# ResearchGate

See discussions, stats, and author profiles for this publication at: http://www.researchgate.net/publication/241127633

# Direct synthesis of nanostructured TiO 2 films with controlled morphologies by stagnation swirl flames

# ARTICLE in JOURNAL OF AEROSOL SCIENCE · FEBRUARY 2012

Impact Factor: 2.24 · DOI: 10.1016/j.jaerosci.2011.10.001

CITATIONS	READS
8	49

# 5 AUTHORS, INCLUDING:



# **Yiyang Zhang**

Institute of Nuclear and New Energy T...



SEE PROFILE



## Qiang Yao

Tsinghua University

245 PUBLICATIONS 871 CITATIONS

SEE PROFILE



# Sili Deng Princeton University 8 PUBLICATIONS 10 CITATIONS

SEE PROFILE

Contents lists available at SciVerse ScienceDirect

# Journal of Aerosol Science



journal homepage: www.elsevier.com/locate/jaerosci

# Direct synthesis of nanostructured TiO<sub>2</sub> films with controlled morphologies by stagnation swirl flames

Yivang Zhang<sup>a</sup>, Shuiqing Li<sup>a,\*</sup>, Sili Deng<sup>a</sup>, Qiang Yao<sup>a</sup>, Stephen D. Tse<sup>b</sup>

<sup>a</sup> Key laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, China

<sup>b</sup> Department of Mechanical and Aerospace Engineering, Rutgers University, Piscataway, NJ 08854, USA

### ARTICLE INFO

Article history: Received 27 February 2011 Received in revised form 4 October 2011 Accepted 4 October 2011 Available online 12 October 2011

Keywords: Nanostructured films Titanium dioxide Stagnation flame Film synthesis Deposition

### ABSTRACT

A novel premixed swirl flame in stagnation point geometry is used to synthesize uniform, high-quality nanostructured TiO<sub>2</sub> films at growth rates of 20–200 nm/s in a single step. The roles of precursor concentration and substrate temperature in controlling film morphology and characteristics are investigated. Increasing precursor concentration, for a given substrate temperature, significantly increases the packing density of the nanoporous film. The specific surface area of the film is mainly dependent on substrate temperature, where two distinct regimes, i.e. in-flame-agglomeration at low temperature and on-substrate-sintering at high temperature, specify film properties. A simplified deposition model for the formation of the nanoporous film structure is proposed, correlating penetration distance of thermophoretically-driven Brownian particles into the film with the resultant morphology. The model predicts the packing density in excellent agreement with experiments, thereby clarifying the complex roles of precursor concentration and substrate temperature. Finally, increasing substrate temperature, at fixed precursor concentration, changes the packing density little, but considerably decreases specific surface area, as sintering becomes dominant among controlling mechanisms.

© 2011 Elsevier Ltd. All rights reserved.

### 1. Introduction

Nanostructured metal-oxide thin films, usually synthesized by the deposition of nanoparticles, are used in a wide range of photovoltaic and photocatalytic applications, including selective catalytic reduction (SCR) of NO<sub>x</sub> (Zheng et al., 2005), dye-sensitized solar cells (Regan & Grätzel, 1991; Benkstein et al., 2003), chemical gas sensors (Li & Kawi, 1997; Leite et al., 2000), diesel soot traps (Seipenbusch & Friedlander, 2004), and pollutant purification for air and water (Takita et al., 1990; Vorontsov et al., 1999). Different from films constructed with micro- or mini-particles, nanostructured films exhibit especiallyhigh specific surface area (SSA) as well as very-low packing density, usually below 10%, with the resultant morphology and nanostructure governing their specific performance. For examples, gas sensors constructed by well-sintered ultrafine nanoparticles exhibit higher sensitivity (Wang et al., 1995); dye-sensitized cells composed of properly-sintered primary TiO<sub>2</sub> nanoparticles possess higher SSA, absorbing more dye for better electron transport (Thimsen et al., 2008); and pollution remediation devices made of high-SSA anatase TiO<sub>2</sub> can achieve larger degradation/oxidation rates for volatile

<sup>\*</sup> Corresponding author. Tel.: +86 10 62773384; fax: +86 10 62794068. E-mail address: lishuiqing@tsinghua.edu.cn (S. Li).

<sup>0021-8502/\$-</sup>see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.jaerosci.2011.10.001

organic compounds (Sirisuk et al., 1999). As such, the control of particle morphology of nanostructured films during the synthesis process can play a crucial role in their practical applications.

Flame synthesis of nanostructured films has received much interest due to characteristically high growth rates, uniformity, and polycrystralline deposition quality (Bertagnolli et al., 1998). Compared to wet chemistry routes (e.g., sol–gel), flame synthesis has the advantage that it can produce nanostructured films in a single step, which innately incorporates all the requisite basic mechanisms. In a single continuous operating process, precursors are converted to monomers by oxidation, producing a supersaturated vapor that undergoes nucleation to form primary particles, which then grow via surface growth and agglomeration to form aggregate nanoparticles, finally depositing and sintering on a substrate to construct a porous film. These produced nanostructured films can be described by two key parameters, i.e. porosity and SSA, which indicate their abilities for adsorption and diffusion of relevant species. Wang and co-workers (Tolmachoff et al., 2009) used laminar divergence-stabilized stagnation flames to attain uniform TiO<sub>2</sub> nanofilms with a porosity of 90%. Mädler et al. (2006a) synthesized relatively-high-porosity (98%) Pt/SnO<sub>2</sub> nanofilms using spray flames impinging on a substrate. Thimsen and Biswas (2007) synthesized TiO<sub>2</sub> nanofilms using premixed stagnation jet flames. They found two distinct morphologies: a granular morphology with a larger number of grain boundaries and higher SSA, and a highly crystalline columnar morphology with more complete sintering and lower SSA, by controlling the substrate temperature and precursor concentration.

Recently, we have employed a novel, turbulent, premixed stagnation swirl flame (SSF) to synthesize ultrafine  $TiO_2$  nanoparticles (Li et al., 2010; Wang et al., 2011). Improved flame stabilization and increased lateral turbulent mixing from the swirl make the SSF a promising system for consistent and homogeneous large-scale production. As reported, the SSF can produce small non-agglomerated nanoparticles of narrow size distribution, along with uniform deposition coverage. Furthermore, the precursor loading mass flux can be drastically increased while maintaining these characteristics (Wang et al., 2011). As a result, the synthesis of nanostructured films with well-controlled morphologies is a logical extension.

Nevertheless, stagnation flame synthesis of films possesses two main aspects that require further investigation and optimization. Although it is a convenient one-step method, the control of operational parameters (e.g., substrate temperature, precursor concentration) to produce desired morphologies can be complex due to the coupled relationships between formation, deposition, and sintering of nanoparticles during the process. For example, increasing precursor concentration may simultaneously affect the nucleation and coagulation of nanoparticles within the flame flow field and at the deposition region. Increasing substrate temperature not only directly facilitates sintering of deposited particles, forming larger ones, but also establishes smaller temperature gradients that reduce thermophoretic deposition of particles, producing larger primary particles in the flow field. To better understand these interactions calls for more thorough and systematic work on studying the effects of operating parameters on the as-synthesized film morphologies. Our previous work on SSF synthesis of TiO<sub>2</sub> nanoparticles (Wang et al., 2011) focused on their formation in the flame zone (given their quenching at a cooled substrate); here we examine their successive deposition/sintering to form a film on a heated substrate.

In thin film deposition, the contribution of inertial impact of nanoparticles can be neglected, given Stokes numbers that are far below the critical value of 0.24. Without the influence of externally applied fields (Zhao et al., 2008), only thermophoresis and Brownian diffusion remain to play crucial roles in the deposition of nanoparticles, among which thermophoresis is particularly important when there is a cold surface that establishes a large temperature gradient within the boundary layer (Mädler et al., 2006a). Since photovoltaic and photocatalytic abilities of nanofilms are strongly dependent on film morphology and structure (Thimsen et al., 2008), theoretical work has been attempted to simulate and analyze the deposition mechanisms of nanoparticles. Brownian dynamics have been employed, for example in conjunction with Monte Carlo, to investigate deposition on a plane or fiber surface, which have indicated that tree-like fractal structures with larger SSA will be constructed if the particle sizes are small and very 'sticky' (Meakin, 1984; Meakin et al., 1986; Ramarao et al., 1994; Mädler et al., 2006b). From the simulations, the porosity and SSA of nanofilms have been found to be sensitive to interparticle interactions (Kulkarni & Biswas, 2004) and to particle sintering on the substrate (Kulkarni & Biswas, 2003), where the modeling parameters are still not very well known and more empirical data from systematic experiments are needed.

Considering the above issues, the objective of this work is to understand the effects of process parameters on the deposition/sintering of nanoparticles during one-step  $TiO_2$  film synthesis using our novel SSF reactor. Specifically, the dependencies of packing density on precursor concentration and of SSA on substrate temperature are investigated. A simplified model, based on the Brownian motion and thermophoresis of nanoparticles during deposition, is proposed and compared to experimental results.

#### 2. Experimental methods

#### 2.1. Film synthesis setup

The schematic of the SSF burner setup for  $TiO_2$  nanostructured film synthesis is shown in Fig. 1. The system is composed of three main parts, i.e. a delivery system for reactant gases and precursor, a downward stainless steel tube of 18 mm i.d with a vane swirler inside, and a temperature-controlled silicon substrate on which film deposition occurs. Mass flow controllers meter the delivery of CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. Nitrogen also serves as the carrier gas for the liquid precursor



Fig. 1. Schematic of the SSF burner setup for nanostructured film synthesis.

(titanium tetraisopropoxide, TTIP, Aldrich, 97%), which is heated to  $80 \pm 2$  °C by an electrical mantle to achieve a high vapor pressure. The precursor concentration is calculated based on the assumption that the loading rate is proportional to the carrier nitrogen flow rate. Downstream lines are heated to 130 °C to avoid precursor condensation prior to delivery to the burner. The vane swirler, which is 14 mm long with eight 45° blades, is situated inside the burner tube at a position of 73 mm above the burner exit. It introduces swirling flow to the main gas stream, greatly stabilizing the flame impinging on the substrate. The outer diameter of the vanes is 18 mm, while that of the central bypass channel is 8.0 mm. This design of the vane swirler with an open center-channel allows a portion of reactants to remain un-swirled, which inhibits vortex breakdown and promotes flow divergence—the key aerodynamic feature for the low-swirl flame stabilization method (Cheng et al., 2009). The swirl number can be altered by adjusting the rates of center bypass flow and, in this work, is fixed at 0.248, meeting the low-swirl limit value of 0.6. A characteristic SSF image is also shown in Fig. 1.

The silicon substrate on which the  $TiO_2$  nanofilms are synthesized is placed on a temperature-controlling device, which consists of an aluminum sheet (embedded with a K-type thermocouple), quartz glass blocks, and a heat sink with cooling water. The substrate temperature can be precisely set by adjusting the thickness of the quartz glass blocks which serve as thermal resistance, as well as the flow rate of cooling water. The substrate temperatures examined in this work range from 100 °C to 550 °C, with a controlling accuracy of  $\pm 10$  °C.

#### 2.2. Film characterization

m

The morpology and thickness of nanostructured  $TiO_2$  films are observed using a Hitachi S-5500 field emission scanning electron miscroscope (FESEM) operating at 5 kV. The films along with the substrate are cleaved prior to observation, ensuring that the cross sections inside the films can be visualized. A JEOL 2010 transmission electron microscope (TEM) operating at 200 kV images nanoparticle elements composing the films. The packing density of the film is calculated using

$$\varepsilon = \frac{m_f}{\rho A_f h_f} \tag{1}$$

where  $\rho$  is the density of TiO<sub>2</sub>, (taken as 3840 kg/m<sup>3</sup>);  $m_f$  is the weight of the film (measured by a microbalance, CAHN C-35, with an accuracy of 1 µg);  $A_f$  is the area of the film; and  $h_f$  is the thickness of the film (determined by SEM imaging). SSA is measured by gas physisorption and chemisorption analyzer (Micromeritics ASAP 2010), where 20 mg samples are used typically for measurements.

#### 2.3. Experimental procedure

This work focuses on examining the effects of precursor concentration and substrate temperature on  $TiO_2$  nanofilm characteristics. Table 1 presents the experimental cases. For all runs, the flow rates of CH<sub>4</sub>, O<sub>2</sub>, and total N<sub>2</sub> are 2.25, 6.60, and 24.9 L/min, respectively, corresponding to a fixed flame equivalence ratio of 0.682. All experiments are conducted at atmosphere pressure. The N<sub>2</sub> carrier-gas flow rate can be adjusted to vary precursor loading, but the total N<sub>2</sub> flow rate delivered to the burner is held constant (by adjusting the inert balance). 1 L/min of carrier gas is measured to deliver 0.0249 g/min of TTIP. Accordingly the precursor concentrations in this work range from 29.1 to 291.0 ppm.

Case number	Precursor concentration (ppm)	Substrate temperature (K)	Synthesis time (s)	Film characterization
1	29.1	763	1200	SEM & packing density
2	58.2	763	600	SEM & packing density
3	116.4	763	300	SEM & packing density
4	174.6	763	200	SEM & packing density
5	232.8	763	150	SEM & packing density
6	291.0	763	120	SEM & packing density
7	58.2	763	3600	SSA
8	116.4	763	1800	SSA
9	174.6	763	1200	SSA
10	232.8	763	900	SSA
11	291.0	763	720	SSA
12	29.1	383	1200	TEM
13	116.4	383	300	TEM
14	232.8	383	150	TEM
15	116.4	473	300	SEM & packing density
16	116.4	633	300	SEM & packing density
17	116.4	686	300	SEM & packing density
18	116.4	383	1800	SSA
19	116.4	423	1800	SSA
20	116.4	584	1800	SSA
21	116.4	681	1800	SSA

Table 1Experimental conditions for TiO2 film synthesis.<sup>a</sup>

<sup>a</sup> CH<sub>4</sub>, O<sub>2</sub>, and total N<sub>2</sub> flow rates are 2.25, 6.60, and 24.9 L/min, respectively.

The substrate temperatures studied range from 383 K to 763 K. For all experiments, the synthesis duration is inversely proportional to the precursor concentration, in order to maintain the same total amount of precursor added to the flame (since longer synthesis durations for lower precursor concentrations are needed to meet a minimum weight requirement for SSA measurements). Finally, an additional case with very low substrate temperature (383 K) is conducted for TEM observation of less-sintered nanoparticles.

### 3. Results and discussion

#### 3.1. Effect of gas-phase precursor concentration

Fig. 2 shows SEM images of the side view of nanostructured TiO<sub>2</sub> films synthesized by the one-step SSF. Again, the total precursor amount added for each case is the same, and the substrate temperature is fixed at 763 K. As can be seen, film morphology is dependent on precursor concentration. For low precursor concentration, i.e. 29.1 ppm (Fig. 2(a)), the film is characterized by separated dendrites that are unevenly distributed. As the precursor concentration increases to 116.4 ppm (Fig. 2(b)), the film becomes more uniform and evinces a tree-like fractal structure, with film thickness  $\sim$  30  $\mu$ m. This structure is quite similar to the simulated structures of Meakin (1998), as well as the experimental structures of Biswas and co-workers (Thimsen & Biswas, 2007; Thimsen et al., 2008). These types of structures have been attributed to the "adhesive" or "sticky" nature of nanoparticles, arising from either van der Waals interactions or strong ionic bonds between the surface atoms of contacting particles (Yan et al., 2010; Wang et al., 2011). For ultrafine particles at nanoscale, particle inertia is usually very small, and particle motion is strongly affected by surface interaction forces. For example, on a 763 K substrate, upon particle collision, rapid reduction of surface energy creates a strong attraction between incident and deposited particles that can form small particle agglomerates, preventing further penetration of incoming particles (Mädler et al., 2006b). Moreover, the Brownian velocity is usually much larger than the deposition velocity for the nanoparticles, increasing the collision probability before a particle can penetrate deeper. Thus, ultra-low packing and treelike film structures are formed, as shown in Fig. 2(b). With further increase of the precursor concentration to 232.8 ppm, the film exhibits tree-like structures and appears to be more dense and uniform. The distances between individual branches are shorter, indicating higher packing density. Finally, for a precursor concentration of 291.0 ppm, the film becomes so densely packed that the branching tree-like structures disappear. Similarly, Tolmachoff et al. (2009) obtained dense-packed structures without discernible tree-like morphology for a high precursor concentration of 1070 ppm, using stagnation flat-flame synthesis.

The TiO<sub>2</sub> nanofilms shown in Fig. 2 are quantified in terms of packing density using Eq. (1). Fig. 3 presents the film packing density as a function of precursor concentration, where the error bars indicate the standard error of repeated measurements. The substrate temperature is 763 K. Within the ranges of experimental conditions examined in this work, the packing densities of deposited films are ultralow. For example, for a precursor concentration of 58.2 ppm, the packing density is as low as 1.41%. The packing density increases monotonically with precursor concentration, reaching 2.76% at 291.0 ppm. The data are in good agreement with the theoretical values of 3.1% reported by Kulkarni and Biswas (2004)



**Fig. 2.** SEM images of the side view of nanostructured TiO<sub>2</sub> films for various precursor concentrations (with total amount of precursor added kept the same) at a substrate temperature of 763 K: (a) 29.1 ppm, (b) 116.6 ppm, (c) 232.8 ppm, and (d) 291.0 ppm.



Fig. 3. Packing density of  $TiO_2$  films synthesized for different precursor concentrations. The error bars are the standard errors of measured packing densities.

using Brownian dynamics simulation, and of 2.5–10% reported by Mädler et al. (2006b) using a particle transport model based on the Langevin equation. This ultralow value of packing density implies that the deposition of nanoparticles on the substrate is dominated by particle diffusion rather than particle inertia, as characterized by very small Peclet numbers.

The effect of precursor concentration can be quite complex because its variation can readily change the size, agglomeration, and concentration of particles to be deposited. To better clarify its role, we investigate three cases, with precursor concentrations of 29.1, 116.4, and 232.8 ppm, corresponding to the cases of Fig. 2, but with a low substrate temperature of 383 K, to eschew sintering at the substrate. Recently, using molecular dynamics (MD) simulation, we showed that two particles neck, but cannot completely sinter into one larger particle at such relatively low temperatures (Wang et al., 2011). Indeed, from TEM imaging of the TiO<sub>2</sub> particles collected from the substrate for different precursor concentrations, Fig. 4 shows the lack of particle sintering upon deposition; moreover, agglomeration between the nanoparticles is quite weak, producing only soft particle agglomerates and no hard aggregates. As confirmed in our previous work (Wang et al., 2011), particles sampled from the gas-phase flow field just above the substrate exist mainly as individual particles and not agglomerates, which are actually similar in size with the primary particles among agglomerates collected from the substrate under low temperature. Fig. 4(d) shows the relationship between particle size and precursor concentration. The filled



**Fig. 4.** Effect of precursor concentration on primary particles of  $TiO_2$  films with a low substrate temperature of 383 K, avoiding the post-deposition sintering. (a), (b), and (c) TEM images at 29.1 ppm, 116.4 ppm, and 232.8 ppm, respectively; (d) variation of the diameter of primary particles (with the filled circles representing the measurements from TEM images and the curved line representing the prediction based on the assumption that synthesized particle concentrations remain constant independent of precursor concentration).

circles are the experimental data, where each datum represents the average diameter of more than 30 identifiable primary particles of 4–5 different aggregates from TEM images. The size of the primary particles increases with the precursor concentration, a trend consistent with that also found by others using conventional flame synthesis (Xing et al., 1996; Pratsinis, 1998). We then develop a simplified analysis to clarify the role of precursor concentration on particle size. From the precursor concentration (116.4 ppm) and the related particle diameter (10.3 nm) at Point B in Fig. 4(d), we calculate the concentration of synthesized particles in the gas-phase to be  $\sim 1.91 \times 10^{16} \text{ m}^{-3}$ , just prior to deposition. Next, we assume that this particle concentration is the same for different cases, despite differing amounts of precursor loading. The curved line in Fig. 4(d) represents the predicted diameters of primary particles for precursor concentrations from 25 ppm to 300 ppm, using this assumption of same particle concentration for different cases. Interestingly, the predicted values coincide with the measured diameters, with errors of only 4.4% at 29.1 ppm (Point A) and 1.1% at 232.8 ppm (Point C). Thus it seems that increasing precursor concentration remaining the same. This result implies that increased particle nucleation due to increased precursor loading is offset by particle coalescence, where the characteristic time for particle sintering is much shorter than that for particle collision, leading to instantaneous coalescence. Therefore, increasing packing density of the TiO<sub>2</sub> films with increasing precursor concentration can be attributed to larger primary particles before deposition. A detailed analysis will be given later.

Upon deposition of synthesized particles, the sintering process inside the films may reconstruct the morphology of primary particles, which can be inferred from the SSA of the TiO<sub>2</sub> films, as shown in Fig. 5. When the substrate temperature is low (i.e. 383 K), SSA dramatically decreases from 313.1 m<sup>2</sup>/g to 188.3 m<sup>2</sup>/g, as precursor concentration increases from 29.1 ppm to 116.4 ppm (for the same total amount of precursor added). On-substrate sintering is quite weak due to low local temperature, with particles "frozen" upon deposition. The SSA of produced films is mainly dependent on the in-flame collision-sintering process prior to deposition, which we term as the 'in-flame-agglomeration controlled' regime, shown as circles in Fig. 5. In contrast, when the substrate temperature is high (i.e. 763 K), SSA dependence on precursor concentration is much weaker, with SSA varying in a narrow range from 91.4  $m^2/g$  to 129.7  $m^2/g$ . With a slight increase in SSA as precursor concentration increases from 58.2 to 116.4 ppm, SSA exhibits a general trend of slow decrease as precursor concentration increases from 116.4 ppm to 291.0 ppm. The relatively low SSA of 107.7 m<sup>2</sup>/g at the low precursor concentration of 58.2 ppm may be attributed to the effects of long synthesis duration (i.e. 3600 s) in keeping the total amount of precursor addition the same for all cases, resulting in significant sintering of the upper layers of the films, where the local temperatures are higher than at the substrate due to the high thermal resistance of the  $TiO_2$  films. Subplots (A) and (B) of Fig. 5 display TEM images of TiO<sub>2</sub> films for precursor concentrations of 116.4 ppm and 291.0 ppm, respectively, with the substrate at 763 K. The size of primary particles in subplot B (291.0 ppm) is only slightly larger than that in subplot A (116.4 ppm), although precursor concentration is about 2.5 times larger. Compared to the TEM images in Fig. 4 at low substrate temperature (383 K), on-substrate sintering of primary particles after deposition greatly reconstructs the



**Fig. 5.** Specific surface area (SSA) of TiO<sub>2</sub> nanofilms for different precursor concentrations. Open circles represent the data for a substrate temperature of 383 K, while the filled squares correspond to a substrate temperature of 763 K. The TEM images on the right-hand side show the morphologies of the nanofilms at (A) 116.4 ppm and (B) 291.0 ppm, for a substrate temperature of 763 K.

 $TiO_2$  film morphology. At a low precursor concentration, just deposited particles are relatively small, as shown in Fig. 4, but rapidly enlarge via sintering due to the high substrate temperature. At high precursor concentration, the sintering rate of deposited particles decreases because the sintering process is size-dependent. For solid-state diffusion in the  $TiO_2$  films, the characteristic time for sintering of two identical particles can be described as (Friedlander & Wu, 1994),

$$\tau_f = \frac{3kT}{64\pi\nu_0 D\sigma}\nu\tag{2}$$

where  $\tau_f$  is the characteristic time of sintering, v the volume of the sintering particles,  $v_0$  the volume of the diffusing vacancy, D the solid-state diffusion coefficient, and  $\sigma$  the surface tension. As can be seen, the characteristic time of sintering is proportional to the third power of particle diameter, resulting in markedly reduced sintering rate for larger particles. Therefore, the degree of on-substrate reconstruction of TiO<sub>2</sub> film structure is less for the cases with higher precursor concentrations. Even for cases of low precursor concentration, at the final stage, sintering gradually becomes slower with increasing sizes of particles that have been already sintered. Thus, for a given substrate temperature, the sintering-drive increase of particle sizes is not infinite, but has an upper limit. Consequently, after long sintering duration on the substrate, the final sizes of primary particles in the TiO<sub>2</sub> films are almost the same for all cases notwithstanding different precursor concentrations, and SSA is found to be in the narrow range of 91.4–129.7 m<sup>2</sup>/g. We term this regime as 'on-substrate-sintering controlled,' which is represented by filled squares in Fig. 5. It should be noted that with further increase of precursor concentration, particle size prior to deposition may be too large to sinter on the substrate. For these cases, particles (due to their size) will experience little sintering after deposition despite a high substrate temperature, and the SSA dependence will revert back to the 'in-flame-agglomeration controlled' regime that often occurs for low substratetemperature cases. Generally, the criterion to distinguish these two regimes is based on the ratio of length scales between the sizes of particles upon deposition and the upper sizes of primary particles driven by temperature-limited sintering on the substrate.

#### 3.2. Simplified deposition model for particle packing

Based on the above experimental results, a simplified model is developed to describe the deposition process of  $TiO_2$  nanoparticles during film synthesis, which is greatly different from that for micro-size particles. Strong nanoscale surface forces and small particle inertia make the nanoparticles 'stick' together with relatively small sliding, rolling, or separating effects after first contact. As a result, once an incident particle contacts a deposited one, its penetration into the film stops. In our model, we assume that the deposition process is mainly controlled by two kinds of particle motion: (*i*) Brownian motion induced by the impact of gas molecules, and (*ii*) directional thermophoresis toward the substrate due to the local temperature gradient. Since, in this work, average Brownian velocity ( $\sim 2-10 \text{ m/s}$ ) is about one order of magnitude larger than average thermophoretic velocity ( $\sim 0.2 \text{ m/s}$ ) for the particles, the hypothesis is that particles will maintain their "perpendicular" penetration into the film structure. By determining the mean penetration time, the corresponding penetration distance can be calculated. It is reasonable to assume that higher packing density of the films results when the particles penetrate deeper.

The average Brownian velocity is calculated by applying the principle of equipartition of energy to the translational energy of the particles (Einstein, 1905)

$$\frac{1}{2}m_p\overline{u_B^2} = \frac{3}{2}kT\tag{3}$$

where  $m_p$  is the mass of particles; and  $u_B$  is the average Brownian velocity. It is quite difficult to determine the possibility of capture for particles undergoing Brownian motion inside the complex tree-like fractal structure of nanofilms shown in Fig. 2. Considering that the fractal structures of the films for different precursor concentrations are quite similar, the size of the primary particles can represent the size of the branches to some extent. For simplification, we postulate that the incident particles travel through a space that is uniformly filled with primary particles of a constant size. Although this simplification may reduce the mean free time of the depositing particle, the final prediction of packing density should not be significantly affected. Since the Peclet number does not vary much in the experiments  $(10^{-3}-10^{-4}, within an order,$ near the diffusion limited regime), the cluster structures are similar for different cases (i.e. the fractal dimension does not change much). Therefore, the simplification reduces the mean free time in a nearly constant ratio for different precursor concentrations. The concentration of the primary particles in the film structure can be obtained from the packing density of the film, by keeping the same volume loading,

$$c_f = \frac{\varepsilon f}{d_{pf}^3} \tag{4}$$

where  $c_f$  is the concentration of primary particles;  $d_{pf}$  is the diameter of primary particles calculated from SSA; and  $\varepsilon$  is the average packing density of the film. We define f as a correction factor representing the ratio of the packing density at the top layer of the film to that of the whole bulk film. Since the top layer of the film is a transition zone with packing density varying from the bulk film value to zero, f ranges from 1 to 0 and is set as 0.5 in this work. The film packing density  $\varepsilon$  in Eq. (4) is obtained iteratively, together with Eqs. (5)–(9).

The total travel distance of a depositing nanoparticle inside porous film structures before its final capture can be predicted from basic collision theory in the free molecule regime (Vincenti & Kruger, 1965, Friedlaner, 2000). In a highly porous structure, the product of particle travel distance and the effective cross-sectional area of collision is just the average volume occupied by a particle, which is expressed as

$$l_p = \frac{1/c_f}{S_e} \tag{5}$$

where  $l_p$  is the total travel distance of a depositing (incident) nanoparticle in the film;  $c_f$  is the concentration of primary particles in the space; and  $S_e$  is the effective cross section area for collision, which can be expressed as,

$$S_e = \beta \frac{\pi}{4} (d_{pi} + d_{pf})^2 \tag{6}$$

where  $d_{pi}$  is the diameter of incident particles ready for deposition;  $d_{pf}$  is the diameter of primary particles inside the film; and  $\beta$  is the enhancement factor for collision rate due to van der Waals force. The attraction induced by van der Waals force enhances the collision rate, which is significant in the free molecule regime. Also, the trajectories of particles can be "bent" due to van der Waals force as if the capture radius were larger. Here, the classical derivation by Marlow (1980a, 1980b) is applied to estimate the enhancement factor. The mean penetrating time of nanoparticles  $\tau_p$ , i.e., the residence time of particles traveling through the film before capture, can be expressed by dividing the total travel distance by the Brownian velocity

$$\tau_p = \frac{l_p}{\nu_B} \tag{7}$$

The thermophoretic velocity of nanoparticles is calculated as (Friedlander et al., 1988)

$$v_{th} = -0.55 \frac{\eta_{\text{gas}}}{\rho_{\text{gas}}} \nabla \ln T.$$
(8)

The temperature gradient is considered to be uniform in the stationary layer, in which particle transport by thermophoresis and Brownian diffusion is dominant compared with axial convection (Mädler et al., 2006a), above the substrate. The temperature difference across the stationary layer is estimated by the temperature measured in the flame and that at the aluminum sheet, together with thermal resistance calculation comprising the aluminum sheet, silicon substrate, thermal paste, and nanofilm. The thickness of the stationary layer is estimated to be 100  $\mu$ m (Mädler et al., 2006a). In the free molecular regime, thermophoretic velocity is independent of particle size (Friedlander et al., 1988; Guha, 2008), resulting in similar penetration distance for particles of different sizes. The penetration distance  $l_{pene}$  into the film can be expressed as

$$l_{pene} = \tau_p v_{th}.$$
(9)

To predict the packing density, a quantitative relationship between the penetration distance and the packing density needs to be established. For simplicity, we assume the packing density to scale with the penetration distance. The precursor concentration of 232.8 ppm is chosen as a reference point to determine the coefficient of proportionality between the packing density and the penetration distance. Since the packing density of the film is dependent on the relative values of penetration distance rather than the absolute values, a characteristic film temperature is sufficient to correlate the parameters. Iterating Eqs. (4)–(9) together with the above coefficient of proportionality, the packing density of the film can be determined. Fig. 6 shows the comparison of packing densities between the experiments and the model



Fig. 6. Comparison of packing density between experiments and model predictions for different precursor concentrations.



Fig. 7. Effect of substrate temperature on film morphologies and measured packing densities of nanostructured TiO<sub>2</sub> films: (a) 473 K, (b) 663 K, (c) 763 K and (d) packing density.

predictions. Beside the reference case at 232.8 ppm, the predicted packing densities at 116.4, 174.6, and 291.0 ppm compare very well with the experimental data, with differences much smaller than experimental errors. The relationship between packing density and precursor concentration can be explained as follows. As precursor concentration increases, larger primary particles form in the flow field to be deposited. The smaller Brownian velocity of a larger particle results in a longer residence time within (or penetrating time into) the film structure before collision (and capture). Since the thermophoretic velocity (assumed here to be the velocity of particle penetration into the film) is independent of particle size in the free molecule regime, the result is a longer penetration distance, producing a TiO<sub>2</sub> film with higher packing density.

#### 3.3. Effect of the substrate temperature

As shown previously in Fig. 5, low and high substrate temperatures correspond to 'in-flame-agglomeration controlled' and 'on-substrate-sintering controlled' regimes, respectively, for film SSA. Fig. 7 shows the effect of substrate temperature on film morphology as well as packing density. Side-view SEM images of the TiO<sub>2</sub> films at 473, 633, and 763 K divulge similar tree-like structures for all cases. Fig. 7(d) shows a moderate effect of substrate temperature on packing density, with an overall decrease from 2.32% to 1.70%, for substrate temperatures ranging from 473 to 763 K. Change in substrate



Fig. 8. Effect of substrate temperature on specific surface area of TiO<sub>2</sub> film.

temperature embodies multiple aspects, some of which seem conflicting. For example, an increase in substrate temperature can cause a smaller temperature gradient in the deposition zone, resulting in a smaller thermophoretic velocity, which would tend to "loosen" the film. Additionally, it can produce a higher temperature in the deposition zone, increasing the Brownian velocity of incident particles, which would decrease packing density. However, it can also generate a larger sintering rate of deposited particles on the substrate, which would densify the TiO<sub>2</sub> film. The resulting effects can be quite complex as these aspects are coupled and nonlinear. When the substrate temperature is in the low range, the effects of thermophoretic velocity and Brownian velocity dominate, decreasing packing density with increasing substrate temperature. When the substrate temperature is in the high range, the 'on-substrate-sintering controlled' regime holds, causing slightly increasing packing density with increasing substrate temperature. The characteristic time for particle sintering is both temperature and size dependent, which can be expressed empirically by  $\tau_f \propto d_p^3 T \exp(A/T)$  (Ehrman et al., 1998; Xing et al., 1996). The exponential temperature dependence causes a steep reduction in film packing density at temperatures between 633 K and 686 K, as shown in Fig. 7(d). However, compared to the effect of precursor concentration on the film packing density, the effect due to substrate temperature is relatively weak.

In contrast, the effect of substrate temperature on SSA is dramatic, as revealed in Fig. 8. As the substrate temperature increases from 383 K to 763 K, SSA drops precipitously from 188.3  $m^2/g$  to 129.7  $m^2/g$ , corroborated by TEM images of primary TiO<sub>2</sub> particles in the films. For example, even compared to the sizes of primary particles at 643 K, those at much higher temperature (e.g., 763 K and even 833 K) are obviously larger. As confirmed in a previous section, the size of particles before deposition is fixed for a given precursor concentration. Therefore the variation of SSA of TiO<sub>2</sub> films can be attributed to the sintering rate of nanoparticles after their deposition. At high enough temperatures, severe sintering produces low SSA, but relatively unchanged packing density.

#### 4. Conclusions

Morphologically-controlled nanostructured  $TiO_2$  films are synthesized in a one-step process through the use of a novel stagnation swirl flame. This work clarifies the detailed roles of two parameters, i.e. precursor concentration and substrate temperature, in controlling film properties, namely, SSA and packing density. The main conclusions are summarized below.

- (1) For a given substrate temperature, as precursor concentration increases from 58.2 to 290.1 ppm, packing density of TiO<sub>2</sub> films increases considerably, reaching 2.76%, along with the disappearance of tree-like fractal structures. Through TEM observation and analysis of non-sintered primary particles in the films, the role of precursor concentration is found to affect mainly the size of primary particles prior to deposition, but not their concentration.
- (2) The effects of precursor concentration on film SSA are strongly dependent on substrate temperature. Two distinct regimes are discovered. The 'in-flame-agglomeration controlled' regime is typified by significant decrease of SSA with increased precursor concentration, occurring at low substrate temperatures. The 'on-substrate-sintering controlled' regime is exemplified by overall mild decrease of SSA with increased temperature. A general criterion to distinguish the two regimes can be based on the length ratio between the size of particles just prior to deposition and the upper size of primary particles driven by on-substrate sintering.
- (3) A simplified deposition model, based on thermophoretic and Brownian motion of nanoparticles and their overall travel distances within the porous film structure, is developed to predict the packing density of films. The predicted packing densities agree well with the experimental data. The model further explains the role of precursor concentration, where for increased precursor concentration, larger primary particles with smaller Brownian velocities are formed in the SSF, leading to longer residence times (and penetration depths) during their deposition. Larger penetration depths of nanoparticles correspond to more densely-packed films.

(4) For a given precursor concentration, increasing substrate temperature (e.g. up to 763 K) has much less effect on film packing density than that on SSA. This result arises because substrate temperature simultaneously affects Brownian velocity, thermophoretic velocity, and sintering rate of primary particles, which have counteracting effects during film formation. However, increasing substrate temperature appreciably decreases film SSA, due to the dominance of sintering among the aforementioned aspects driven by temperature and temperature gradient.

#### Acknowledgments

This work was supported mainly by the National Natural Science Fund of China (No. 50776054) and the National Program for New Century Excellent Talents in University, as well as partially from the U.S. Army Research Office (grant no. W911NF-08-1-0417) for coauthor, SDT. Special thanks are due to Prof. Pratim Biswas and Richard Axelbaum at WUSTL, Prof. Lutz Madler at Bremen, and Prof. Hai Wang at USC for stimulating and helpful discussions.

#### References

- Benkstein, K.D., Kopidakis, N., van de Lagemaat, J., & Frank, A.J. (2003). Influence of the percolation network geometry on electron transport in dye-sensitized titanium dioxide solar cells. *Journal of Physical Chemistry B*, 107, 7759–7767.
- Bertagnolli, K.E., Lucht, R.P., & Bui-Pham, M.N. (1998). Atomic hydrogen concentration profile measurements in stagnation-flow diamond-forming using three-photon excitation laser-induced fluorescence. Journal of Applied Physics, 83, 2315–2326.
- Cheng, R.K., Littlejohn D., Strakey, P.A., &Sidwell T. (2009). Laboratory investigations of a low-swirl injector with H<sub>2</sub> and CH<sub>4</sub> at gas turbine conditions. In: *Proceedings of the Combust. Inst.*, 32, pp. 3001–3009.
- Ehrman, S.H., Friedlander, S.K., & Zachariah, M.R. (1998). Characteristics of SiO<sub>2</sub>/TiO<sub>2</sub> nanocomposite particles formed in a premixed flat flame. Journal of Aerosol Science, 29, 687–706.
- Einstein, A. (1905). The motion of elements suspended in static liquids as claimed in the molecular kinetic theory of heat. Annalen Der Physik, 17, 549–560. Friedlander, S.K., de la Mora, J.F., & Gokoglu, S.A. (1988). Diffusive leakage of small particles across the dust-free layer near a hot wall. Journal of Colloid and
- Interface Science, 125, 351–355. Friedlander, S.K., & Wu, M.K. (1994). Linear rate law for the decay of the excess surface area of a coalescing solid particle. *Physical Review*, 49, 3622–3624. Friedlander, S.K. (2000). Smoke. Dust. and Haze. Oxford: New York.
- Guha, A. (2008). Transport and deposition of particles in turbulent and laminar flow. Annual Review of Fluid Mechanics, 40, 311-341.
- Kulkarni, P., & Biswas, Pratim (2004). A Brownian dynamics simulation to predict morphology of nanoparticle deposits in the presence of interparticle interactions. *Aerosol Science and Technology*, 38, 541–554.
- Kulkarni, P., & Biswas, Pratim (2003). Morphology of nanostructured films for environmental applications: simulation of simultaneous sintering and growth. Journal of Nanoparticle Research, 5, 259–268.
- Leite, E.R., Weber, I.T., Longo, E., & Varela, J.A. (2000). A new method to control particle size and particle size distribution of SnO<sub>2</sub> nanoparticles for gas sensor applications. Advanced Materials, 12, 965–968.
- Li, G.J., & Kawi, S. (1997). High-surface-area SnO<sub>2</sub>: a novel semiconductor-oxide gas sensor. Materials Letters, 34, 99-102.
- Li, S.Q., Zhang, Y.Y., Wang, J.J., Deng, S.L., & Tse, S.D. (2010). Synthesis of titania nanoparticles by premixed stagnation flames with different stabilization techniques. In: Proceedings of the 6th World Congress on Particle Technology, April 26–29, Nuremberg.
- Mädler, L., Roessler, A., Pratsinis, S.E., Sahm, T., Gurbo, T., Barsan, N., & Weimar, U. (2006a). Direct formation of highly porous gas-sensing films by in situ thermophoretic deposition of flame-made Pt/SnO<sub>2</sub> nanoparticles. *Sensors and Actuators B: Chemical*, 114, 283–295.

Mädler, L., Lall, A.A., & Friedlander, S.K. (2006b). One-step aerosol synthesis of nanoparticle agglomerate films: simulation of film porosity and thickness. Nanotechnology, 17, 4783–4795.

Marlow, W.H. (1980a). Derivation of aerosol collision rates for singular attractive contact potentials. Journal of Chemical Physics, 73, 6284–6287.

Marlow, W.H. (1980b). Lifshitz-van der Waals forces in aerosol particle collisions. I. Introduction: water droplets. Journal of Chemical Physics 73, 6288-6295.

- Meakin, P. (1984). Diffusion-controlled deposition on surfaces: Cluster-size distribution, interface exponents, and other properties. *Physical Review B* 30, 4207–4214.
- Meakin, P., Ramanlal, P., Sander, L.M., & Ball, R.C. (1986). Ballistic deposition on surfaces. Physical Review A, 34, 5091–5103.

Meakin, P. (1998). Fractals, Scaling and Growth Far from Equilibrium. Cambridge University Press: Cambridge.

- Pratsinis, S.E. (1998). Flame aerosol synthesis of ceramic powders. Progress in Energy and Combustion Science, 24, 197-219.
- Ramarao, B.V., Tien, C., & Mohan, S. (1994). Calculation of single-fiber efficiencies for interception and impaction with superposed Brownian-motion. Journal of Aerosol Science, 25(2), 295-313.
- Regan, B.O., & Grätzel, M. (1991). A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. Nature, 353, 737-740.
- Sirisuk, A., Hill, C.G., & Anderson, M.A. (1999). Photocatalytic degradation of ethylene over thin films of titania supported on glass rings. *Catalysis Today*, 54, 159–164.
- Seipenbusch, M., & Friedlander, S.K. (2004). Catalytic soot oxidation in microscale experiments: simulation of interactions between co-deposited graphitic nanoparticle agglomerates and platinum nanoparticles. *Journal of Nanoparticle Research*, 6, 605–611.

Takita, Y., Yamada, H., Hashida, M., & Ishihara, T. (1990). Conversion of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) over TiO<sub>2</sub>-supported metal and metal oxide catalysts. *Chemistry Letters*, 221, 715-718.

- Tolmachoff, E.D., Abid, A.D., Phares, D.J., Campbell, C.S., & Wang, H. (2009). Synthesis of nano-phase TiO<sub>2</sub> crystalline films over premixed stagnation flames. *Proceedings of the Combustion Institute*, 32, 1839–1845.
- Thimsen, E., Rastgar, N., & Biswas, P. (2008). Nanostructured TiO<sub>2</sub> films with controlled morphology synthesized in a single step process: performance of dye-sensitized solar cells and photo watersplitting. *Journal of Physical Chemistry*, 112, 4134–4140.

Thimsen, E., & Biswas, P. (2007). Nanostructured photoactive films synthesized by a flame aerosol reactor. AIChE Journal, 53, 1727-1735.

Vincenti, W.G., & Kruger, C.H. (1965). Introduction to Physical Gas Dynamics. Wiley: New York.

- Vorontsov, A.V., Kurkin, E.N., & Savinov, E.N. (1999). Study of TiO<sub>2</sub> deactivation during gaseous acetone photocatalytic oxidation. *Journal of Catalysis* 186, 318–324.
- Wang, J.-J., Li, S.-Q., Yan, W., Tse, S.D., & Yao, Q. (2011). Synthesis of TiO<sub>2</sub> nanoparticles by premixed stagnation swirl flames. Proceedings of the Combustion Institute, 33, 1925–1932.
- Wang, X., Yee, S.S., & Carey, W.P. (1995). Transition between neck-controlled and grain-boundary-controlled sensitivity of metal-oxide gas sensors. Sensors and Actuators B: Chemical, 24–25, 454–457.
- Xing, Y., Köylü, Ü.O., & Rosner, D.E. (1996). Synthesis and restructuring of inorganic nano-particles in counterflow diffusion flames. Combustion and Flame, 107, 85–102.

Yan, W., Li, S.-Q., Zhang, Y.-Y., Yao, Q., & Tse, S.D. (2010). Effects of dipole moment and temperature on the interaction dynamics of titania nanoparticles during agglomeration. *Journal of Physical Chemistry C*, 114, 10755–10760.
 Zhao, H., Liu, X., & Tse, S.D. (2008). Control of nanoparticle size and agglomeration through electric-field-enhanced flame synthesis. *Journal of Nanoparticle*

Research, 10, 907-923.

Zheng, Y., Jensen, A.D., & Johnsson, J.E. (2005). Deactivation of  $V_2O_5$ - $WO_3$ - $TiO_2$  SCR catalyst at abiomass-fired combined heat and power plant. *Applied Catalysis B: Environmental*, 60, 253–264.