Control of nanoparticle size and agglomeration through electric-field-enhanced flame synthesis

Hong Zhao · Xiaofei Liu · Stephen D. Tse

Received: 8 November 2007 / Accepted: 15 November 2007 / Published online: 6 December 2007
© Springer Science+Business Media B.V. 2007

Abstract The isolated study of electrophoretic transport of nanoparticles (that are innately charged through thermionic emission), with no ionic wind, has been conducted under uniform electric fields. Titania nanoparticles are produced using a burner-supported low-pressure premixed flame in a stagnation-point geometry from corresponding organometallic vapor precursor. The material processing flow field is probed in-situ using laser-induced fluorescence (LIF) to map OH-radical concentrations and gas-phase temperatures. The experimental results of particle growth under different applied electric fields are compared with computations using monodisperse and sectional models. The results show that such electric field application can decrease aggregate particle size (e.g. from 40 to 18 nm), maintain metastable phases and particle crystallinity, and non-monotonically affect primary particle size (e.g. from 6 to 5 nm) and powder surface area. A specific surface area (SSA) for anatase titania nanopowder of 310 m²/g, when synthesized under an applied electric field of 125 V/cm, is reported. Results are also given for the synthesis of alumina nanoparticles.

Keywords Nanoparticles · Electrical field · LIF · Residence time · Synthesis · Processing

Introduction

Among the many techniques that have been developed for the production of nanoparticles, flame processes offer the advantage of scalability and thus manufacture of commercial quantities of nanopowders (Kammler et al. 2001). However, agglomeration (i.e. the adhesion of particles to each other due to Van der Waals forces) presents a limiting problem. The use of non-agglomerated nanoparticles as the starting material is essential due to the difficulties associated with aggregated nanoparticles in dispersing in a liquid medium, mixing uniformly, sintering to full density, forming coatings, and preserving nanoscale quantum properties (Chen et al. 1997). Moreover, these aggregated masses of nanoparticles can be difficult to cleave into their individual primary particles. Thus, despite having small primary nanoparticles, the formation of large aggregates (>100 nm) due to particle coalescence can obviate the point of creating a high-surface-area powder (Singhal et al. 1999).

Subjecting an external electric field to nanoparticles during their formation has been found to have a noticeable effect on primary particle size, agglomerate size, and crystallinity. Early on, Hardesty and Weinberg (1973) demonstrated influence over the size of primary particles in silica agglomerates in the

H. Zhao · X. Liu · S. D. Tse (✉)
Department of Mechanical and Aerospace Engineering,
Rutgers, The State University of New Jersey,
98 Brett Road, Piscataway, NJ 08854, USA
e-mail: sdytse@rci.rutgers.edu

presence of an electric field. They injected hexamethyldisiloxane (HMDS) vapor into a Meker-burner-supported, premixed methane/air flame, with an electric field applied coincident to the gas-stream lines. The primary particle size of the resulting SiO_2 powders was reduced by a factor of three for a 6 kV potential. They attributed the results to decreased particle residence time for sintering of the thermionically-positively-charged SiO_2 particles in the oxidizer-rich, high-temperature, product gas. However, Katz and Hung (1990, 1992) found an opposite trend in particle size due to an applied electric field (e.g. 1,250 V/cm). They injected precursors such as SiCl_4 , SiH_4 , and GeCl_4 into a H_2/O_2 counterflow diffusion flame, with an electric field applied parallel to the issued flow velocities. Regardless of the polarity of the bottom electrode, dynamic laser scattering and TEM probing data showed a significant *increase* in the diameter (3–10 times) of the particles produced (e.g. TiO_2 , SiO_2 , and GeO_2) compared with those synthesized without an electric field. The laser scattering data indicated that the particles exited the burner at an earlier location (corresponding to decreased particle residence time) when the electric field was applied.

Much of the recent work in electrically-assisted flame synthesis of particles has been done by Pratsinis et al. (Vemury and Pratsinis 1995a; Vemury et al. 1997; Morrison et al. 1997; Kammler and Pratsinis 2000). Vemury and Pratsinis (1995a) produced ultrafine titania particles generated from a CH_4 /air/Ar jet diffusion flame using a corona discharge to charge the particles (for repulsion and dispersion) and to reduce residence time through ionic wind effects by flow mixing. Increased electric potential reduced the particle size and the rutile content. Vemury et al. (1997) produced TiO_2 , SiO_2 , and SnO_2 nanopowders generated by burner-stabilized flat flames and non-stabilized laminar (bunsen-like) flames. The fields (applied perpendicular to the direction of flow) were created either by needle electrodes to introduce ions and wind in the flame or by plate electrodes to attract flame-generated ions. The electric fields reduced the primary particle size of TiO_2 , the agglomerate size of SnO_2 , and both the agglomerate and primary sizes of SiO_2 . Kammler and Pratsinis (2000) were able to reduce primary particle diameter (by a factor of two) of fumed silica produced at high rates (up to 87 g/h) using a co-flow

double diffusion flame with needle electrodes. Their results have been met with much success in terms of influencing particle size, agglomerate size, and crystallinity; and their investigation of electrically-assisted flame synthesis in various geometries have paved the way for such research. However, an isolated, fundamental study of the electrophoretic effect, without ionic wind influence (Chattock 1899), on nanoparticle synthesis is still needed. At the same time, the contrasting results of Katz and Hung (1990, 1992) warrant further study.

The present investigation utilizes a flame synthesis configuration based on the axi-symmetric stagnation point flame (characterized by a simple, well-defined, quasi-one-dimensional flow field), along with a uniform electric field applied between the burner and the (cooled) substrate. This strategic geometry facilitates experimental comparisons with modeling and computations. Since small particles residing in a flame, with or without an electric field, tend to become charged either due to charge transfer from naturally ionized flame species or electron emission, electrostatic manipulation can provide additional time/temperature histories for the particles beyond that capable of flow transport. For a given temperature distribution, electrophoretic effects should aid thermophoretic effects in transporting particles faster to a cooled substrate, reducing the residence time. In this one-dimensional geometry, no ionic wind is generated (maintaining fixed gas-phase residence times), thereby isolating the electrophoretic effect on manipulating particle residence time.

Experimental

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 et al. (1998, 1999) and Singhal et al. (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. Ceramic nanopowders such as TiO_2

Fig. 1 Burner setup for electrically-enhanced premixed flame

(and Al_2O_3) are investigated. Liquid precursors (i.e. titanium tetra-iso-propoxide (TTIP) and aluminum tri sec-butoxide (ATSB), respectively) are vaporized and entrained into a carrier gas via a heated and temperature-controlled bubbling unit and then combined with combustible premixed gases (e.g. hydrogen/oxygen) 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 (see Fig. 2). A dual-polarity high-voltage source (0 ± 10 kV, 3–10 mA) establishes the uniform electric field. 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.

The synthesis reactor (Fig. 2) consists of a 47-cm diameter cold-wall vacuum chamber, which is maintained at the desired pressure by a vacuum pump, throttle valve, and closed-loop pressure controller. Inside the chamber, the burner and substrate are fixed rigidly to a mount. Both the burner and substrate are water-cooled, and their temperatures are monitored with type K thermocouples. The chamber is configured with four 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.

The flames examined in this study use premixed hydrogen and oxygen with an equivalence ratio of ~ 0.4 and a system of pressure of ~ 20 torr. We will use the term “negative electric field” to refer to the cases where a negative voltage is applied to the substrate, and “positive electric field” where a positive voltage is applied to the substrate. The burner is grounded. For titania synthesis, a precursor loading rate of 7.185×10^{-4} mol/min of TTIP is used.

In-situ laser-based diagnostics

Non-intrusive laser-based diagnostics (Fig. 3) are utilized in the experiments to obtain the axial

Fig. 2 Low-pressure flame synthesis facility

Fig. 3 Experiment setup for gas-phase LIF

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 (LIF) of the OH radical is collected at right angles to the excitation source with $f/6$ optics into an $f/6.5$ -imaging spectrometer (Acton SpectrPro-2558), with an ICCD camera (Princeton Instruments PIMAX: 1300HQ) as detector. A 50 μm diameter pinhole allows for a 150 μm spatial resolution of the flow field. A 3,600 g/mm UV grating and slit width of 100 μm , gives a 11.5 nm 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 et al. 1998). This eliminates the need for temperature correction to the fluorescence signal profile. The uncertainty of OH concentration measurements is within $\pm 5\%$. For the two-line temperature measurements, $P_2(7)$ and $P_2(9)$

transitions of the (1–0) band of the $A^2\Sigma \rightarrow X^2\Pi$ are excited, as used 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.

Ex-situ characterization

Dynamic light scattering (DLS) measures the aggregate size of the synthesized nanopowder. Multipoint Brunauer–Emmet–Teller (BET) nitrogen adsorption determines the specific surface area (SSA) and the equivalent BET primary particle size. X-ray diffraction (XRD) obtains the phase composition, crystallinity, and crystallite size of the nanoparticles. Transmission Electron Microscopy (TEM) 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) determines the extent of the precursor decomposition (or conversion).

Computational modelling

Gas-phase flame structure

The axial gas-phase flame structure of the premixed flame in the experiment is simulated using the Sandia SPIN code (Coltrin et al. 1991) (generally used for CVD processes), by turning off disk rotation and using the appropriate boundary conditions at the substrate. A flow/chemistry model treats the flow and transport between the burner and the substrate, as well as the chemical reactions occurring in the gas-phase and at the substrate. Gas-phase and surface chemical kinetics are handled by CHEMKIN (Kee et al. 1996) and SURFACE CHEMKIN (Coltrin et al. 1996) subroutines, respectively, while variable transport properties are determined by TRANSPORT (Kee et al. 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 et al. (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.

$$j_k = \dot{s}_k M_k \quad (k = 1, \dots, K_g). \quad (1)$$

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

$$j_k = \rho Y_k u + \rho Y_k V_k \quad (k = 1, \dots, K_g), \quad (2)$$

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

Particle growth

Two models are applied to simulate the nanoparticle growth dynamics: (i) a monodisperse model, assuming a uniform size distribution during the coagulation process; and (ii) a simplified sectional model, which allows for a particle size distribution.

Monodisperse model

The monodisperse model neglects the polydispersity of the aggregates and primary particles. We employ a model developed by Kruis et al. (1993). The simplified General Dynamic Equations (GDEs) are (Koch and Friedlander 1990):

$$\frac{dN}{dt} = -\frac{1}{2} \beta N^2, \quad (3a)$$

$$\frac{dv_a}{dt} = -\frac{1}{N} \frac{dN}{dt} v_a, \quad (3b)$$

$$\begin{aligned} \frac{da_a}{dt} &= -\frac{1}{N} \frac{dN}{dt} a_a - \frac{1}{\tau_f} (a_a - a_s) \quad \text{with } a_s \\ &= \pi \left(\frac{6v_a}{\pi} \right)^{2/3}, \end{aligned} \quad (3c)$$

where N is the particle number concentration, v_a the volume of an aggregate, and a_s the surface area of a completely fused spherical particle.

The equations describe a process where for each collision, there is a reduction of one in the number of particles in a unit volume. Thus, the rate of collisions is numerically equivalent to the rate of change in the number concentration. These equations can be derived by considering a single particle and how other particles diffuse to its collision surface (Hinds 1982). A coalescence term is added to the surface area equation due to the surface area decrease during the process. This term depends on the characteristic coalescence time τ_f and the driving force for coalescence, i.e. the difference between the surface area of aggregates a_a and that of the completely fused spherical particle a_s .

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 H₂/O₂ flames (Glumac et al. 1998); (ii) the critical size of homogeneously nucleated nanoparticles is 1 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.

By introducing the collision factor s , the particle shape and the accessible surface area are taken into consideration in the collision frequency function (Xiong et al. 1992). The characteristic coalescence time for fusion of two primary particles (Kobata et al. 1991) and group-wise coalescence for aggregates (Lehtinen et al. 1996; Schwade and Roth 2004; Giesen et al. 2004) are applied in the calculation of the aggregate characteristic coalescence time. The initial particle concentration at precursor decomposi-

tion is estimated from the precursor-loading rate and the total volume flow rates of the gas mixture. The density of the TiO_2 nanoparticles is taken to be the same as the bulk density of $3.84 \times 10^3 \text{ kg/m}^3$.

Sectional model

In this work, the one dimensional, zero-order sectional model based on Prakash et al.'s (2003) work is utilized and extended. The validation of this sectional model was carried out by the authors for coagulation using an initially monodisperse aerosol. The size sections are defined for volume; and within each volume section, all particles are of the same size though not necessarily fully coalesced. Instead, particles are assumed to have an average surface area within each volume section (Vemury et al. 1994; Muhlenweg et al. 2002). Another surface area equation, which takes coalescence into consideration, is added to the volume sectional model. Assuming that the density of newly formed particles have the same density as the initial primary particles, coalescence changes neither the particle number nor particle volume; it only changes the surface area. Thus the coalescence term appears only in the surface area equation. As stated previously, group-wise coalescence of aggregates as proposed by Lehtinen et al. (1996), and as applied by Schwade and Roth (2004) and Giesen et al. (2004), is assumed. For example, an n -primary-particle aggregate is divided into n/m groups, in each of which the coalescence law holds; and coalescence in larger aggregates occurs in steps. The characteristic coalescence time for aggregates is defined as

$$\tau_{fm} = \tau_{fm}(v^*) \sum_{i=0}^{k-1} m^{4i/3}$$

where $k = \ln n / \ln m$ (Schwade and Roth 2004; Giesen et al. 2004). The value of m is taken as 3 in this work (see Schwade and Roth 2004).

Particle volumes with sizes ranging from 10^{-27} to 10^{-20} m^3 are considered (which correspond to diameters of range from $\sim 1 \text{ nm}$ to $\sim 0.3 \mu\text{m}$) by defining 102 size sections at a geometric spacing factor q of 1.2 on a logarithmic volume scale. Equations for population balance (Prakash et al. 2003) and average surface area (Muhlenweg et al. 2002) are solved considering precursor decomposition (Tsantilis et al. 2002),

homogeneous particle nucleation (Girshick and Chiu 1990), coagulation (Friedlander 2000), coalescence (Kobata et al. 1991; Lehtinen et al. 1996; Schwade and Roth 2004; Giesen et al. 2004), and surface growth (Prakash et al. 2003). Monomers of TiO_2 are given a diameter of 0.4 nm, corresponding to the volume equivalent diameter of a titania molecule.

Particle transport and external forces

In many particle-laden gas flows, the aerosol concentrations are dilute. Hence, the aerosol dynamics do not affect mass and momentum transfer in the carrier gas, and the overall mass and momentum balance equations can be solved independently of the GDE. Employing this assumption, 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), thermophoretic force, and electrophoretic force. The density of the solid particle is assumed 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.

The electrophoretic force (i.e. $F_{ES} = qE$, where q is the charge on a particle, and E the electric field) affects particles when they acquire positive charges due to thermo-ionization. By taking the ionization energy for TiO_2 to be 3 eV (Campbell et al. 1999), the electrons emitted per particle per second N_e can be calculated from the Richardson–Dushman equation:

$$J = AT^2 \exp\left(\frac{-W}{k_B T}\right), \quad (4)$$

$$N_e = 4\pi r^2 J / e, \quad (5)$$

where J is the emitted current density, W the work function (or ionization energy), h the Planck's

constant, m and e the mass and charge of an electron, respectively, and A the Richardson's constant, i.e.

$$A = \frac{4\pi m k_B^2 e}{h^3} = 1.20173 \times 10^6 (\text{A/m}^2/\text{K}).$$

As seen from Fig. 4, the number of electrons emitted increases dramatically with increasing temperature at a turning point around 1,400–1,500 K. As a result, we assume that nanoparticles become positively charged once they reach a critical temperature of 1,450 K.

We also assume that aggregate particles carry one unit charge since unit charge is dominant from charging theory (Fuchs 1963). Singly charged particles have also been confirmed in similar synthesis environments (Janzen and Roth 2001). For the $\text{H}_2\text{-O}_2$ flame, two primary charge carriers, H_3O^+ and e^- , are found naturally from chemi-ionization (Fialkov 1997). Due to the high mobility of the electrons, the outer region of the reaction zone can be negatively charged by electrons, while the inner flame region is likely to be positively charged by positive ions. Therefore, the particles are initially neutral if not positively charged. When the temperature reaches 1,400–1,500 K, particles start to eject an electron due to thermal-impact ionization, resulting in one unit of positive charge. As they travel through the flame structure, inter-particle collisions allow the particles to grow larger, while the charge redistributes on the particle surface. Some electrons return to the growing particle surface, and the particles remain singly charged. Note that we do not consider electrostatic or Van der Waals forces between particles.

Fig. 4 Electrons emitted per aggregate particle per integral step as a function of temperature

Flame structure characterization (isolation of the electrophoretic effect)

In flame synthesis, gas-phase temperature history plays a critical role in particle growth and evolution. Therefore, it is important to know precisely the flame structure and flow field. Particle image velocimetry (PIV) and laser Doppler velocimetry (LDV) are two methods to measure the velocity of flow fields. In both cases, tracer particles (larger than the nanoparticles produced in this study) are seeded into the flow; and the tracer velocity is extracted through Mie scattering either from measuring the movements of those particles, or from the Doppler signals collected. Assuming that the particles follow the flow, the flow velocities are then deduced. However, given the strong thermophoretic and electrophoretic forces in this synthesis system, the trajectories of the tracer particles are not expected to follow the streamlines. As such, the velocity of seed particles may not correctly represent the flow field velocities. In fact, it is the very manipulation of nanoparticle trajectories with respect to the flow field that is being sought.

In this work, simulation of the gas-phase flame structure is performed using the Sandia SPIN code, which is written for a quasi-1-D stagnation flow. The flame structure is then probed in-situ using 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 can be revealed.

The axial gas-phase temperature and OH concentration profiles in the synthesis flame (mass flux = 2.498 mg/s/cm^2 , $\text{H}_2/\text{O}_2 = 0.833$) with (e.g. – 500 V applied to substrate and burner grounded) and without an electric field are shown in Figs. 5 and 6, respectively. As shown in Fig. 5, the measurements compare very well with the simulation for the temperature profile. Furthermore, the LIF measurements reveal that there are negligible differences between cases with and without uniform electric field application. Therefore, there is virtually no influence on the gas-phase temperature by the electric fields imposed.

The electric field effect is also examined with respect to chemical species. With the OH radical being a key combustion intermediate, the OH concentration profiles from the LIF measurements

Fig. 5 Axial gas-phase temperature profile without precursor. Comparison between simulation, with (i.e. -500 V is applied to the substrate and the burner is grounded) and without an electric field at 20 torr. The symbols are the results of the LIF measurements, and the line is the model prediction

Fig. 6 Axial gas-phase OH radical mole fraction without precursor. Comparison between simulation, with (i.e. -500 V is applied to the substrate and the burner is grounded) and without an electric field at 20 torr. The symbols are the results of LIF measurements, and the line is the model prediction

in the synthesis flames with and without electric field are compared to the ones predicted by the simulation, as shown in Fig. 6. Similarly, there is good agreement between computations and measurements; and again, the application of electric fields has negligible effect on the OH concentration. Although not shown, there is no noticeable change in flame chemiluminescence when negative/positive voltages are applied to the substrate. These results imply that although chemical effects induced by transposing and redistributing ionic species by the action of the electrical fields may exist, they seem to play a very minor role in terms of our synthesis flow field. As such, we can be sure that, for this geometry, the

electrophoretic effect is isolated, and its effect on manipulating particle residence time under fixed gas-phase conditions is what is being studied. In addition, the agreement between the quasi one-dimensional model and the experimental measurements for these stagnation point flames suggests that the model predicts accurately the material processing flow field. Thus, the temperature and velocity profiles from the simulations can be used for particle transport and growth modeling.

Experimental results and discussion

Effect on aggregate particle size and extent of agglomeration

The aggregate particle sizes of the as-synthesized TiO_2 powders produced under different electric fields are obtained using DLS, as shown in Fig. 7 using

Fig. 7 Mean aggregate particle size (as measured by DLS of titania powder collected from substrate post-experiment) synthesized under different electric fields (with voltages applied to substrate with burner grounded): (a) using the number-weighted method, (b) using the volume-weighted method

number-weighted and volume-weighted methods, respectively.

For negative/positive voltages applied to the substrate, the hydrodynamic diameters of the aggregates (for both weighting methods) decrease/increase significantly due to the shorter/longer residence times, confirming that the particles are positively charged by the flame. However, under higher applied voltages (e.g. -500 V for TiO_2 in Fig. 7), the aggregate particle size increases. The simulations verify that this result is not due to small particles bouncing off the substrate due to their high acceleration. Instead, the reason is likely due to charging of the small particles by the highly negatively-biased substrate. As the local particles acquire negative charges, they are repelled, or levitated (Baron and Willeke 2001), from the substrate, with only larger particles remaining. As such, not only is the electric field itself a parameter but also the magnitude of the voltage applied. For this reason, the x -axis of Fig. 7 is labeled as it is, with the actual voltage applied divided by the gap distance.

Establishing electric fields by applying negative/positive voltages to the burner with the substrate grounded generated different results than those by applying voltage to the substrate with the burner grounded, even for the same electric field. Larger agglomerated particles are always attained. Again, the magnitude of the voltage itself plays a role. It is likely that the decomposition of the precursor near the burner is affected, resulting in larger particles. Nonetheless, more study is needed. In all experiments reported otherwise, voltages are applied to the substrate with the burner grounded, as shown in Fig. 7.

The morphologies and primary particle sizes of the TiO_2 nanoparticles produced without an electric field and with -300 V applied to the substrate are examined by TEM. Without an electric field, the particles are agglomerated (Fig. 8a), whereas the agglomeration with negative electric fields has been decreased significantly as shown in Fig. 8b. The primary particle sizes in Fig. 8a and b vary from 4 to 7 nm, with average primary particle sizes of about 5.9 nm for the case without an electric field and about 5.2 nm for the one with -300 V applied to the substrate. These results further confirm that the nanoparticles are positively charged and are transported through the flow field with shorter residence

times. HRTEM, Fig. 8c, shows that the nanoparticles possess high crystallinity, as indicated by the circled particle fringes and confirmed by the SAD pattern (inset in Fig. 8c).

Effect on SSA and primary particle size

DLS measurements substantiate that the use of the electric fields can be advantageous for process control in terms of minimizing aggregate particle size (i.e. degree of agglomeration). The SSA of the powders also increases when the electric field application is concurrent with the flow direction (negative electric field), as verified by BET.

As seen from Fig. 9, higher negative electric fields result in nanopowders of higher surface areas, and thus smaller primary particle sizes. Surprisingly, the SSA of TiO_2 also increases when the electric field application is countercurrent to the flow direction (positive electric field). The reason for this is that primary particle size can also decrease due to a longer characteristic coalescence time (which is highly dependent on the temperature), during which larger aggregate particles are produced through coagulation. This effect is confirmed in the computations and discussed in more detail in Sect. “Computational results and discussion (TiO_2)”. The 0 V case, or no electric field, appears to be a local minimum. However, as will be discussed in Sect. “Computational results and discussion (TiO_2)”, it is only by coincidence that the minimum occurs at 0 V here. It will be seen that the voltage (or electric field) corresponding to minimum SSA is highly dependent on the specific conditions (e.g. particle residence time) involved under different operating conditions.

The SSA of the TiO_2 nanopowder is as large as $310 \text{ m}^2/\text{g}$ for the -500 V case. Note that this is one of the largest SSA values for TiO_2 nanopowder to be reported in the literature. The average primary particle sizes calculated from TEM images compare well to the average particle sizes calculated from the SSA, further demonstrating that the particles have limited degrees of agglomeration. Typically, in flame synthesis, the average primary particle size from TEM is smaller than that obtained by BET because necking between the particles increases the corresponding particle diameter.

Fig. 8 (a) TEM image of TiO_2 particles synthesized without electric field application. (b) TEM image of loosely agglomerated TiO_2 particles synthesized with -300 V applied to the substrate. (c) HRTEM image of TiO_2 with -300 V applied to the substrate. The circles in the figure highlight individual primary particle fringes; the primary particle size is about 5.2 nm. The insert is an SAD pattern of TiO_2 particles

Fig. 9 Specific surface area of titania powder synthesized as a function of applied electric field. d_{BET} represents the equivalent particle diameter based on BET surface area measurement

Effect on crystallinity and phase composition

Despite the reduced particle residence times, electric field application does not seem to affect the crystallinity for the TiO_2 system. XRD analysis of all TiO_2 samples collected from the substrate evinces that the nanoparticles are anatase dominant, as illustrated in Fig. 10. Although rutile is thermodynamically more stable than anatase, anatase is readily formed at low temperatures due to its relatively fast crystallization kinetics (Rulison et al. 1996). In our flame, peak temperature is around $1,600$ K, and electrical fields exert no effect on the temperature profile. Formation of rutile from anatase requires ~ 1 s at $1,200^\circ\text{C}$ to finish the atomic

Fig. 10 XRD pattern of TiO_2 nanopowder synthesized with -300 V applied to the substrate and the burner grounded. A: anatase, R: rutile

rearrangement (where oxygens are in a distorted face-centered cubic arrangement for anatase, while for rutile, they are in a distorted hexagonal arrangement (Shannon and Pask 1964)). However, in our setup, particle residence time is on the order of 12–30 ms. Given the low temperature profile, short residence time, and fast crystallization kinetics for anatase, we invariably produce crystalline anatase in our flame. From the relative intensity of its primary peak in the XRD pattern, rutile is determined to be less than 5% weight fraction in the powder. Moreover, the peaks in Fig. 10 agree with the SAD pattern in Fig. 8c. Due to the particle size effect, the diffraction peaks show broadening. It is seen in Fig. 10 that the (103), (004), and (112) peaks are overlapped, as well as the (105) and (211) peaks (PDF#71-1166).

The crystalline particle size is determined to be about 4–8 nm from the Scherrer equation. However, because the primary particle sizes are extremely small, the size difference calculated from the XRD peak widths is not discernable. For flame-generated powders, it has been shown that XRD crystallite sizes are consistently smaller than BET-determined particle sizes (Vemury and Pratsinis 1995b). The lack of a significant difference in the particle crystallinity suggests that the pre-residence time required for forming the TiO_2 crystalline primary particles is much shorter than that for some other ceramic oxides (e.g. Al_2O_3 , to be discussed in Sect. “Alumina synthesis”).

Effect on extent of precursor decomposition (or conversion)

TGA was conducted for samples produced with 0 V and -500 V applied to the substrate to examine the extent of TTIP pyrolysis (or conversion). Prior to TGA measurement, the samples are heat treated at $\sim 80^\circ\text{C}$ in an oven overnight to avoid additional moisture absorption onto the powder surface. As shown in Fig. 11, the initial weight loss, up to a temperature of 200°C , is due to loss of water that is physically adsorbed on the high-area surfaces of the nanoparticles. Although the two samples are heat treated for the same time duration, nanoparticles produced under -500 V contain more water, which from another point of view verifies that the sample has more surface area.

Also seen from the curves in Fig. 11, for both conditions at 0 and -500 V, there is only about a 3.2–3.5% weight loss due to unpyrolyzed precursor. It can be concluded that the powders are almost fully pyrolyzed, displaying only a small weight loss (gain) during post heat treatment. A small amount of weight gain near the tail end is probably due to the samples having a very small percentage of TiO or Ti_2O_3 , which when exposed to an O_2 -containing environment under elevated temperature, is converted into TiO_2 . Moreover, even for the case of -500 V, where the residence time is much shorter compared to the 0 V case (as will be seen in the temperature residence time histories of Fig. 14), the TTIP precursor is still almost fully pyrolyzed, which substantiates that

Fig. 11 TGA curves of TiO_2 nanopowder synthesized with no electric field application and with -500 V applied to the substrate, showing weight loss of the powder as a function of temperature

shorter residence time has little effect on the pyrolysis process. This is consistent with the previous statement that the electric field seems to have no obvious effect on crystallinity because the precursor has enough residence time to pyrolyze completely, for the cases studied. Thus, the experiments with the application of electric fields are not in the regime where shorter residence times lead to insufficient pyrolysis, where partially pyrolyzed precursor species would condense to form bigger aggregates. However, since residence times can be readily manipulated, this implies that the crystallinity can also be controlled through electric field application.

Alumina synthesis

Presented briefly, the trends for electric field effect on nanoparticle characteristics for Al_2O_3 synthesis is also experimentally examined. As seen from Fig. 12, the aggregate particle size shows a similar trend, decreasing/increasing significantly due to the shorter/longer residence times, when applying negative/positive voltages to the substrate. However, the charging effect (from large voltage biases on the substrate) may not be as strong for the Al_2O_3 system. More investigation is needed. Note that the modeling and computation of Al_2O_3 particle growth are not presented in this work.

Figure 13 divulges the crystalline structure of γ phase alumina produced without electric field

Fig. 12 Mean aggregate particle size, as measured by DLS of alumina powder collected from substrate post-experiment, synthesized under different electric fields (with voltage applied to the substrate and the burner grounded) using the intensity-weighted method (Intensity-weighted distribution gives the fraction of the total scattered light intensity of the particles contributed by particles in any size range)

Fig. 13 XRD pattern of Al_2O_3 nanopowder synthesized without electric field application

application. XRD shows that the application of intense electric fields can be detrimental, resulting in more amorphous structures for alumina, with TGA showing incomplete pyrolysis. Both particle agglomeration and particle crystallinity are strongly affected by residence time and temperature. As such flame structure and electrical field conditions must be optimized to realize high nanoparticle crystallinity at significantly reduced agglomeration.

Computational results and discussion (TiO_2)

The experiment cases in Sect. “Experimental results and discussion” for titania synthesis are simulated using both the monodisperse model and the sectional model. Since particles are positively charged due to thermo-ionization in the flame, applying electric fields (concurrently) in the direction of the axial flow velocity (by applying negative voltages to the substrate) will accelerate the particles towards the substrate and thus shorten the residence times, as shown in Fig. 14. However, applying electric fields countercurrent to the axial flow velocity (by applying positive voltages to the substrate) will decelerate the movement of the particles. Worse yet, particles could be forced back to the burner due to a combination of electrophoretic and thermophoretic effects (note: a large temperature gradient exists between the burner and the flame zone), as shown in Figs. 14 and 15 (e.g. case +700 V), growing into larger particles and then retracing their steps towards the substrate.

Fig. 14 Sectional model assessment of the influence of electric field application on particle temperature history, for titania

Fig. 15 Assessment of the influence of electric field application on the aggregate particle size as a function of position in the flow field using (a) the sectional model and (b) the monodisperse model, for titania. *Note:* the branch point is thermo-ionization point

Fig. 16 Assessment of the influence of electric field application on the aggregate particle size as a function of particle residence time using (a) the sectional model and (b) the monodisperse model, for titania

Therefore, as seen from Figs. 15 and 16, when applying negative (concurrent) electric fields, the synthesized nanoparticles leave the reaction zone earlier, leading to fewer particle-to-particle collisions. The aggregate particle sizes decrease as the negative (concurrent) electric field intensity increases. However, in applying positive (counter-current) electric fields, the electrophoretic effect keeps the nanoparticles longer in the reaction zone, and the aggregate particle sizes increase as the positive (countercurrent) electric field intensity increases. The trends in the aggregate particle size are in good agreement with the experimental results presented in Sect. “Experimental results and discussion”.

The evolution of the GSDs, as shown in Fig. 17, changes only slightly with respect to the applied electric field magnitude, except for the case in which

Fig. 17 Geometric standard deviation of particle size distribution (computed using the sectional model) as a function of particle position in the flow field, for different electric field application, for titania

the nanoparticles are attracted back to the burner (e.g. +700 V), as discussed previously. When the equivalent solid sphere diameter is much smaller than the mean-free path of the gas, chemical reactions are rapid; and particle growth is dominated by coagulation in the free molecule regime rather than by surface reaction. In this case, particles grow by Brownian coagulation and reach an asymptotic self-preserving size distribution. All of the GSDs converge to a similar value between 1.460 and 1.462 (the limit for the free molecular regime of the polydispersity of particles grown by coagulation) by the time these nanoparticles reach the substrate. As seen from Fig. 17, the processes of nucleation and TTIP decomposition are not affected by electric-field application because they are accomplished before the nanoparticles become thermally ionized and carry unit charge.

In contrast to the trends in aggregate particle size, the trends in primary particle size can be non-monotonic as a function of applied substrate voltage, as experimentally shown in Fig. 9. Similarly, Figs. 18 and 19 show that, depending on the precursor-loading rate, there is a local maximum for the primary particle size with respect to electric field strength. In Fig. 19a, with the primary particle size peaking around +300 V, as computed by the sectional model, increasing the negative field strength or the positive field strength larger than this critical value (i.e. +300 V) results in a smaller primary particle size. In the monodisperse model calculations, the local maximum primary particle size occurs at an

Fig. 18 Assessment of the influence of electric field application on primary particle size as a function of particle position in the flow field using (a) the sectional model and (b) the monodisperse model, for titania

electric field of +20 V/4 cm, corresponding to Fig. 19b. As the precursor-loading rate increases, the position where the peak value of the primary particle size occurs moves towards larger magnitudes of negative electric field. This non-monotonic trend in the primary particle size with the application of electric fields agrees with the experimental results presented previously in Sect. “Experimental results and discussion”, where the BET SSA increases with increasing field strength under both concurrent and countercurrent electric fields (since the SSA equivalent particle size, to some extent, can be treated as the primary particle size as shown in Fig. 9). In the hot flame, the particles start growing from molecular size by coagulation. They coalesce as they collide, where they gradually partially coalesce after collisions due to the longer characteristic coalescence time for the aggregates. With a group-wise coalescence process occurring, the more primary particles there are within an aggregate, the longer it takes an aggregate to

Fig. 19 Assessment of the influence of electric field application on primary particle size as a function of particle residence time using (a) the sectional model and (b) the monodisperse model, for titania

coalesce into a single solid spherical particle. At high temperatures, coalescence of particles can cause rapid sintering; while at medium or lower temperatures, the collision time can be shorter than this characteristic group-wise coalescence time, resulting in agglomeration or partial coalescence. It seems that the long characteristic coalescence times associated with our moderate flame temperatures can, under certain conditions, prohibit the growth of primary particles; and the coalescence within aggregates can be negligible. Thereafter, each collision just increases the number of primary particles per aggregate, and the primary particle size is frozen. At the turning point, by applying the electric field concurrent to the axial flow velocity, the residence time decreases, which results in a smaller primary particle. By applying the electric field countercurrent to the axial flow velocity (although the residence time is longer), the primary

particle growth “freezes” at a smaller value due to its bigger aggregate size having more primary particles within it, resulting in a longer characteristic time needed for coalescence.

Comparison of the simulations of the monodisperse model and the sectional model shows similar trends in particle growth with the application of uniform electric fields. This correspondence confirms again that the main particle growth mechanisms under our flame synthesis conditions are coagulation and coalescence. Matched up to the experimental results, both the monodisperse model and the sectional model predict the trends very well for aggregate and primary particle sizes. The small discrepancy between these two models (e.g. the critical value of the electric field where the maximum primary particle occurs) probably results from the different initial conditions, other assumptions, and inherent model characteristics.

Concluding remarks

The application of uniform electric fields to control particle growth characteristics is investigated. For the electric fields applied, gas-phase temperature and chemical species profiles are unaffected (as verified by LIF), and only transport of the innately-charged nanoparticles (due to thermionic emission) is induced. As such, it can be sure that, for this geometry, the electrophoretic effect is isolated and its influence on manipulating particle residence times is studied. Electric fields in the direction of the axial flow velocity (concurrent) are shown to significantly decrease the aggregate particle size. Interestingly, the SSA of TiO_2 increases with increasing field strength under both concurrent and countercurrent (antiparallel to axial flow velocity) electric fields. The controlling mechanism for this non-monotonic result is the competition between particle coalescence and coagulation. Depending on the conditions, primary particle size can decrease due to the longer characteristic coalescence time for the larger aggregate particles. Moreover, the turning point in primary particle size behavior can occur for different electric field magnitudes, since particle temperature history is the key parameter. The crystallinity of TiO_2 is not influenced by the magnitudes of electric field examined. The anatase phase remains dominant in the

synthesized powders due to fast crystallization kinetics, moderate flame temperatures, and short residence times. Even with electric field application, TGA reveals that the precursor is still almost fully converted, indicating that the experiments with the application of electric fields are not in the regime where short residence times can lead to insufficient pyrolysis, with partially pyrolyzed precursor species condensing to form bigger aggregates. However, as seen from the nano-alumina results, residence time can greatly affect crystallinity given the overall flame conditions, and electric field application can have a significant effect by shifting particle residence time into another formation regime.

Acknowledgments This work was supported by the National Science Foundation through grants NSF-CTS-0213929 and NSF-CTS-0325057. Initial seed funding from the New Jersey Space Grant Consortium is acknowledged. Special thanks are due to Joshua Dewanaga, Venkata Rapaka, Fusheng Xu, and John Petrowski for their help with the experiments.

References

- Aghalayam P, Bui PA, Vlachos DG (1998) The role of radical wall quenching in flame stability and wall heat flux: hydrogen-air mixtures. *Combust Theory Model* 2:515–530
- Baron P, Willeke K (2001) *Aerosol measurement: principles, techniques, and applications*. Wiley & Sons, New York
- Ben-Yakar A, Kamel M, Morris C, Hanson RK (1998) Hypersonic combustion and mixing studies using simultaneous OH-PLIF and schlieren imaging. Paper AIAA-1998-940 presented at the 36th aerospace sciences meeting and exhibit, Reno, NV, 12–15 January 1998
- Campbell SA, Kim HS, Gilmer DC, He B, Ma T, Gladfelter WL (1999) Titanium dioxide (TiO₂) based gate insulators. *IBM J Res Dev* 43:383–392
- Chattock AP (1899) On the velocity and mass of ions in the electric wind in air. *Philos Mag* 48:401–420
- Chen Y, Glumac N, Kear BH, Skanden G (1997) High rate synthesis of nanophase materials. *Nanostruct Mater* 9:101–104
- Coltrin ME, Kee RJ, Evans GH, Meeks E, Rupley FM, Grcar JF (1991) SPIN: a Fortran program for modeling one-dimensional rotating-disk/stagnation-flow chemical vapor deposition reactors. Technical report SAND91-8003, Sandia National Laboratories
- Coltrin ME, Kee RJ, Rupley FM, Meeks E (1996) Surface Chemkin-III: a Fortran package for analyzing heterogeneous chemical kinetics at a solid-surface—gas-phase interface. Technical report SAND96-8217, Sandia National Laboratories
- Fialkov AB (1997) Investigations on ions in flame. *Prog Energy Combust Sci* 23:399–528
- Friedlander SK (2000) *Smoke, dust and haze*. Oxford University Press, Oxford
- Fuchs NA (1963) On the stationary charge distribution on aerosol particles in a bipolar ionic atmosphere. *Geofis Pura Appl* 56:185–193
- Giesen B, Orthner HR, Kowalik A, Roth P (2004) On the interaction of coagulation and coalescence during gas-phase synthesis of Fe-nanoparticle agglomerates. *Chem Eng Sci* 59:2201–2211
- Girshick SL, Chiu CP (1990) Kinetic nucleation theory: a new expression for the rate of homogeneous nucleation from an ideal supersaturated vapor. *J Chem Phys* 93:1273–1277
- Glumac NG, Chen YJ, Skandan G (1998) Diagnostics and modeling of nanopowder synthesis in low pressure flames. *J Mater Res* 13(9):2572–2579
- Glumac NG, Skandan G, Chen YJ, Kear BH (1999) Particle size control during flat flame synthesis of nanophase oxide powders. *Nanostruct Mater* 12:253–258
- Hardesty DR, Weinberg FJ (1973) Electrical control of particulate pollutants from flames. *Proc Combust Inst* 14:907–918
- Hinds WC (1982) *Aerosol technology, properties, behavior, and measurement of airborne particles*. John Wiley & Sons, New York
- Janzen C, Roth P (2001) Formation and characteristics of Fe₂O₃ nano particles in doped low pressure H₂/O₂/Ar flames. *Combust Flame* 125:1150–1161
- Kammler HK, Pratsinis SE (2000) Electrically-assisted flame aerosol synthesis of fumed silica at high production rates. *Chem Eng Process* 39:219–227
- Kammler HK, Madler L, Pratsinis SE (2001) Flame synthesis of nanoparticles. *Chem Eng Technol* 24(6):583–596
- Katz JL, Hung CH (1990) Initial studies of electric field effects on ceramic powder formation in flames. *Proc Combust Inst* 23:1733–1738
- Katz JL, Hung CH (1992) Ultrafine refractory particle formation in counterflow diffusion flames. *Combust Sci Technol* 82:169–183
- Kee RJ, Dixon-Lewis G, Warnatz J, Coltrin ME, Miller JA (1986) A Fortran computer code package for the evaluation of gas-phase multicomponent transport properties. Technical report SAND86-8246, Sandia National Laboratories
- Kee RJ, Rupley FM, Meeks E, Miller JA (1996) Chemkin-III: a Fortran chemical kinetics package for the analysis of gas-phase chemical and plasma kinetics. Technical report SAND96-8216, Sandia National Laboratories
- Kobata A, Kusakabe K, Morooka S (1991) Growth and transformation of TiO₂ crystallites in aerosol reactor. *AIChE J* 37(3):347–359
- Koch W, Friedlander SK (1990) The effect of particle coalescence on the surface area of a coagulating aerosol. *J Colloid Interface Sci* 140(22):419–427
- Kruis FE, Kusters KA, Scarlett B, Pratsinis SE (1993) A simple model for the evolution of the characteristics of aggregate particles undergoing coagulation and sintering. *Aerosol Sci Technol* 19:514
- Lehtinen K, Windeler R, Friedlander S (1996) A note on the growth of primary particles in agglomerate structures by coalescence. *J Colloid Interface Sci* 182:606–608

- Morrison PW Jr, Raghavan R, Timpone AJ, Artelt CP, Pratsinis SE (1997) In situ fourier transform infrared characterization of the effect of electrical fields on the flame synthesis of TiO_2 particles. *Chem Mater* 9:2702–2708
- Mueller MA, Kim TJ, Yetter RA, Dryer FL (1999) Flow reactor studies and kinetic modeling of the H_2/O_2 reaction. *Int J Chem Kinet* 31:113–125
- Muhlenweg H, Gutsch A, Schild A, Pratsinis SE (2002) Process simulation of gas to particle synthesis via population balances: investigation of three models. *Chem Eng Sci* 57:2305–2322
- Prakash A, Bapat AP, Zachariah MR (2003) A simple numerical algorithm and software for solution of nucleation, surface growth, and coagulation problems. *Aerosol Sci Technol* 37:892–898
- Rulison AJ, Miquel PF, Katz JL (1996) Titania and silica powders produced in a counterflow diffusion flame. *J Mater Res* 11:3083–3089
- Schwade B, Roth P (2004) Simulation of nano-particle formation in a wall-heated aerosol reactor including coalescence. *J Aerosol Sci* 34:339–357
- Shannon RD, Pask JA (1964) Topotaxy in the anatase-rutile transformation. *Am Mineral* 49:1707–1717
- Singhal A, Skandan G, Wang A, Glumac N, Kear BH, Hunt RD (1999) On nanoparticle aggregation during vapor phase synthesis. *Nanostruct Mater* 11:545–552
- Singhal A, Skandan G, Glumac N, Kear BH (2001) Minimizing aggregation effects in flame synthesized nanoparticles. *Scripta Mater* 44:2203–2207
- Tsantilis S, Kammler HK, Pratsinis SE (2002) Population balance modeling of flame synthesis of titania nanoparticles. *Chem Eng Sci* 57:2139–2156
- Vemury S, Pratsinis SE (1995a) Corona-assisted flame synthesis of ultrafine titania particles. *Appl Phys Lett* 66(24):3275–3277
- Vemury S, Pratsinis SE (1995b) Dopants in flame synthesis of titania. *J Am Ceram Soc* 78:2984–2992
- Vemury S, Kusters KA, Pratsinis SE (1994) Modeling of coagulation and sintering aggregates. *Proc First Int PTF AICHE* 2:350
- Vemury S, Pratsinis SE, Kibbey L (1997) Electrically controlled flame synthesis of nanophase TiO_2 , SiO_2 , and SnO_2 powders. *J Mater Res* 12:1031–1042
- Xiong Y, Pratsinis SE, Weimer A (1992) Modeling the formation of boron carbide particles in an aerosol reactor. *AIChE J* 38(11):1685–1692