not long enough for the coalescence to complete. Fractal agglomerates will be formed, and the size of primary particles will be ‘frozen’ around 15 nm. At 1400 K, the collision time is always shorter than coalescence time. However, it should be noted that Eq. (2.8) is fitted from experiments of particles around 10 nm. There could be significant deviation when applied Eq. (2.8) to much smaller particles, e.g., 3 nm. From Fig. 2.5, we could see that the time scales of collision and coalescence range from 10^{-7} to 10^{-1} s, covering the scale of flow time which is usually 10^{-2} to 1 s. Therefore, the collision-coalescence process controls the morphology and structure of final products.

Particle deposition occurs in the boundary layer with a characteristic time of ~ 0.05 s. The transport of particles inside the boundary layer determines the deposition flux and deposited structures, which will be discussed in details in Chap. 5. The sintering effect after deposition mainly depends on substrate temperature. Considering a deposition time of 60 min, the sintering is almost negligible for 400 K. If the substrate temperature is 700 K, particles could sinter/coalesce up to 12 nm. Therefore, the sintering after deposition can be well controlled by adjusting substrate temperature.

The analysis in this section indicates that the collision-coalescence process is the controlling step for particle growth. Next section will study this process using population balance method.

2.2.2 Modeling of Particle Coagulation in Flames

This section will employ population balance method to investigate particle collision-coalescence in stagnation flames. Population balance method is based on general dynamics equation (GDE) or Smoluchowski equation,

$$\frac{\partial n_k}{\partial t} = \frac{1}{2} \sum_{i+j=k} \beta(i, j) n_i n_j - \sum_{i=1}^{\infty} \beta(i, k) n_i n_k + \alpha_{k+1} s_{k+1} n_{k-1} - \alpha_k s_k n_k \quad (2.9)$$

Left-hand side of Eq. (2.9) is the changing rate of number concentration n_k for particles with size class k . The first and second terms in the right-hand side are the changes due to coagulation, which has no contribution to the total volume fraction. The first term represents the increase of class k particles due to the coagulation of smaller particles, with $1/2$ denoted that the same coagulation event has been counted twice. The second term represents the decrease of class k particles due to coagulation with other class particles, to form larger particles. The third and fourth terms are source terms due to gas-particle transformation. As mentioned in the previous section, for TTIP-TiO₂ flame synthesis system, the processes of chemical reaction and nucleation can be regarded as instantaneous. Hence, source terms can be neglected in post-flame gas, which results in a pure collision-coalescence process corresponding to only the first and second terms.

From TEM photographs shown in Fig. 2.3, we could see that particles keep nearly uniform sizes during coagulation. Hence here we introduce monodisperse assumption for simplicity. According to Tsantilis et al. (2002), the deviation due to this assumption in flame synthesis modeling is usually below 5%. Monodisperse assumption reduces Eq. (2.9) to,

$$\frac{dn}{dt} = -\frac{1}{2} \beta n^2 \quad (2.10)$$

where n is the number density of particles. The expression in free-molecular regime is used for collision kernel,

$$\beta = \left(2^{\frac{5}{2}}\right) \left(\frac{3}{4\pi}\right)^{\frac{1}{6}} \left(\frac{6kT}{\rho_p}\right)^{\frac{1}{2}} \left(v_p^{\frac{1}{6}}\right) \quad (2.11)$$

where ρ_p is particle density, 3.84 g/cm³ and v_p is particle volume.

Rayleigh scattering measurements in Chap. 3 will show that the temperature field within the projection of combustor nozzle is quite uniform for post-flame area, which leads to a similar temperature history for particle growth. Hence, we will only discuss particle coagulation along the axis as a representative. The temperature profile along the axis is measured by Raman scattering, as shown in Fig. 2.6. The detailed measuring procedure can be referred in Chap. 3.

The velocity profile is described by potential flow field,

$$U = ar; \quad W = -2az \quad (2.12)$$

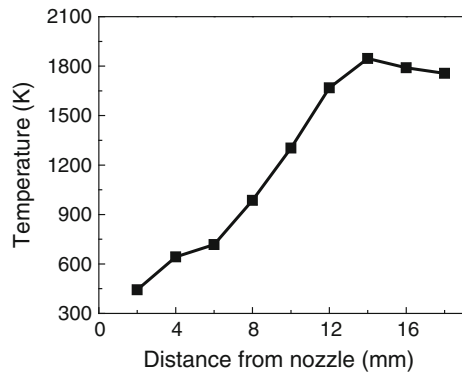
where U is radial velocity, W is axial velocity, r is radial coordinate, z is axial coordinate, and a is global strain rate. A modification is needed which accounts for the acceleration due to thermal expansion of post-flame gas,

$$W = -2az \frac{T}{T_0} \quad (2.13)$$

where T is local temperature, and T_0 is the gas temperature at nozzle exit. It should be noted that the velocity field used here is a quite strong simplification considering the existence of low swirling. However, the particle residence time mainly depends on axial velocity. Moreover, it will be shown later that for stagnation flame synthesis, the influence of gas velocity on particle size is not strong.

Additionally, the thermophoresis in the near-wall region must be accounted for. The thermophoretic velocity in the free-molecular regime can be described by Waldmann's formula (Waldmann and Schmit 1966),

Fig. 2.6 Temperature profile along the axis measured by Raman scattering



$$\vec{V}_{th} = \frac{-3v\nabla T}{4\left(1 + \frac{\pi\alpha}{8}\right)T} \quad (2.14)$$

where v is gas kinematic viscosity, and α is momentum accommodation coefficient which denotes the ratio of specular and diffuse scattering, usually taken as 0.9 (Friedlander 2000). Figure 2.7 shows the effect of introducing thermophoresis. If thermophoretic velocity is not included, there will be an unrealistic abrupt jump for particle size near the substrate as highlighted by the red circle, which is induced by

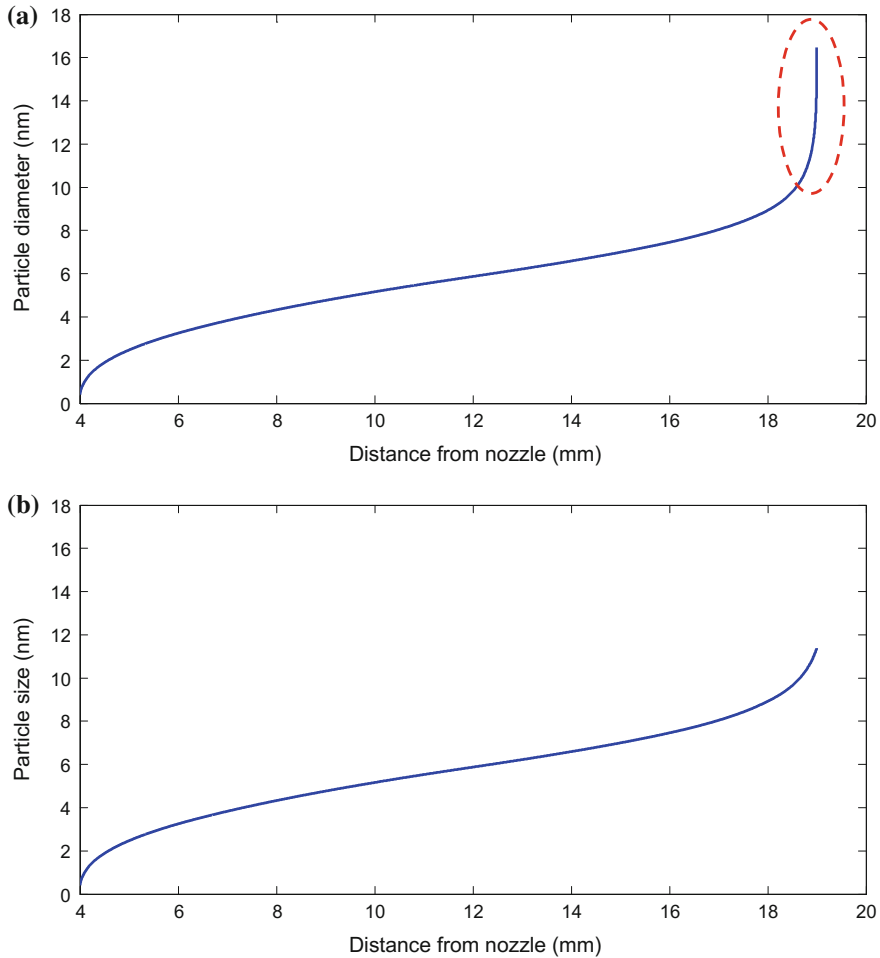


Fig. 2.7 Particle size along the axis **a** with or **b** without including thermophoretic velocity (Color figure online)

the incorrect estimation of residence time in the near-wall region. By including thermophoretic velocity, the unrealistic jump disappears as shown in Fig. 2.7b).

The last problem is the competition of collision and coalescence. In the initial stage where particles are small and temperature is high, the coalescence time is shorter than collision time, which indicates that the coalescence process is finished before next collision occurs, or ‘instantaneous coalescence’ from a macroscopic view. However, when particles travel to near-wall region, where particles are relatively large and the temperature goes down due to cooled substrate, the coalescence time becomes comparable and eventually longer than the collision time. After this intersection point, the collisions of particles will form agglomerates with primary particle size nearly ‘frozen.’ In order to determine this point, we first solve Eq. (2.10) with the assumption of instantaneous coalescence, as shown in Fig. 2.8a. The final particle size is 7.4 nm for 58.2 ppm precursor concentration case and 12.8 nm for 232.8 ppm precursor concentration case. The experimental results from BET surface area deduction are 6.7 nm for 58.2 ppm and 10.8 nm for 232.8 ppm, both smaller than modeling predictions. The deviation rises from the instantaneous coalescence assumption which is not valid when approaching substrate. Hence, we

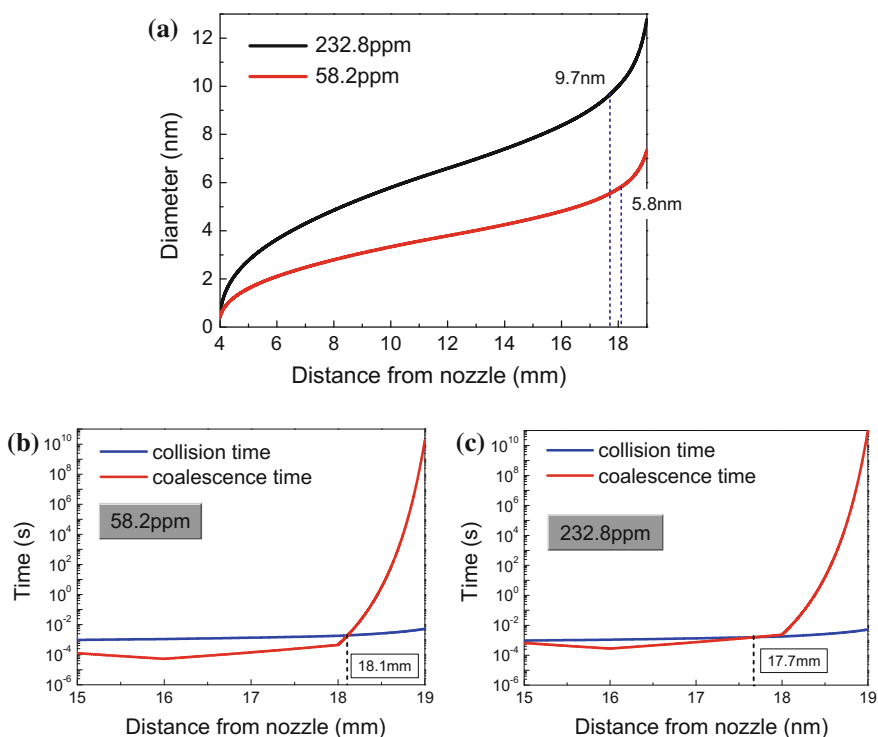


Fig. 2.8 a Particle size growth with the assumption of instantaneous coalescence and comparison of coalescence time and collision time for a precursor concentration of b 58.2 ppm and c 232.8 ppm

need to figure out the intersection point of coalescence and collision times. Figure 2.8b, c show the variation of coalescence and collision times along the axis, with coalescence time calculated by Eq. (2.8). The variation of coalescence time is much larger than collision time for its much stronger dependence on temperature. For 58.2 and 232.8 ppm case, the coalescence time exceeds the collision time at 18.1 and 17.7 mm away from nozzle exit, respectively. The intersection point slightly moves upstream for larger precursor concentration. After this point, the coalescence time rapidly increases so that the size of primary particle is nearly ‘frozen.’ Hence, we take the size at this intersection point to be the size of final products. We perform in situ thermophoretic sampling to investigate the morphology of particles in the flame, as shown in Fig. 2.9. The sampling position is 2 mm above the substrate, i.e., 17 mm away from the nozzle exit. It is shown that most particles keep monodisperse without aggregation, which agrees with the analysis that the coalescence time is shorter than the collision time up to this position.

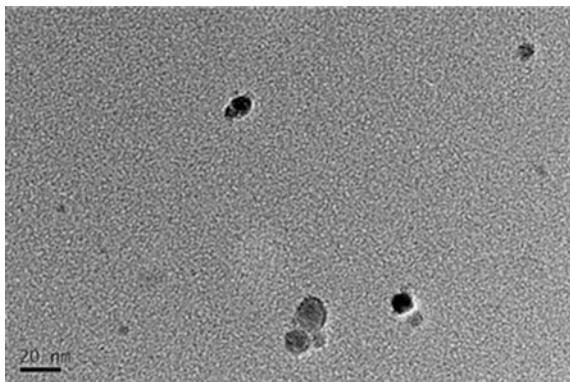
2.2.3 Modeling Results and Comparison with Experiments

Based on the analysis in Sect. 2.2.2, we are now able to predict the final size of TiO_2 nanoparticles. Considering that a universal theory for nanoparticle coalescence has not been established yet, besides Ehrman et al.’s (1998) formula (Eq. 2.8), we also check other two empirical formulas, i.e., Kobata et al.’s (2004) formula,

$$\tau_f = 1.19 \times 10^{18} T_p^4 \exp \left[\frac{258 \text{ kJ/mol}}{RT} \right], r_p \text{ in m}, \quad (2.15)$$

where r_p is particle radius, and Xiong and Pratsnis’s (1993) formula,

Fig. 2.9 TEM photograph of TiO_2 nanoparticles sampled by thermophoretic sampler at 2 mm above the substrate



$$\tau_f = 8.3 \times 10^{24} T d_p^4 \exp\left(\frac{3700}{T}\right), d_p \text{ in m.} \quad (2.16)$$

Figure 2.10 shows the modeling results of final particle sizes for different precursor concentrations. All the three coalescence formulas give fairly good agreement with average deviation below 20%, which validates the analysis and modeling based on GDE in Sect. 2.2.2. The modeling particle sizes are about 10% smaller than experimental results when using Ehrman's formula for coalescence time. And the trends with increasing precursor concentration are the same. The overall agreement is better when using Kobata's formula, but the deviation of the trend is larger, which suggests that Kobata's formula may underestimate the dependence on particle size. When using Xiong's formula, the agreement is very good below 232.8 ppm precursor concentration but rapidly becomes worse for larger precursor concentration. Above 465.6 ppm, we cannot derive any reasonable result by using Xiong's formula since the coalescence time appears to be longer than collision time at the very beginning. These facts suggest that Xiong's formula overestimates the dependence on particle size.

All the results in Fig. 2.10 show that the particle size significantly increases with precursor concentration. This is because the precursor concentration in lab-scale experiments is usually low, and thus collision time becomes the limiting factor for particle growth. It should also be noted that the increasing trend becomes slower for larger precursor concentration, as shown in the inset figure of Fig. 2.10. Since the coalescence time is more sensitive to particle size than collision time, the coalescence process will reach 'saturation' earlier as particles grow larger. The 'saturation' of coalescence termed here indicates that the coalescence time becomes comparable to particle residence time. Or from a view of operating parameters, the effect of precursor concentration drops while the residence time becomes more dominant, which is related to the global strain rate in the stagnation flame. The

Fig. 2.10 Particle size predicted by population balance modeling with different coalescence time formulas and comparison with experimental results

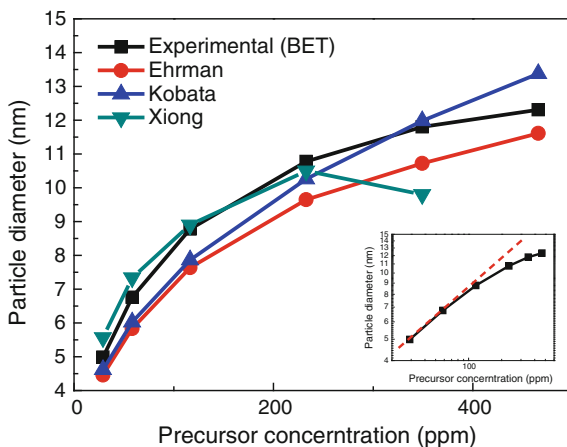
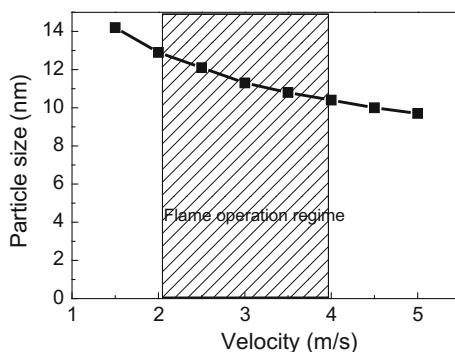


Fig. 2.11 Particle size variation with gas velocity at nozzle exit



saturation of coalescence is more significant in larger scale productions, which will be presented in Sect. 2.4.

Figure 2.11 shows the effect of gas velocity on the final particle size, with a precursor concentration of 232.8 ppm. The particle size exhibits a weak dependence on gas velocity because the saturation of coalescence is not reached yet at this precursor concentration. Actually for the premixed stagnation flame used here, the operational range of gas velocity is 2–4 m/s, which makes the possible effect of gas velocity even more limited.

Additionally, we also investigate the effect of equivalence ratio. By adjusting dilution ratio at the same time, the flame temperature is kept unchanged for different equivalence ratios. The experimental results show that the particle size and structure are basically not affected by equivalence ratio, which indicates that the formation of TiO_2 particles is not coupled with minor species in flame chemistry.

2.3 Synthesis of TiO_2 Nanoporous Films by Stagnation Swirl Flame

In a lot of applications, TiO_2 nanoparticles functionalize in the form of nanoporous films, for instance gas sensors (Tolmacheff et al. 2011), dye-supporting films in dye-sensitized solar cells (O'Regan and Gratzel 1991; Chung et al. 2012), photo-catalytic films for pollution degradation (Vorontsov et al. 1999). Stagnation flames can be used to synthesize nanoporous films in one step by direct deposition of in situ formed nanoparticles, which is already demonstrated in the case of gas sensors (Tolmacheff et al. 2011) and DSSC (Thimsen et al. 2008). We also successfully synthesized 5–0- μm -thick TiO_2 films with porosity higher than 95%, by placing a silicone plate on the water-cooling substrate. Figure 2.12 shows side view SEM photographs of TiO_2 nanoporous films synthesized in one step by stagnation swirl flame. The particle size before deposition is about 12 nm, and the substrate

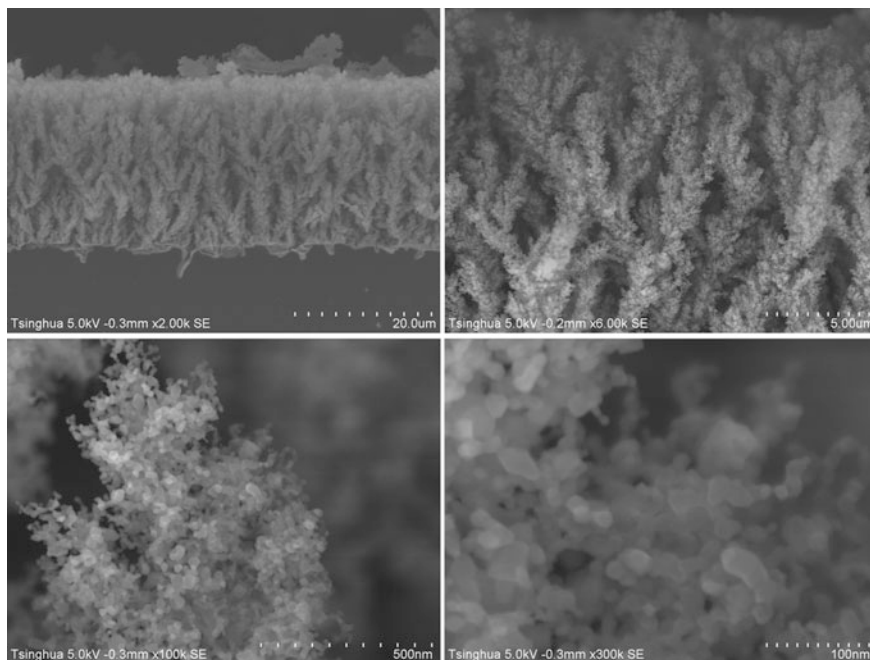
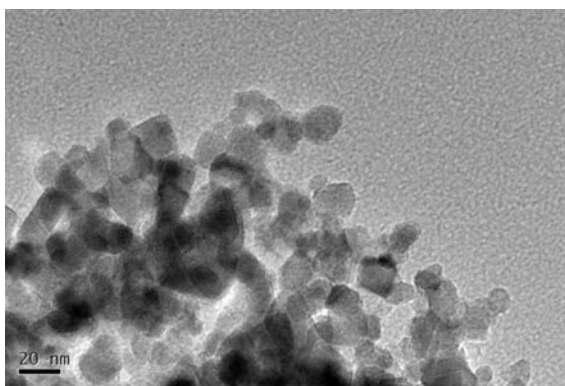


Fig. 2.12 Side view SEM photographs of TiO_2 nanoporous films synthesized in one step by stagnation swirl flame

Fig. 2.13 TEM photographs of primary particles that construct the deposited nanoporous film



temperature is 745 K. The four photographs are from the same sample with magnification ratio increasing from 2 to 300 K. The first photograph shows a tree-like structure ‘rooted’ on a silicon substrate. Larger magnifications reveal that this is a typical fractal structure with smallest units to be 15–20 nm primary particles. Figure 2.13 shows TEM photographs of primary particles that construct the film. The particle size is nearly 20 nm with significant necks, which indicates notable

sintering after deposition due to relatively high substrate temperature. The deposition of nanoparticles in stagnation flames will be discussed in details in Chap. 5.

2.4 Pilot-Scale Experiments of TiO₂ Nanoparticle Synthesis by Stagnation Swirl Flame

Based on the systematic analysis, a pilot-scale synthesis experiment was conducted to study scale-up characteristics of stagnation swirl flame. The combustor used is similar to the lab-scale experiment, with inner diameter enlarged to 33 mm. A horizontal reactor of 1.5 m length and 1 m diameter is chosen. TiCl₄ is chosen to be the precursor, which is heated to 120 °C and delivered by clean dry air. Flue gas goes through filtration and de-chlorine devices before ventilated. 20% of TiO₂ nanoparticles are collected from substrate, and 80% are collision from filtration device. Figure 2.14 shows the reactor and gas delivery system of pilot-scale synthesis setup. Figure 2.15 shows the flame with and without precursor feeding.



Fig. 2.14 The reactor and gas delivery system of pilot-scale synthesis setup

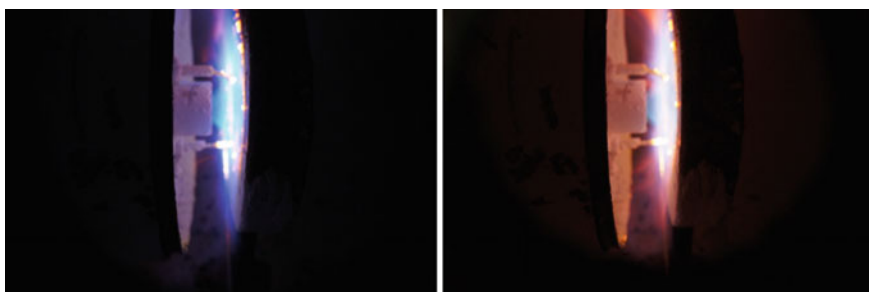
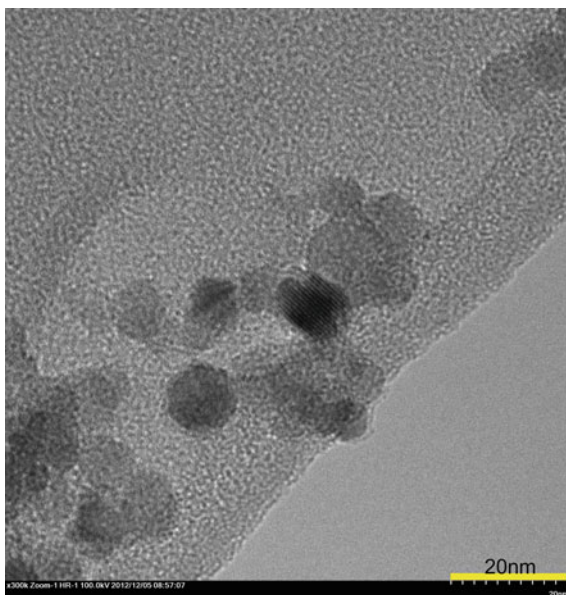


Fig. 2.15 The stagnation swirl flame in pilot-scale synthesis experiment with (*right*) and without (*left*) precursor feeding

Fig. 2.16 TEM photographs of collected particles, indicating a particle size below 20 nm



The precursor loading rate in the pilot-scale experiment is about 0.3 kg/h, which 200 times of lab-scale experiments. Considering that the combustor nozzle cross area is 3.36 times larger, the precursor loading per unit nozzle area is enlarged by 60 times. Section 2.2.3 mentioned that when precursor concentration increased by 4 times (from 58.2 to 232.8 ppm), particles size increases 1.6 times (from 6.76 to 10.78 nm), roughly scaling with cube root of precursor concentration. If this relationship holds up to pilot-scale experiment, the particle size would be 26.5 nm, corresponding to a SSA of $58 \text{ m}^2/\text{g}$. However, the SSA of TiO_2 particles synthesized by pilot-scale synthesis experiments is about $85 \text{ m}^2/\text{g}$, 47% higher than the cube root prediction. Figure 2.16 shows TEM photographs of collected particles, which indicates a particle size below 20 nm and agrees well with SSA measurements. These facts again verify the saturation effect of coalescence mentioned in Sect. 2.2.3, which demonstrates that when precursor concentration is high, the particle coagulation process is more limited by coalescence time, rather than collision time. Therefore, the relation between particle size and precursor concentration becomes weaker. Meanwhile, the effect of residence time becomes more dominant. In pilot-scale experiments, we found that the particle size is significantly reduced by decreasing nozzle-to-substrate distance. The saturation effect of coalescence is very important for industrial flame synthesis of nanoparticles because this effect ensures particle size to keep small when production rate scales up.

2.5 Summary

In this chapter, we successfully synthesized high purity anatase nanoparticles and nanoporous films by effectively combining swirl flame and stagnation flow. A simplified model based on aerosol dynamics equation is established to investigate the collision-coalescence process of nanoparticles in stagnation flames. The main conclusions are as following:

- (1) A novel flame configuration, stagnation swirl flame, is developed to synthesize high purity anatase nanoparticles with size below 10 nm. The collision-coalescence process is found to be dominant for particle morphology and structure, by comparing different characteristic time scales of chemical reaction, nucleation, collision, and coalescence. Based on the population balance modeling and parametric experiments, we investigate the effects of equivalence ratio, precursor concentration, and residence time. Particularly, for low precursor concentration situation, the particle size is limited by collision time and thus roughly scales with cube root of precursor concentration. For high precursor concentration situation, the coalescence of particles is easily 'saturated' and becomes the limiting factor. The effect of residence time turns to be more important, which is related to global strain rate of stagnation flames. The parametric study provides basis for scaling up synthesis. In pilot-scale experiments when precursor concentration is increased by 60 times, TiO_2 particle size only increases by 2.5 times, which again verifies the saturation of coalescence for high precursor loadings.
- (2) The particle size predicted by population balance modeling agrees well with lab-scale experiments. Different formulas of coalescence time are tested. For the conditions studied here, Kobata et al.'s (2004) formula underestimates the dependence on particle size while Xiong and Pratsnis's (1993) formula could not fit large precursor concentration. The overall agreement is best when using Ehrman et al.'s (1998) formula.

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