Effects of pressure and precursor loading in the flame synthesis of titania nanoparticles

Hong Zhao, Xiaofei Liu, Stephen D. Tse*

Department of Mechanical and Aerospace Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA

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ABSTRACT

The synthesis of TiO2 nanoparticles is investigated experimentally and computationally in low-pressure H2/O2/N2 burner-stabilized flat stagnation flames, using titanium tetra-iso-propoxide as precursor. The flow field is modeled with detailed chemical kinetics and transport, and is compared with measurements using laser-induced fluorescence to map gas-phase temperature and OH-radical species concentration. A sectional model, coupled with the simulated flow field and flame structure, is employed to model particle growth dynamics, computing aggregate particle size distribution, geometric standard deviation, and average primary particle size. The computations are compared with the experiments, for which in situ characterization of the nanoparticles in the flow field is accomplished by a low-pressure aerosol sampling system connected to a nano-scanning mobility particle sizer. Effects of operating pressure and precursor-loading rate on particle growth are examined experimentally and are compared with computational modeling. Higher pressures produce larger aggregate particles, but also smaller primary particles, due to longer residence times, as seen in both the experiments and computations. For higher precursor-loading rates, aggregate particle size is larger (for both experiments and computations), while primary particle size remains constant for the experiments and decreases slightly for the computations in the corresponding range.

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1. Introduction

Precursor-loading rate has been found to significantly affect primary particle size, aggregate particle size, crystallinity, and degree of agglomeration. Pratsinis, Zhu, and Vemury (1996) studied the effect of precursor-loading rate on the specific surface area (SSA) of synthesized particles. Injecting TiCl4 vapor into a concentric coflow CH4/Air/Ar flame, they found that the BET surface area of the synthesized TiO2 nanopowder was reduced for increased precursor-loading rates. However, different flame geometries (with different corresponding flame temperature profiles) presented different rates of decrease in the SSA. The results were attributed to higher coagulation rates for higher TiCl4 loadings, leading to increased sintering among the primary particles and thus decreased SSA. Arabi-Katbi, Pratsinis, Morrison, and Megaridis (2001) also found that increasing the precursor-loading rate resulted in larger primary particles, where increasing the flow rate of titanium tetra-iso-propoxide (TTIP) increased both the mass concentration of particles and the characteristic flame temperature. Higher flame temperatures and higher particle concentrations favored coagulation and sintering, leading to larger primary particles.

* Corresponding author. Tel.: +1 732 445 0449; fax: +1 732 445 3124.
E-mail address: sdytse@rci.rutgers.edu (S.D. Tse).
However, Briesen, Fuhrmann, and Pratsinis (1998) found that different precursors had different concentration effects on particle SSA. In making SiO₂ nanoparticles, they compared SiCl₄ and hexamethyldisilazane (HMDS) precursors, in a CH₄/O₂/N₂ premixed flame, finding that increased HMDS concentration decreased the SSA of the generated powders, whereas increasing the SiCl₄ concentration initially increased but then drastically decreased the SSA. These results indicated that increased coagulation rates from increased concentrations could not be the sole reason for changes in SSA. They then investigated the role of flame temperature in the precursor-loaded flames. For the HMDS-loaded flame, the organic component of the precursor increased flame temperature, which enhanced powder sintering, resulting in decreased SSA of the produced SiO₂ powder. For the SiCl₄-loaded flame, the presence of chlorine decreased the flame temperature. For their investigated concentration range, the increased coagulation rate at the relatively lower temperatures of their experiments would mainly enhance the aggregation of the particles, but not necessarily lower the SSA.

A few groups have investigated low-pressure flame synthesis. Glumac, Skandan, Chen, and Kear (1999) synthesized SiO₂ nanoparticles by injecting HMDS into a H₂/O₂ premixed flat flame. They found decreasing mean primary particle size with increasing HMDS concentration. The results were attributed to the increase of total equivalence ratio (due to the organic precursor) making the flames at higher precursor concentrations more oxygen deficient. Janzen and Roth (2001) produced Fe₂O₃ nanoparticles by injecting iron pentacarbonyl (Fe(CO)₅) into a 22.8 Torr H₂/O₂/Ar premixed flat flame. Increasing the precursor concentration had little effect on the primary particle size. In the same flame geometry, Simanjenkov, Ifeacho, Wiggers, Knipling, and Roth (2004) used tetramethyl germanium (Ge(CH₃)₄) as precursor to make germanium oxides. They found that higher precursor concentration led to the formation of larger primary particles. Chen (2000) observed a transition from large coalesced particles to small agglomerated primary particles as the precursor feed rate was increased.

As seen from above, the effect of precursor loading rate on particle growth can be intertwined with other parameters such as synthesis temperature, precursor chemistry, and flame geometry. In this work, specific parameters are isolated, while all others are fixed, in examining its influence.

The effect of pressure on particle characteristics needs more investigation, with most flame-synthesis studies having been conducted at one atmosphere. Early on, Xiong and Pratsinis (1991) calculated that increasing ambient pressure increased the geometric mean particle diameter of titania produced in a turbulent reactor (at 4, 7, and 10 atm), due to longer reactor residence times and higher particle concentrations. However, in low-pressure flame synthesis, Chen (2000) found that pressure had little effect on SiO₂ primary particle size, keeping total mass flow rate, fuel-to-oxidizer ratio, and other operating parameters constant. Using the same setup, Colibaba-Evulet (2000) found that, with increasing ambient pressure, XRD measurements of zirconia showed a very small increase in the crystalline size, while BET surface area measurements revealed constant primary particle size at different pressures. Orthner and Roth (2002) synthesized iron oxide powders in a hot wall flow reactor. In reducing the reaction pressure, the surface area of the powders increased due to shorter residence times associated with increased flow velocities from decreased pressures (for the same mass flow rate). More recently, Tsantilis and Pratsinis (2004) modeled titania formation by TTIP oxidation and found that particle size (diameter of average particle volume) increased with pressure (e.g., ~40 nm at 0.1 atm, ~92 nm at 1 atm, and ~144 nm at 10 atm, for 10 s residence time), although they have not been compared with experiments.

In the foregoing studies, the effect of ambient pressure is coupled with other factors. For example, pressure increase can result in not only hotter flames but also longer residence times (due to lower characteristic flow velocities for the same mass flow rate). Furthermore, for higher-pressure flames, the same precursor-loading rate results in a change in the initial precursor concentration. Therefore, it is difficult to identify which parameter mainly contributes to the final particle properties. Varying pressure will change the temperature profile if the H₂/O₂/N₂ ratios and the total mass flow rates are kept constant. In this work, the N₂ dilution ratio and total mass flow rates are purposely adjusted (while maintaining a constant equivalence ratio of ~0.4) to fix the temperature profile at 20, 30, and 40 Torr. Varying ambient pressure will change precursor-loading concentrations if precursor-loading rates are kept constant. Therefore, in this work, the initial precursor concentrations for different pressures are purposely fixed by adjusting the flow rates of carrier gas while keeping the bubbler temperature unchanged. With these strategies, we systematically investigate each aspect by performing flow field characterization, particle characterization (both in situ and ex situ), and particle growth modeling. Specifically, we examine the titania system, which apart from its potential fundamental contributions, is an important material in the manufacture of pigmentary TiO₂—a $9B/year business producing 4.5 million tons worldwide (Doan, 2006), as well as in the manufacture of anatase TiO₂, with its photocatalytic (Howe & Gratzel, 1987) and gas sensing (Fujishima, Hashimoto, & Watanabe, 1999) applications.

2. Experimental setup

2.1. Synthesis apparatus

The employed setup utilizes operation at low pressures, which increases characteristic gas-flow velocities (for the same mass flow rate) and increases thermophoretic velocities, minimizing residence time and thus aggregate particle size and agglomeration, as found in works by Glumac, Chen, and Skandan (1998), Glumac et al. (1999), and Singhal, Skandan, Glumac, and Kear (2001). The axi-symmetric, stagnation-point premixed flame (Fig. 1) is formed by flowing premixed reactants, seeded with chemical precursor vapor, through a flat-flame burner impinging onto a cold substrate. TiO₂ ceramic nanopowder is investigated. Liquid precursor, i.e. TTIP, is vaporized and entrained into a carrier gas via a heated (and temperature controlled) bubbling unit and then combined with inert (i.e. 99.999% N₂) and combustible premixed (i.e. 99.999% H₂ and 99.994% O₂) gases and delivered to
the burner. The flow system is metered with mass flow controllers, and the flow lines are heated (and temperature controlled) to prevent precursor condensation. The chemical precursors pyrolyze and oxidize in the flame and condense into nanoparticles as the gases cool upon reaching the substrate, where they deposit thermophoretically.

Utilizing an empirical relationship for vapor pressure of TTIP versus temperature, i.e. \( \log_{10}(P(Torr)) = 9.837 - \frac{3193.7}{T(K)} \) (Siefering & Griffin, 1990), and assuming the carrier gas to be completely saturated with precursor vapor, exiting the bubbler at a pressure \( P_0 \), the precursor-loading rate can be estimated from the relation (Hersee & Ballingall, 1990; Mayer, Collins, & Walton, 2001):

\[
F_r = \frac{F_c P_r}{P_0 - P_r},
\]

where \( F_r \) is the flow rate of the precursor vapor at the standard temperature and pressure (STP), \( F_c \) the flow rate of the carrier gas (set with the MFC) at STP, \( P_0 \) the pressure immediately downstream of the bubbler, and \( P_r \) the thermodynamic vapor pressure of precursor at the bubbler temperature. The bubbler temperature is set to 358 K, which corresponds to a vapor pressure of 8.2 Torr for all of the experiments. Eq. (1) gives a fairly accurate description of the reagent flow for output pressures in the range \( P_0 > 3P_r \).

Nevertheless, the amount of precursor delivered is also measured gravimetrically for the experiments, with the determined precursor-loading rate comparing very well with that calculated using the formulation above.

The burner is made of aluminum and is composed of an array of 360 holes that are 1.0 mm in diameter, arranged in a hexagonal pattern (~2 in in diameter). The synthesis reactor consists of a 47-cm diameter cold-wall stainless-steel chamber, which is maintained at the desired pressure by a vacuum pump, throttle valve, and closed-loop pressure controller. Both the burner and substrate are water-cooled, and their temperatures are fixed by temperature-controlled water baths/circulators. The chamber is configured with three orthogonal quartz view ports for optical access, and the entire chamber is mounted to a 3-axis positioner to enable spatial probing of the flame structure by laser-based diagnostics.

2.2. In situ laser-based diagnostics

Non-intrusive laser-based diagnostics (Fig. 2) are utilized in the experiments to obtain the axial temperature and OH concentration profiles. An injection-seeded, frequency-doubled, 532 nm Nd:YAG laser (Spectra-Physics Quanta Ray LAB-170) pumps a Sirah dye laser (PrecisionScan D-24) circulating Rhodamine 6G dye. The output of the dye laser is frequency doubled and then attenuated from 0.2 to 0.014 W by the use of beam splitters, which pass part of the laser beam to a photodiode for power monitoring. A 500 mm focal length fused-silica lens focuses the main beam to a small probe volume on the axial centerline between the burner and the substrate. Laser-induced fluorescence of the OH radical is collected at right angles to the excitation source with f/6 optics into f/6.5-imaging spectrometer (Acton SpectrPro-2558), with an ICCD camera (Princeton Instruments PIMAX: 1300 HQ) as detector. A 50 \( \mu \)m diameter pinhole allows for a 150 \( \mu \)m spatial resolution of the flow field. A 3600 g/mm UV grating and slit width of 100 \( \mu \)m gives an 11.5 mm spectral coverage with a resolution of 0.01 nm. The ICCD camera, with a 100 ns gate width, is externally triggered by the 10 Hz Q-switch pulse from the Nd:YAG laser.
The $Q_1(7)$ transition is chosen to measure the relative OH concentration profile, since the relative population does not change much over the range of temperatures in the setup (Ben-Yakar, Kamel, Morris, & Hanson, 1998), eliminating the need for temperature correction to the fluorescence signal profile. The uncertainty of OH concentration measurements is within ±5%.

For the two-line temperature measurements, $P_2(7)$ and $P_2(9)$ transitions of the $(1–0)$ band of the $A^2\Sigma → X^2\Pi$ are excited, as employed by Glumac et al. (1998). These transitions have similar values of $B(g_1 + g_2)/g_2$, where $B$ is the Einstein absorption coefficient and $g_1$ and $g_2$ are the upper and lower state degeneracies, respectively, so that the saturation effect on the derived temperature is reduced, and a linear steady-state regime can be assumed (Glumac et al., 1998). The uncertainty in the LIF temperature measurements is ±25 K.

2.3. In situ characterization of particle size distribution (PSD)

The synthesized nanoparticles are characterized in situ by spatially sampling the local aerosol in the flow field, quenching it quickly (to freeze further chemical reactions and particle growth through large volume dilution with nitrogen), and then sending the well-diluted aerosol to a nano-scanning mobility particle sizer (nano-SMPS). A novel low-pressure aerosol sampling system was designed (based on the works of Ober, Mayer, Buttner, & Ebert, 2002; Whitby & Hoshino, 1995) and constructed, coupling the probe with the commercial nano-SMPS instrument (TSI Inc. model 3085 nano-DMA and model 3025A ultrafine CPC) that operates at atmospheric pressure. This sampling system includes a translatable probe, an intermediate aerosol chamber, and three stages of dilution (as shown in Fig. 1) to enable proper characterization of the nanoparticles. The scanning particle size ranges from 2 to 67 nm. The design of the nano-DMA and its optimization for nanoparticle measurements are described by Chen et al. (1998).

To validate the operation of the sampling system for the nano-SMPS, the “memory effect” and the influence of $N_2$ dilution on the PSDs were assessed. The “memory effect” is associated with the process where a certain percentage of particles deposits on the walls of the aerosol chamber, the sampling probe, or the transport lines, and then re-enters the aerosol sampled in subsequent measurements. In order to check the significance of this effect, the synthesis chamber was purged and refilled with clean $N_2$ (to 20 Torr), immediately after aerosol sampling, and then re-sampled. The particle concentration was measured to be less than 50 cm$^{-3}$, which substantiated that any “memory effect” from a previous run of aerosol sampling is negligible.
When no flow or only a small flow rate is introduced at the first stage of N₂ dilution, the measured PSD is highly dependent on the flow rates, i.e. degree of dilution. Without the first stage of N₂ dilution (see Fig. 1), particles entering the sampling probe could coagulate faster and grow into larger particles during aerosol transport, resulting in a decrease in particle number concentration. Higher dilution flow rates would dilute the sampled aerosol more and effectively suppress particle coagulation and growth. On the other hand, higher flow rates could also entrain more particles (or aerosol) into the sampling probe, increasing inter-particle collision frequency. An optimum N₂ dilution of 0.6 L/min for the first stage to minimize such effects was determined experimentally.

2.4. Ex situ characterization

Dynamic light scattering (DLS) (Brookhaven ZetaPals particle sizer) measures the aggregate size of the synthesized nanopowder. Prior to DLS characterization, as-synthesized powders are dispersed in ethanol (8–10 mg/ml) and ultrasonicated for 30 min, to break down soft agglomerates. Multipoint Brunauer–Emmet–Teller (BET) (Gemini 2375, Micromeritics) nitrogen adsorption determines the specific surface area (SSA) and the equivalent BET primary particle size. X-ray diffraction (XRD) (Siemens D500 X-ray Diffractometer) obtains the phase composition, crystallinity, and crystallite size of the nanoparticles. Transmission electron microscopy (TEM) (TOPCON 002B) characterizes the morphologies of the synthesized nanoparticles and ascertains their grain sizes. High resolution TEM (HRTEM) reveals the atomic-level structures of the nanoparticles. Selected area diffraction (SAD) evaluates the crystallinity and phase composition of individual (and groups of) nanoparticles. Thermogravimetric Analysis (TGA) (Perkin-Elmer TGA 6.0) determines the extent of the precursor decomposition or conversion.

3. Computational modeling

3.1. Gas-phase flame structure

The axial gas-phase flame structure of the premixed flame in the experiment is simulated using the Sandia SPIN (Coltrin et al., 1991) code for stagnation flow geometry. Gas-phase and surface chemical kinetics are handled by CHEMKIN (Kee, Rupley, Meeks, & Miller, 1996) and SURFACE CHEMKIN (Coltrin, Kee, Rupley, & Meeks, 1996) subroutines, respectively, while variable transport properties are determined by TRANSPORT (Kee, Dixon-Lewis, Warnatz, Coltrin, & Miller, 1986). Conservation equations are solved for continuity, radial and circumferential momentum, thermal energy, and chemical species, along with a pressure-explicit equation of state. The detailed chemical kinetic mechanism of Mueller, Kim, Yetter, and Dryer (1999) for hydrogen chemistry involving nine species and 21 elementary reactions is applied for the gas phase.

The boundary conditions are: (i) experimentally specified inlet mass flux and temperature at the burner; (ii) no-slip condition and constant surface temperature at the substrate; (iii) recombination of H, O, OH, and HO₂ with unit sticking probability at the substrate surface; and (iv) the gas-phase mass flux of each species to the substrate \( j_k \) balanced by the creation or depletion of that species by surface reactions, i.e.

\[
\dot{j}_k = \dot{s}_k M_k \quad (k = 1, \ldots, K_g). \tag{2}
\]

The gas-phase mass flux of species \( k \) at the substrate is a combination of diffusive and convective processes, i.e.

\[
\dot{j}_k = \rho Y_k u + \rho Y_k V_k \quad (k = 1, \ldots, K_g), \tag{3}
\]

where \( V_k \) is the diffusion velocity of the \( k \)th species. The surface reactions of Aghalayam, Bui, and Vlachos (1998) are employed at the substrate, where surface recombination reactions are taken to have zero activation energy.

3.2. Particle growth

Two models are applied to simulate the nanoparticle growth dynamics: (i) a monodisperse model, which neglects the polydispersity of the aggregates and primary particles and (ii) a simplified sectional model, which allows for a particle size distribution.

3.2.1. Monodisperse model

The model developed by Kruis, Kusters, Scarlett, and Pratsinis (1993) is employed. We assume that (i) the precursor decays instantaneously at a fixed temperature (800 K) that is chosen based upon the location of the emission features in our metalorganic \( \text{H}_2/O_2 \) flames (Glumac et al., 1998); (ii) the critical size of homogeneously nucleated nanoparticles is 0.4 nm in diameter; (iii) the particle velocity is the same as that of the gas-phase at the location of instantaneous nucleation; and (iv) there is a negligible difference in time/temperature histories for particles that are formed at different radii near the centerline.

The characteristic coalescence time for fusion of two primary particles (Kobata, Kusakabe, & Morooka, 1991) and group-wise coalescence for aggregates (Giesen, Orthner, Kowalik, & Roth, 2004; Lehtinen, Windeler, & Friedlander, 1996; Schwade and Roth, 2004) are applied in the calculation of the aggregate characteristic coalescence time. The initial particle concentration at precursor decomposition is estimated from the precursor-loading rate and the total volume flow rate of the gas mixture. The density of the TiO₂ nanoparticles is taken to be the bulk density of \( 3.84 \times 10^3 \text{ kg/m}^3 \).
3.2.2. Sectional model

The 1-D, zero-order sectional model based on the work of Prakash, Bapat, and Zachariah (2003) is utilized and extended (e.g. for particle surface growth). As for the model above, group-wise coalescence of aggregates (as proposed by Lehtinen et al., 1996, and as applied by Giesen et al., 2004; Schwade & Roth, 2004) is applied. With an n-primary-particle aggregate divided into n/m groups, coalescence in aggregates occurs in steps, where the characteristic coalescence time for aggregates is defined as

\[ \tau_{cl} = \tau_{стал}(q, K, T) \sum_{i=1}^{n} \frac{1}{k_i} \frac{m}{A} \]

and

\[ k_i = \ln \left( \frac{n}{10^5} \right) \exp \left( -15155.16/T \right) \]

where \( A \) is the specific surface area of the aggregate, \( k_i \) is the rate constant for the \( i \)-th reaction, and \( T \) is the temperature. The driving force for condensation or evaporation depends on the difference between the vapor pressure of monomers and the Kelvin-effect-adjusted saturation vapor pressure for a particular particle size. Monomers of TiO₂ are given a diameter of 0.4 nm (the same as for the monodisperse model), corresponding to the volume equivalent diameter of a titania molecule.

3.3. Particle transport

Since the aerosol concentrations are dilute, we assume that aerosol dynamics do not affect mass and momentum transfer in the flow field. Particle surface growth can be a sink/source for gas-phase species that can affect particle growth rates, which is not treated in this work. Coupling chemistry and particle growth is a complex task (e.g. in terms of addressing the full precursor kinetic mechanism and individual species diffusion coefficients, within the overall mechanism for the reacting flow) that is also computationally intensive, and as such, is not addressed by most works. Moreover, there are many parameters involved for which the values are not known, and attempting such a detailed computation may actually introduce additional problems into the system, yielding less certain results. For example, the value of the H atom diffusion coefficient is not well known, much less those for intermediate Ti-based metalorganic intermediate species. Furthermore, many parameters are difficult to isolate (e.g. local flow velocity or temperature increase due to exothermic heat release from metalorganic precursor combustion), so the trend in primary particles growth from considering this coupling is not readily predicatable.

Although the coupling of gas-phase kinetics and particle growth can be important and has been addressed in a few works (Kremer et al., 2003; Sun, Axelbaum, & Davis, 2004), the present work aims to uncover physicochemical trends rather than produce quantitative matching of the experimental data in terms of particle growth dynamics; and we believe that our approach is valid. Our simplifications should be appropriate considering that we are working with extremely dilute concentrations of precursor vapor and particles, where source/sink species involved with gas-phase and particle interactions should affect the results (e.g. temperature, major species) of the overall detailed chemical mechanism negligibly. The main affecting contribution would be due to exothermic heat release from the metalorganic precursor, which would increase local temperatures slightly, as shown in Fig. 3. As we will be discussed later, such temperature effects (which can be accounted for without a rigorous coupling) likely dominate the system in terms of affecting particle growth.

As such, our solution procedure involves two steps. In the first step, the SPIN code solves the mass and momentum balance, as well as the energy equations to obtain the velocity profile, temperature profile, and thermodynamic properties. In the second step, GDE is solved making use of the solutions from the first step, and a Lagrangian approach is used to numerically compute the nanoparticle trajectory.

We solve the equation of motion for a spherical particle in a moving fluid subjected to Stokes viscous drag (including slip coefficient) and thermophoretic force (Sung, Law, & Axelbaum, 1994). The density of the solid particle is assumed to be much greater than that of the gas mixture, so that the pressure gradient force on the particle, the fluid resistance to an accelerating sphere, and the drag force associated with unsteady motion can be neglected.

4. Standard flame synthesis case (validation and benchmark)—local PSDs

A typical synthesis condition (\( \text{H}_2/\text{O}_2/\text{N}_2 = 1.0:1.2:0.75 \)) with a mass flux of 2.498 mg/s/cm² and a precursor-loading rate of 3.83×10⁻⁴ mol/min at 20 Torr) is specified as the standard case, which has been optimized to obtain nanoparticles with small primary particle sizes and high crystalline structure. Using the nano-SMPS, particles are sampled in situ at discrete axial locations in the flow field and measured for their size and particle size distribution (PSD), which is then compared to particle growth simulations using monodisperse and sectional models. Nanoparticles collected from the substrate are characterized post-experiment to ascertain their aggregate particle size, primary particle size, phase, crystallinity, morphology, specific surface area, and extent of pyrolysis.
4.1. Flame structure characterization

The gas-phase flame structure is simulated using the Sandia SPIN code, which assumes a quasi-1-D stagnation flow. The flame structure is then probed in situ using laser-induced fluorescence (LIF) to map the OH radical concentrations and gas-phase temperature distributions along the axial centerline. By comparing the simulation and measurements, the nature of the material processing flow field is revealed.

The temperature and OH concentrations profiles in the same synthesis flame with and without the addition of precursor TTIP (with a typical precursor loading rate of $3.83 \times 10^{-4}$ mol/min) are given in Fig. 3. The addition of precursor (TTIP) has only a small effect on the flame temperature. Increasing OH concentrations are observed on the burner side of the reaction zone, and the peak value increases by about 10%. However, closer to the substrate side, the decay of OH concentration is similar to that without precursor. This behavior is similar to that seen in hydrogen/oxygen flames to which a trace hydrocarbon is added, showing that the precursor decomposes in a manner similar to a hydrocarbon fuel additive (Glumac et al., 1999).

Usually the loading of a precursor will increase the flame temperature compared to the precursor-free flame, due to oxidation of TTIP and further oxidation of intermediate products such as C$_3$H$_6$. The carbon content can be presumed to have burned away by the midway point of the burner-substrate-gap as seen from the OH concentrations given in Fig. 3. On the other hand, the presence of TiO$_2$ particles can increase radiative losses from the flame (as seen from the strong luminescence when the precursor is loaded—the result of particle incandescence thermally radiating at high temperatures), lowering the flame temperature. These two factors seem to cancel each other out, which might be the reason that the gas-phase temperatures with precursor loading only experience a slight temperature increase (2%, 28 K in Fig. 3) over that of the precursor-free flame. This is an important result because, in our particle modeling effort, we use the TTIP-free flame temperature distribution.

4.2. In situ aggregate particle size

The in situ aggregate PSDs of the as-synthesized nanoparticles, along the axial centerline of the flow field for different locations from the burner to the substrate, are fit very well by log-normal functions, consistent with most single-source aerosols (Hinds, 1982). The width of the log-normal distribution (geometric standard deviation, GSD) is 1.19 at 5 mm from the burner, and increases to 1.32 and 1.35 at 10 and 20 mm, respectively, showing particle growth extending to larger particle size ranges. It is not surprising to see that the mean particle size also increases from 7.90 to 10.5 to 13.2 nm with increasing distance (and residence time) from the burner.

In comparing the measured PSDs with the computations from the sectional model, we consider continued particle growth within the sampling line and the aerosol chamber, from when particles enter the sampling probe until they arrive at the nano-SMPS inlet. Within the sampling system, we find that only particle-to-particle coagulation occurs, since coalescence is suppressed at room temperature, and other particle growth mechanisms (i.e. nucleation and surface growth) are negligible. From the in-take of the aerosol to the sampling probe to the transport of the aerosol to the nano-SMPS inlet, four steps comprise our setup. For the given flow and dilution rates, it takes: (i) 4 ms for the aerosol to traverse the 6-cm sampling probe with the temperature assumed to decrease linearly from 1600 to 300K; (ii) 8 s flow time with a dilution ratio $f_{d_1}$ for the first stage of N$_2$ dilution; (iii) 20 s to bring the aerosol pressure in the intermediate chamber to 1 atm (this second dilution does not change the particle number.
Fig. 4. Comparison of the nano-SMPS results and the simulations, for the 20 Torr standard synthesis condition: (a) at 5 mm from the burner, (b) at 10 mm from the burner, and (c) at 20 mm from the burner.

concentration during this process); and (iv) 130 ms to transport the diluted aerosol to the nano-SMPS inlet with another dilution ratio $f_{d2}$ for the third stage of dilution (see Fig. 1).

Fig. 4 compares the nano-SMPS measurements and the computations at different locations along the axial centerline of the flow field. Step 0 represents the aggregate PSD simulated at the sampling locations within the flow field at the tip of the sampling probe. Step 1 signifies the PSD when the aerosol arrives at the end of the 6-cm sampling probe. Step 2 denotes the PSD of the aerosol when the pressure of the intermediate chamber is raised to 1 atm. Step 3 represents the PSD when the diluted aerosol arrives at the nano-SMPS inlet. The normalized PSDs of steps 2 and 3 are identical, showing that the aerosol transported to the nano-SMPS in the last stage no longer experiences particle growth. The vertical dashed line indicates the aggregate particle size as computed by the monodisperse model. As expected, the aggregate particle sizes computed by the monodisperse model are larger than that computed by the sectional model as well as that measured in the experiments.

The sectional model simulation results match well with the nano-SMPS results as shown in Fig. 4. Fig. 4(a) shows the early dominance of combined nucleation and surface growth, resulting in nearly monodisperse particles (or narrower particle size distribution) at 5 mm from the burner as well as the subsequent dominance of coagulation leading to the self-preserving distribution at 10 mm (Fig. 4(b)) and at 20 mm (Fig. 4(c)). The mean particle diameters measured at different locations are in good agreement with the sectional model simulation; however, a slight discrepancy in the GSD exists for all of the probing locations between the measurements and the simulations, with the lognormal distribution for the experimental data narrower than that for the computations.

At an axial location of 5 mm downstream from the burner, the simulation predicts a bi-modal distribution due to nucleation (see step 0 of Fig. 4(a)). At the same time, surface growth decreases particle number concentration in the smaller size range while increases the particle number concentration in the larger size range. However, particle growth occurs within the sampling probe because small particles and/or monomers quickly form larger particles by coagulation due to the initially high temperature in the probe. As a result, the in situ bi-modal distribution existing in the flow field cannot be detected by the nano-SMPS due to particle evolution in the sampling probe itself.

4.3. Ex situ characterization of nanopowder collected from substrate (post-experiment)

Fig. 5 shows the aggregate PSD, as obtained using DLS, using the number-weighted and the volume-weighted methods, respectively. The number-weighted hydrodynamic diameter is a single mode distribution with a mean hydrodynamic diameter
of 16.4 nm, while the volume-weighted hydrodynamic diameter is a multimode distribution with mean hydrodynamic diameters of 17.5 and 69.0 nm. This multimode volume distribution is also observed by others (Friedlander, 2000). The sectional model simulation predicts a final aggregate particle size of 18.2 nm, which agrees well with the DLS measurement, if only the single mode or the first mode of the multimode distribution is considered.

When the equivalent solid sphere diameter is much smaller than the gas mean free path, overall chemical-reaction rate is rapid, and particle growth is dominated by coagulation in the free molecular regime rather than by surface reaction. In this case, particles grow by Brownian coagulation and reach an asymptotic distribution. The GSD of the produced nanoparticles is 1.55, which is a little-bit higher than that for the limit of polydispersity of particles grown by coagulation (i.e. 1.46 for spherical particles in the free molecular regime, Landgrebe & Pratsinis, 1989). The sectional model simulation predicts a GSD value of 1.463 for particles reaching the substrate. However, the broader particle size distribution found in our experiments is reasonable and not unexpected, considering that non-spherical aggregate particles can possess a GSD of 1.61 (Vemury & Pratsinis, 1995), with a given fractal dimension, in the free molecular regime.

XRD confirms that the nanoparticles are predominantly anatase, with the rutile phase determined to be less than 5% weight fraction of the produced powder. The crystalline size is calculated to be 4–8 nm from Scherrer’s equation. Although rutile is thermodynamically more stable than anatase, anatase is readily formed at low temperatures due to its relatively fast crystallization kinetics (Rulison, Miquel, & Katz, 1996). In our flame, the peak temperature is ∼1600 K. Formation of rutile from anatase requires about 1 s of residence time at 1473 K to finish the atomic rearrangement (oxygen atoms are in a distorted face-centered cubic arrangement for anatase, while for rutile, they are in a distorted hexagonal arrangement, Shannon & Pask, 1964). However, in our synthesis flow field, the particle residence time is about 12–30 ms. Therefore, the low temperature history, the short residence time, and the fast crystallization kinetics for anatase are the main reasons for the dominance of anatase in this flame synthesis configuration, consistent with other flame synthesis studies, e.g. Akhtar, Xiong, and Pratsinis (1991) and Ehrman, Friedlander, and Zachariah (1998).

HRTEM imaging (Fig. 6) reveals the polyhedral shape of the nanoparticles, along with the lattice fringes, showing the well-defined atomic structures. The inset shows the SAD ring pattern, which matches all of the peaks obtained from the XRD pattern, further confirming that the TiO2 nanoparticles are polycrystalline anatase. A statistical evaluation of 120–150 particles from the TEM images reveal primary particles that exhibit a narrow size distribution, with an average primary particle size of 6.09 nm. The mean primary particle sizes predicted by the monodisperse and sectional models are a bit larger, at 8–9 nm.

The SSA of the as-synthesized TiO2 nanoparticles is determined using BET, and found to be 254.8 m2/g. Assuming uniform spherical particles, the surface area equivalent particle size is calculated to be 6.13 nm, which compares well with the average primary particle size deduced from TEM imaging.

TGA measurement assesses the extent of pyrolysis or conversion efficiency of the precursor. The initial weight loss, up to a temperature of 473 K, is due to the loss of water physically adsorbed on the surfaces of nanoparticles. From 473 to 1173 K, the 3.5% weight loss is attributed to release of bound water. This weight loss percentage is consistent with other flame-made titania powders, e.g. Muller, Kammler, Wegner, and Pratsinis (2003), with an SSA of 235 m2/g and no detectable impurities. The TGA data indicates that the precursor (TTIP) is almost fully pyrolyzed under this standard flame synthesis condition. This result is in agreement with the computations (Fig. 7), which show that the conversion of TTIP completes within a quarter of the substrate-burner-gap, i.e. ∼1 cm from the burner.

5. Results and discussion

The parametric cases examined in this work are summarized in Table 1. For flames at 20, 30, and 40 Torr, almost identical temperature profiles are achieved by strategically adjusting the N2 dilution ratio (which does not affect the equivalence ratio) and total mass flow rates. Fig. 8 shows the computed temperature profiles, for the flame conditions listed in Table 2.
The aggregate particle sizes of the as-synthesized TiO$_2$ nanoparticles are obtained using DLS. The left column of Fig. 9 shows the aggregate PSDs for cases 1, 2, and 3 (examining the pressure effect) of Table 1 using the number-weighted method. Statistical evaluation of the TEM images (of 120–150 particles) give the primary particle size distribution and average diameter, as shown in the right column of Fig. 9. As can be seen, the primary particles exhibit a narrow particle size distribution. The evaluation of
### Table 1
Summary of the experimental cases investigated.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Cold gas velocity (cm/s)</th>
<th>Pressure (Torr)</th>
<th>Precursor-loading rate (initial precursor concentration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>20</td>
<td>$6.3864 \times 10^{-4}$ mol/min ($8.0 \times 10^{21}$ #/m$^3$)</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>30</td>
<td>$4.68337 \times 10^{-4}$ mol/min ($8.0 \times 10^{21}$ #/m$^3$)</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>40</td>
<td>$3.83185 \times 10^{-4}$ mol/min ($8.0 \times 10^{21}$ #/m$^3$)</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>30</td>
<td>$3.83185 \times 10^{-4}$ mol/min ($6.5 \times 10^{21}$ #/m$^3$)</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>30</td>
<td>$2.8101 \times 10^{-4}$ mol/min ($4.8 \times 10^{21}$ #/m$^3$)</td>
</tr>
</tbody>
</table>

$\text{H}_2/\text{O}_2(\phi = 0.42)$, TTIP bath temperature $= 358 \text{ K}$, maximum flame temperature $1620 \pm 20 \text{ K}$, burner-substrate-gap $= 4 \text{ cm}$.

*Precursor-loading rates at 20 Torr (case 1) and 40 Torr (case 3) are calculated to obtain equal precursor-loading concentrations as that at 30 Torr (case 2).

![Fig. 8. Temperature profiles of the synthesis flames at 20, 30, and 40 Torr.](image)

### Table 2
Operating parameters of the experiments.

<table>
<thead>
<tr>
<th></th>
<th>Fuel $\text{H}_2$ (L/min)</th>
<th>$\text{O}_2$ (L/min)</th>
<th>$\text{N}_2$ (L/min)</th>
<th>Carrier $\text{H}_2$ (L/min)</th>
<th>Total mass flow flux (g/s/cm$^2$)</th>
<th>Flow velocity (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 Torr</td>
<td>1.1820</td>
<td>1.4338</td>
<td>0.8720</td>
<td>0.03083 (case 1)</td>
<td>$2.519 \times 10^{-3}$</td>
<td>150</td>
</tr>
<tr>
<td>30 Torr</td>
<td>0.9015</td>
<td>1.0935</td>
<td>1.8416</td>
<td></td>
<td>$3.064 \times 10^{-3}$</td>
<td>110</td>
</tr>
<tr>
<td>40 Torr</td>
<td>0.7943</td>
<td>0.9635</td>
<td>2.4275</td>
<td></td>
<td>$3.480 \times 10^{-3}$</td>
<td>90</td>
</tr>
</tbody>
</table>

these particles through observation of lattice planes and the SAD ring patterns divulge that the TiO$_2$ nanoparticles produced in all of the cases are crystalline anatase.

#### 5.1. Precursor-loading rate effect

At the same ambient pressure (i.e. 30 Torr), aggregate particle size increases with increasing precursor-loading rates, for the experiments (see Fig. 10). With more precursor vapor in the flame, the initial particle number concentration increases, resulting in higher coagulation rates and larger denser aggregates of primary particles with more contact points between them.

Interestingly, but not surprisingly, the primary particle sizes are smaller (albeit only slightly) when applying larger precursor-loading rates, for the experiments (see Fig. 10). Coalescence between the contacting primary particles within an aggregate is limited by the longer coalescence time associated with a moderate flame temperature. At sufficiently high temperatures,
Fig. 9. Left column: aggregate PSDs by DLS. Right column: primary particle size distribution from TEM image counting. (a) Case 1, (b) Case 2, and (c) Case 3 of Table 1.

c o a l e s c e n c e of particles can cause a rapid sintering regardless of the magnitude of precursor loading. In the works of Arabi-Katbi et al. (2001) and Zhao et al. (2005), temperatures in the flame zone are as high as 2000 K, enabling instantaneous sintering of primary particles. Under such conditions, the primary particle sizes always increase as the precursor-loading rate increase. In contrast, at moderate or lower temperatures, the collision time can be shorter than the group-wise coalescence time, resulting in agglomeration or partial coalescence. Then, the primary particle sizes either decrease, e.g. Glumac et al. (1999), or do not change much as the precursor-loading rates increase, e.g. Janzen and Roth (2001). For the concentration range involved in this work, the increased coagulation rate at the relatively low temperatures (~1620 K peak temperature) would mainly increase the aggregation of the particles, leading to larger aggregate particles but not necessarily larger primary particles. Instead, smaller primary particle sizes result when increasing the precursor-loading rate, due to formation of larger aggregates and their correspondingly longer coalescence times.

The LIF measurements indicate that the maximum flame temperature increases by only 2.0% (28 K) with the addition of TTIP at low pressures, which helps to explain the nearly constant primary particle size. At atmospheric pressure, Arabi-Katbi et al. (2001) noticed a high temperature increase, up to 17%, in the adiabatic flame temperature over that of a TTIP-free flame, when increasing the TTIP loading rates in their CH₄/O₂ premixed flame. As a result, their change in primary particle size was significant.

For the cases at 20 Torr, an increase in aggregate particle size and a slight decrease in primary particle size are also obtained, similar to the 30 Torr case when increasing the precursor-loading rate from 3.83185×10⁻⁴ to 6.3864×10⁻⁴ mol/min (case 1), as
explained by the reasons above. Therefore, two competing mechanisms affect primary particle growth in this flame synthesis system. Group-wise coalescence within aggregates limits primary particle growth for larger precursor-loading rates, while increased organic-based precursor loading results in higher flame temperatures, which enhance fusing and growth of the primary particles.

The three precursor-loading rates at 30 Torr (experimental cases 5, 4, and 2, respectively) are simulated using both monodisperse and sectional models. The temperature residence time histories are almost identical for all of the precursor-loading rates investigated, as shown in Fig. 11. In calculating TTIP conversion, we find that they are the same for different precursor-loading rates. However, the number of monomers obtained from decomposition of the precursor is proportional to the precursor-loading rate, which gives slightly different nucleation rates and GSDs. Eventually, the GSDs converge to a similar value between 1.463 and 1.464, for different precursor-loading rates.
When increasing the precursor-loading rate, the aggregate particle size increases as shown in Fig. 12, which agrees with the experimental data. Quantitatively, the experimental values themselves are within the range spanned by the monodisperse and sectional models. Primary particles display a size decrease as shown in Fig. 13, with increasing initial precursor concentration. Again, the experimental values are quantitatively within the range predicted by the monodisperse and sectional models; however, the experimental size of the primary particles is weakly affected by precursor loading whereas the theoretical results predict a considerable influence. The reason for this is not clear, and needs more study. It is worth noting that in the computations, temperature increases due to precursor addition, though small (see Fig. 3), was not considered. Small temperature increases can significantly shorten characteristic coalescence times, which go nonlinearly as $T \exp(\text{const}/T)$, and thus increase primary
Fig. 14. Aggregate particle sizes (mass equivalent diameter) for different ambient pressures. SM: sectional model. MM: monodisperse model. Experimental data are: 20 Torr: 17.3 nm; 30 Torr: 31.5 nm; 40 Torr: 33.4 nm.

particle sizes. Coupling chemistry/transport and particle growth in the simulations would be the most correct manner to make the predictions for primary particle size.

The relationship of the precursor-loading rate versus particle size is illustrated in Fig. 10, with three smaller loading rates simulated using the sectional model. The aggregate particle size increases monotonically as the precursor-loading rate increases, agreeing with the experimental results. When the precursor-loading rate is sufficiently large, the assumption of homogeneous nucleation may not be valid since unpyrolyzed TTIP precursor molecules could initiate heterogeneous nucleation.

Fig. 10 shows the trend for primary particle size. Starting from a sufficiently small precursor loading concentration, i.e. $1.5 \times 10^{21}$ #/m$^3$, the primary particle size increases as the precursor-loading rate increases until it reaches a peak value at a precursor-loading concentration of $\sim 3.5 \times 10^{21}$ #/m$^3$. As a larger flow rate of carrier gas brings more precursor vapor into the flame, the initial particle number concentration increases, resulting in higher collision rates. Under these conditions, the flame temperature/enthalpy can handle the fusing of more primary particles within the larger aggregates (due to larger precursor-loading rates), which leads to larger primary particles. When the precursor-loading rate continues to increase after this threshold, the primary particle size decreases since the longer characteristic coalescence time for the larger aggregates impedes fusing of the primary particles, and the primary particle size freezes at a smaller value.

However, the experimental results show a nearly constant primary particle size with increasing precursor-loading rates. For the purpose of verification, an additional experimental datum is taken at 30 Torr with a loading concentration of $3.5 \times 10^{21}$ #/m$^3$.

The primary particle size does not experience the increase as predicted by the simulation, meriting further study. Thus, in combining Figs. 12 and 13 with Fig. 10, it seems that the present theoretical work may not completely explain the primary particle data nor predict further data points, especially if extrapolated to flame-made TiO$_2$ at atmospheric pressure (which is characterized by shorter characteristic coalescence times and larger primary particle sizes).

5.2. Ambient pressure effect

To examine the ambient pressure effect, experiments are performed at different pressures of 20, 30, and 40 Torr, for the same precursor-loading concentration, i.e. case 1, case 2, and case 3 as given in Tables 1 and 2. The temperature profile and the precursor-loading concentration are fixed for all of the cases. The residence time of the particles increases with increasing ambient pressure due to lower flow velocities (and thus particle velocities). As a result, particles still experience different temperature residence time histories.

It is not unexpected that larger aggregate particles are obtained at higher ambient pressures (Fig. 14) due to longer particle growth times. The particles, residing in the hot flame zone for a longer time, experience more particle-to-particle collisions producing larger aggregate particles.

Interestingly, the primary particle size, counted from TEM images, decreases at higher pressures (Fig. 15). Under our conditions (with peak temperature of $\sim 1620$ K), it seems that characteristic coalescence times are longer than coagulations times, inhibiting sintering and growth of primary particles, resulting in larger aggregate particle sizes. In comparing the standard synthesis condition (20 Torr) with case 5 (30 Torr), which have the same precursor-loading concentration, a similar trend is evinced: an
increase in the aggregate particle size and a decrease in the primary particle size under higher ambient pressures. The three different ambient pressures of 20, 30, and 40 Torr (experiment cases 1, 2, and 3 with the same precursor-loading concentration of $8.0 \times 10^{21}$ #/m$^3$) are also computationally investigated. Re-iterating, the pressure effects on particle growth are isolated during their stay in the flame zone by purposely fixing the temperature profiles (Fig. 8).

Fig. 16 shows the temperature residence time histories for the particles produced at 20, 30, and 40 Torr, respectively. At a lower ambient pressure, calculated TTIP conversion (Fig. 17) completes at a position farther away from the burner, due to the higher flow field velocity. The curves of the nucleation rate and the GSD shift towards the substrate correspondingly. Nevertheless, the GSDs all finally converge to a very close value between 1.462 and 1.464. Therefore, at a higher ambient pressure, the lower flow field velocity delays the traveling of particles in the flame resulting in larger aggregate particles. Concurrently, the primary particle size is smaller at higher pressures for the investigated precursor-loading concentration. These trends in the aggregate and the primary particle sizes obtained by the simulations agree well with the experimental results, for different ambient pressures,
as shown in Figs. 14 and 15. Again, evolution of the primary particle size is a function of both temperature residence time history and characteristic coalescence time (under group-wise coalescence) for the aggregates.

6. Conclusions

A typical synthesis condition is employed to validate and benchmark the particle growth models by in situ sampling and PSD characterization using a nano-SMPS. The as-synthesized TiO₂ nanoparticles are characterized to be well-crystallized anatase, with a high SSA. Both aggregate particle size and primary particle size are evaluated to be smaller than that produced in other flame synthesis studies, e.g. coflow diffusion flame at 1 atm (Kammler, Jossen, Morrison, Pratsinis, & Beaucage, 2003). The precursor TTIP is almost fully pyrolyzed leaving negligible residue in the particles.

The simulations of the monodisperse and sectional models show similar trends in particle growth for different precursor-loading rates and ambient pressures. The similarity confirms that the main (and competing) particle growth mechanisms in our flame synthesis system are coagulation and coalescence. Compared to the experimental results, both monodisperse and sectional models predict the trends very well, especially for the aggregate particle size. The experiments show an almost constant (slightly decreasing) primary particle size with increasing precursor loading and ambient pressures, whereas the simulations indicate an obvious decrease in the primary particle size. There are two likely reasons that may contribute to this discrepancy. One is that the temperature of the precursor-loaded flame does experience an increase (albeit small), especially with increasing precursor-loading rates. Higher temperatures will facilitate fusing of the primary particles and result in larger primary particle sizes. This effect will narrow the differences of the primary particle sizes between different precursor-loading rates. Another (and more likely) reason might be due to parameters in the coalescence model, affecting primary particle growth. In atmospheric synthesis, the instantaneous sintering of primary particles into aggregates is most likely dominant, as predicted in the modeling effort of Tsantilis and Pratsinis (2004). Many coalescence models (Ehman et al., 1998; Kobata et al., 1991; Xiong & Pratsinis, 1993) have also been applied leading to different characteristic coalescence times, assuming two or more particles coming together to become a single spherical particle. In our models, a group-wise coalesce model is applied, where coalescence in a large aggregate occurs between the neighboring m (= 3) primary particles only. Thus coalescence in aggregates is assumed to occur in steps versus in one step, significantly affecting the characteristic coalescence time of the aggregates, which consequently affects the growth of primary particles.

Moreover, some other coalescence effects that could affect primary particle growth are not applied in this modeling effort. For example, sufficiently small particles will have a lower particle melting surface temperature $T_{ms}$ (due to the interface curvature effects); and therefore a larger surface diffusion coefficient would be present until the primary particles stop growing under this prevailing condition (Xing & Rosner, 1999). In another scenario, when two particles coalesce, the formation of new chemical bonds results in energy release, and therefore a significant increase in the particle temperature (Lehtinen & Zachariah, 2001), which would reduce the coalescence time significantly.

Nevertheless, for the most part, the computed aggregate particle sizes agree to within 30% of the experimental results as well as follow the same trend. The primary particle size is within the range predicted by the monodisperse and sectional models. The two models serve as good first estimations in predicting particle properties.
The effects of precursor-loading rate (precursor concentration) and ambient pressure (particle residence time) are examined experimentally for identical temperature profiles. A higher precursor-loading rate produces larger aggregate particles, composed of almost constant-sized (actually slightly smaller) primary particles. A higher pressure produces larger aggregate particles and smaller primary particles. Therefore, in general, the aggregate particle size increases as the residence time or the precursor concentration increase, while evolution of the primary particle size is related to the number of primary particles within aggregates, particle residence time, and temperature. For all cases, crystalline anatase TiO₂ nanoparticles are produced under these flame synthesis conditions.

The effects of precursor-loading rate and ambient pressure are also investigated using the two modeling simulations. The obtained trends are very similar for the monodisperse and sectional models, which confirm that the main (and competing) particle growth mechanisms are coagulation and coalescence. The simulation predicts well the trend in the aggregate particle size for different precursor-loading rates and different ambient pressures. The experimental data is within the range of sizes bracketed by the monodisperse and sectional model predictions.

In comparing the present data and theory with that of flame-made spherical TiO₂ by TTIP oxidation at atmospheric pressure, as found in other works, the main experimental differences are in characteristic residence times and temperatures, associated with pressure, which significantly affect particle properties. Compared to atmospheric-pressure synthesis, low-pressure synthesis is characterized by reduced residence times for given mass flow rates, due to increased flow velocities. This implies that (i) the synthesized particles spend substantially less time in the hot flame zone and (ii) the particles experience fewer potentially agglomerating particle-to-particle collisions, resulting in decreased particle sizes and narrowed particle size distributions. Our residence time is ~20 ms (as shown in Fig. 11), while that for atmospheric-pressure premixed flame synthesis can be ~200 ms (Arabi-Katbi et al., 2001; Tsantilis et al., 2002; Tsantilis & Pratsinis, 2004) and that for diffusion flame synthesis can be ~50–100 ms (Johannessen, Pratsinis, & Livbjerg, 2001).

The characteristic temperatures (peak T~1600 K) in our low-pressure flame synthesis studies are relatively low compared to those (peak T~1900–2400 K) found in atmospheric premixed flame synthesis studies (Arabi-Katbi et al., 2001; Tsantilis et al., 2002; Tsantilis & Pratsinis, 2004). Low temperatures favor anatase formation and high SSA. Moreover, in atmospheric diffusion flame studies, the temperature at the end of flame region can be relatively high—e.g. ~700 K, e.g. Johannessen et al. (2001), where particle growth may not yet be quenched. Thus, atmospheric flame synthesis studies can easily encounter larger particle sizes with more rutile content (Arabi-Katbi et al., 2001). Nevertheless, similar to our results, Johannessen et al. (2001) showed that for atmospheric flames, those with shorter residence times and lower flame temperatures produced powders with dramatically reduced primary particle sizes.

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