Synthesis of TiO$_2$ nanoparticles by premixed stagnation swirl flames

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Abstract

A new turbulent, premixed, stagnation swirl flame (SSF) is used to synthesize titanium dioxide (TiO$_2$) nanopowders. Synthesis conditions under two flame modes, i.e., burner- and substrate-stabilized SSF, are investigated, for the same equivalence ratio, but different inert-dilution ratios. The particles (collected on the substrate) have high anatase purity, with mean diameters of 5–10 nm, determined using BET and TEM, for all cases studied. For the same mean nanoparticle diameter synthesized, the SSF can accommodate higher precursor loading fluxes than that produced by others using laminar premixed stagnation flat flames. Particles in the flow field are determined to be non-agglomerated. For the particles deposited on the substrate, molecular dynamics simulations support the experimental results that sintering and growth of TiO$_2$ nanoparticles do not occur on the substrate after the deposition, and the high anatase-phase purity is maintained.

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1. Introduction

Ultrafine titanium oxides (e.g., TiO$_2$) are expected to play important roles in addressing various environmental and energy challenges, due to their unique properties applicable for solar-energy conversion based on photocatalytic, photovoltaic, and water-splitting devices [1–3]. TiO$_2$ properties are strongly influenced by size, polymorph, and phase purity. For example, anatase titania, rather than rutile, possesses the requisite properties for the above applications [4]. The thermodynamic phase stability of nanocrystalline aggregates during growth is dependent on the initial particle sizes [5]. It has been reported that, for equally sized nanoparticles, anatase is thermodynamically stable for sizes <11 nm, that brookite is stable for sizes between 11 and 35 nm, and that rutile is stable for sizes >35 nm [6].

Photocatalytic activity is enhanced with decreasing TiO$_2$ particle size, with an increasing fraction of atoms located at the particle surface. On the other hand, while the increase in bandgap energy in relation to a decrease in nanoparticle...
size enhances the redox potential of the valence band holes and the conduction band electrons [1], the efficiency of TiO\textsubscript{2} nanoparticles as photocatalysts becomes limited as only a small percentage of the sunlight spectrum can be utilized. As such, studies have been conducted to find optimal sizes for specific photocatalytic reactions. For example, in trying to achieve maximum photocatalytic efficiency in the decomposition of chloroform, Ref. [7] found an improvement in activity when the particle size is decreased from 21 to 11 nm, while the activity decreases when the size is reduced further to 6 nm. In this work, the optimum mean particle size is found to be \(\sim10\) nm, where bulk recombination of charge carriers in larger TiO\textsubscript{2} nanoparticles balances surface recombination in smaller particles. In addition, it has been reported that 7 nm particles show 1.6 times better photocatalytic activity than those of TiO\textsubscript{2}, P25 and other 15- and 30-nm particles in the decomposition of 2-propanol [8]. Therefore, producing anatase-dominated TiO\textsubscript{2} nanoparticles with sizes <10 nm, which is highly dependent on the method and conditions of synthesis, is of considerable interest.

Flame synthesis is an attractive technique, where particle size, crystallinity, and phase purity can be precisely controlled, along with the potential scale up for high-throughput production, giving it an advantage over other methods such as wet-chemical and chemical vapor deposition [3]. Moreover, flame-made catalysts (compared with wet-made catalysts), e.g., TiO\textsubscript{2} composites, can be fabricated with an open-pore structure that should facilitate mass-transfer limited reactions [9]. Reported flame synthesis configurations include co-flow diffusion flame [9,10], counterflow diffusion flame [11], multi-element diffusion flame [12], burner-stabilized premixed stagnation flat flame [13,14], and divergence-stabilized premixed stagnation flat flame (SFF) [3,15]. In the latter two SFF configurations [3,13–15], the cooled stagnation substrate provides many advantages, such as: (i) steep temperature gradient for nanoparticle formation, (ii) controllable temperature histories based on burner–substrate distance, (iii) flame stabilization, (iv) collection source for TiO\textsubscript{2} nanoparticles deposition by thermophoresis, and (v) electric field application. Thus, using the stagnation configuration, synthesis of ultrafine anatase TiO\textsubscript{2} nanocrystals ranging from 3 to 10 nm is readily achieved. Finally, by setting the substrate at an “elevated” temperature, nanoparticles can sinter upon arrival, allowing for one-step continuous synthesis of porous TiO\textsubscript{2} nanocrystal films, e.g., for use in dye-sensitized solar cells [15,16].

Although the SFF can produce ultrafine (<10 nm) TiO\textsubscript{2} photocatalysts, operation in the laminar regime may limit further scale-up to commercial production. Moreover, burners based on shower-head design are subject to particle clogging by upstream thermophoretic transport, making them troublesome for long-term industrial operation [13,14]. The turbulent low-swirl flame, with swirl number \(S<0.6\), has received considerable attention in combustion applications because of its stability, ultralow NO\textsubscript{x} emissions, and ultralean operation [17–19]. In a previous study, using identical methane flow rate and precursor loading rate as that used in this paper, we found that introducing swirl into a free-jet flame (without stagnation substrate) produced finer, less-aggregated TiO\textsubscript{2} nanoparticles [20]. In this work, a novel turbulent flame configuration, termed here as stagnation-point swirl flame (SSF), is utilized for nanomaterials synthesis, combining the advantages of both substrate-established stagnation flames and low-swirl flames. The SSF is always detached from the burner, moderating over-heating and particle deposition. Additionally, the flame can be flexibly stabilized at either the burner or the substrate. As previously mentioned, depending on substrate temperature, as well as temperature gradient along the burner–substrate axis, the sintering or growth of TiO\textsubscript{2} nanoparticles may occur not only in the flow field, but also on the substrate itself. Several publications on modeling have investigated particle growth dynamics in the flow field using the population balance model (PBM) [13,14,21]. Comparatively, theoretical studies on the sintering and growth of TiO\textsubscript{2} particles on the substrate are rare.

The current study aims to demonstrate that anatase-phase TiO\textsubscript{2} of a few nanometers, with a narrow size distribution, can be synthesized using a novel SSF configuration, with promising scale-up prospects for high-throughput production. Specifically, the influences of the substrate-to-burner distance and the precursor loading rate are investigated. Properties such as specific surface area (SSA), morphology and size, and crystalline phase of the particles collected on the substrate are characterized by Brunauer–Emmet–Teller (BET), transmission electron microscopy (TEM), and X-ray diffraction (XRD), respectively. Finally, molecular dynamics (MD) simulation is conducted to compare particle sintering and growth on the substrate with that observed in the experiments.

2. Experimental

Fig. 1 depicts the SSF setup, along with the reactant and precursor delivery system. The SSF setup is composed of three main parts: (i) a downward stainless steel tube of 18 mm i.d., (ii) a swirler located within the tube that is 73 mm above the tube exit, and (iii) a substrate below the burner exit (with adjustable distance). The swirler component consists of circumferential annular vanes with a tubular central bypass fitted with a perfo-
rated screen, as shown in Fig. 2. The swirler is 14 mm long and has eight blades with an angle of 45°. The swirl number is dependent on the ratio of the jet flow in the central bypass to the swirl flow through the annular vanes. The outer diameter of the vane is 18 mm, while that of the central bypass is 8.0 mm. It can be altered by adjusting the mesh density of the perforated screen. The swirl number (S) is measured as 0.248 to ensure operation in low-swirl combustion mode [19,20].

The substrate is a 90 mm x 90 mm plate, which is mounted on a three-axis translation stage. The upper surface of the substrate is an aluminum sheet attached to a copper plate embedded with cooling-water channels. The temperature of the substrate surface (monitored by a 1-mm type K thermocouple located 0.5 mm below the substrate surface) is maintained at 110 ± 5°C, avoiding serious particle sintering and water vapor condensation.

Nitrogen-diluted oxidizer is preheated to 170°C, combined with methane, and passed through a premixing chamber, prior to delivery to the burner. Nitrogen also serves as the carrier gas for the metalorganic precursor (i.e., titanium tetraisopropoxide, TTIP, Aldrich, 97%), which is delivered with the CH₄/O₂/N₂ mixture into the SSF setup. The liquid TTIP is heated by an electrical mantle to 80°C, with the downstream line heated to 130°C to avoid condensation. The reactant flow exiting the premixing chamber is maintained above 130°C.

Three precursor loading rates of TTIP are investigated in this work by adjusting the carrier gas flow rates from 0.5 to 1.5 L/min (where 1.0 L/min gas delivers 0.025 g/min TTIP precursor). For all synthesis runs, the equivalence ratio is purposely fixed at Φ = 0.68, with flow rates of the CH₄ and O₂ set at 2.25 and 6.60 L/min, respectively. We isolate the effects of characteristic temperature by adjusting the dilution ratio of the oxidizer, i.e., α = O₂/(O₂ + N₂), via N₂ dilution with nitrogen flow rates ranging from 20.0 to 27.15 L/min. Using the operation map (Fig. 3, to be discussed later), two N₂ dilution rates are utilized for the synthesis runs: one at 20.0 L/min.
where $x = 0.2481$ (oxygen-enriched air), and the other at 24.9 L/min where $x = 0.2095$ (standard air). The flame temperatures are measured by a 0.25 mm type B thermocouple coated with SiO$_2$ to minimize surface catalytic effects, in which radiation corrections are made for measurement precision. Specifically, a TEM grid is mounted on a holder, which rotates in and out of the flow field, similar to Refs. [3,22]. The vertical distance of the TEM grid to the substrate surface is <1 mm, and the sample collection time for each period is <21 ms. The temperature of the TEM grid is <50 °C.

3. MD simulation

To assess the sintering behavior of nanoparticles on the substrate, atomic-level simulations of TiO$_2$ particle dynamics are performed using the molecular dynamics simulation open code, DL_POLY version 2.18, from Daresbury laboratories [23,24]. The Matsui–Akaogi (MA) potential, which has been validated by experimental data describing the structure and stability of TiO$_2$ particles [25–27], is employed to represent the detailed interactions between the constituent atoms of TiO$_2$ as given below:

$$V_{ij} = \frac{q_i q_j}{r_{ij}} - \frac{\epsilon_i \epsilon_j}{r_{ij}^6} + f(B_i + B_j) \exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right)$$

(1)

where $V_{ij}$ is the interaction energy between atoms $i$ and $j$. The three terms in the right-hand side of the equation represents Coulomb, dispersion, and repulsion interactions, respectively. The values of the parameters in Eq. (1) are given in Table 1. The charges ($q_i$) for titanium and oxygen are +2.196 and −1.098, respectively, in atomic units.

We extend the simulation procedure in Ref. [27] of the interaction of two TiO$_2$ nanoparticles from initial-stage sintering to complete sintering or coalescence. First, a perfect lattice is constructed using parameters for anatase, given that anatase-phase dominates for TiO$_2$ nanocrystals with $d_p < 10$ nm. Then, a 2 nm spherical nanoparticle is “excised” from the lattice structure. The excess titanium ions or oxygen ions are removed from the nanoparticle to obtain neutrality. Second, the neutral nanoparticle is simulated using the canonical ensemble (NVT) for 15 ns (3,000,000 time steps with 5 fs steps), which is sufficient for approaching equilibrium at the given temperature. Third, the particle configuration is replicated and translated along the x-axis, to establish two particles with 1 nm separation distance. Fourth, the sintering of two nanoparticles is investigated using the microcanonical ensemble (NVE). Simulations are run until the time-averaged mean temperature becomes constant, representing system equilibrium. The initial particle temperatures examined are 573, 973, 1273, 1473, and 1673 K, respectively, with the simulation time ranging from 2 to 10 ns.

4. Results and discussion

First, we map the operating limits of the stagnation-swirl flame to determine the appropriate conditions for TiO$_2$ synthesis. With fixed $\Phi$, the dilution ratio $x$ can be varied to determine the dilution blowout (DBO) limit. Fig. 3 illustrates the dilution blowout limit (DBO) and synthesis conditions of the SSF burner with $S = 0.248$, CH$_4 = 2.25$ L/min, and O$_2 = 6.6$ L/min (i.e., $\Phi = 0.64$). As the substrate–burner distance ($d_{s-b}$) increases, the DBO limit decreases, reaching a minimum value of $x = 0.1956$ at $d_{s-b} = 18$ mm, and then increases again. Note that $d_{s-b}$ at the minimum DBO limit ($x$) nearly equals the inside diameter of the burner tube. Using this operating map, we set eight runs for TiO$_2$ synthesis. Three runs are operated at $x = 0.2095$ with $d_{s-b}$ of 12, 18 and 24 mm, respectively. We denote these cases as s-SSF since the flames are stabilized close to the substrate surface, whose flame configurations, with and without the synthesis, are both shown in Fig. 1. The other five synthesis runs are operated at $x = 0.24812$ with $d_{s-b}$ ranging from 6 to 36 mm. We denote these cases as b-SSF because the flames are stabilized close to the burner tip, also shown in Fig. 1. Nevertheless, the SSF is always detached from the burner, permitting long-time operation with negligible powder deposition on the tube tip. All experiments are run for 45 min, ensuring sufficient nanopowder production for collection at the substrate.

Fig. 4 illustrates the effect of substrate–burner distance $d_{s-b}$ on the SSA of as-synthesized TiO$_2$ nanopowders, as determined by BET for all cases. For the b-SSF cases, the SSA decreases from 277 to 184 m$^2$/g as $d_{s-b}$ increases from 6 to 36 mm. Correspondingly, assuming spherical, monodisperse primary particles with homogeneous density ($\rho = 3840$ kg/m$^3$), the calculated average BET particle diameter, $d_{\text{BET}}$, increases from 5.7 to 8.5 nm. This trend is expected as the increase of $d_{s-b}$ from 6 to 36 mm results in both a decrease in the average temperature gradient between the burner and substrate (170–25 K/mm) and an increase in mean particle residence time in the flow field. As shown in Fig. 3, the SSF stabilizes close
to the burner tip, and the maximum flame temperatures are \( \sim 1850 \pm 50 \text{ K} \) for all five \( d_{s-b} \) studied. However, for the s-SSF cases, the SSA remains relatively constant in a range of 274–290 m\(^2\)/g, insensitive to the variation in \( d_{s-b} \). The corresponding \( d_{\text{BET}} \) of the nanoparticles are about 5.4–5.7 nm. In contrast to the b-SSF, the s-SSF is stabilized close to the substrate surface. Precursor oxidation and nanoparticle nucleation/coagulation are likely confined to the thin zone (see Fig. 3) between the flame sheet (1680 ± 40 K) and the substrate (383 ± 5 K), in which the temperature gradient and temperature history of the particles are similar for different \( d_{s-b} \). In addition, this difference between b-SSF and s-SSF may also be attributed to the difference in characteristic flame temperature. Since s-SSF has a relatively low flame temperature, particles may coagulate but not seriously coalesce, with longer burner-substrate distance resulting in growth in aggregate size, but not decrease in SSA.

As can be seen, both b-SSF and s-SSF cases produce ultrafine TiO\(_2\) nanocrystals with sizes of 5–10 nm, satisfying the characteristic size of thermodynamically-stable anatase TiO\(_2\) for use as photocatalysts [1,6]. Moreover, the SSF deposits the TiO\(_2\) nanoparticles uniformly, similar to the laminar burner-stabilized SFF [14] and divergence-stabilized SFFs [15]. For producing the similar \( \sim 6 \text{ nm TiO}_2 \), the TTIP loading rate per burner nozzle flow-area (mass flux) of the s-SSF is about 98.4 g/(min m\(^2\)), while those of burner-stabilized and divergence-stabilized SFFs are 53.7 and 62.4 g/(min m\(^2\)) [14,15], respectively. Again, the SSF in this work is not subject to burner clogging, which may be an issue for burner-stabilized SFFs, e.g., those based on a Mckenna-type burner, thus hindering industrial use. Also, difficulties exist in scaling up burners for premixed laminar flames, since flame shape and stability are strongly influenced by the issuing velocity profile. As such, the SSF possesses advantages over the SFF making it promising for commercial production.

The nanopowders collected from the substrate for all eight runs are analyzed by TEM, with the micrographs appearing very similar for all cases. Two b-SSF cases with \( d_{s-b} = 12 \) and 36 mm are displayed in Fig. 6. For \( d_{s-b} = 12 \text{ mm} \), the size distribution is narrow, within the range of 6.8 ± 1.1 nm; while for \( d_{s-b} = 36 \text{ mm} \), the particles are a larger, 10.2 ± 2.5 nm. The two results correlate well with the average BET diameters of 5.8 from 5.9 to 9.3 nm, in the range of that calculated based on BET.

A case with carrier flow rate of 1.0 L/min that produces TiO\(_2\) nanoparticles of \( d_{\text{BET}} = 5.8 \text{ nm} \) is compared with similar 6 nm TiO\(_2\) nanoparticles produced by burner-stabilized [14] and divergence-stabilized SFFs [15]. For producing the similar \( \sim 6 \text{ nm TiO}_2 \), the TTIP loading rate per burner nozzle flow-area (mass flux) of the s-SSF is about 98.4 g/(min m\(^2\)), while those of burner-stabilized and divergence-stabilized SFFs are 53.7 and 62.4 g/(min m\(^2\)) [14,15], respectively. Again, the SSF in this work is not subject to burner clogging, which may be an issue for burner-stabilized SFFs, e.g., those based on a Mckenna-type burner, thus hindering industrial use. Also, difficulties exist in scaling up burners for premixed laminar flames, since flame shape and stability are strongly influenced by the issuing velocity profile. As such, the SSF possesses advantages over the SFF making it promising for commercial production.

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Fig. 4. SSA of TiO\(_2\) nanopowders synthesized by SSF as a function of substrate–burner distance.

Fig. 5. SSA of TiO\(_2\) nanopowders synthesized by s-SSF as a function of carrier gas flow rate (related to precursor loading rate).

Fig. 6. TEM images of TiO\(_2\) particles collected on the substrate produced by b-SSF (a) \( d_{s-b} = 12 \) mm and (b) \( d_{s-b} = 36 \) mm.
and 8.6 nm, respectively. The collected nanopowders are in aggregate form, posing the question if significant sintering and growth of particles occurs after their deposition on the substrate. From XRD results, Zhao et al. [3] reported that partial phase transformation to rutile, coupled with sintering of anatase crystallites, occurred on the substrate after deposition. Using TEM, they also compared the sizes of particles collected from the substrate with those sampled from a point in the flow field just above it, finding the particle growth factor to be 2–3 upon deposition.

Fig. 7 shows TEM images of the particles obtained in the flow field just above the substrate, for the b-SSF case with \( d_{c-b} = 12 \) mm, using a rapid-insertion sampler. As can be seen, the particles mainly exist as individual particle, which can be attributed to the sintering time of ultrafine particles (<10 nm) being much smaller than the collision time in flow field [16,28]. The particle size is 6.4 ± 0.8 nm, which is very close to the 6.8 ± 1.1 nm of the particles collected from the substrate shown in Fig. 6 (left). The results indicate that sintering and growth processes are weak after particle deposition, different from the findings of Ref. [3]. XRD (Fig. 8) shows that the particles collected on the substrate, for all eight runs, are anatase dominant, with almost negligible rutile content. In contrast, Zhao et al. [3] reported particle sizes >10 nm with high rutile content, despite a cool substrate temperature of 50°C.

Thus, to assess further particle sintering on the substrate, MD simulations on the sintering of two

Fig. 7. TEM images of TiO_2 particles sampled from a position in the flow field <1 mm above the substrate by rapid-insertion technique (b-SSF with \( d_{c-b} = 12 \) mm).

Fig. 8. XRD pattern of TiO_2 particles collected from the substrate produced by b-SSF.

TiO_2 nanoparticles are performed at 573, 973, 1273, 1473, and 1673 K. In this work, the collected particles from the experiments are about 5 nm. Simulations of particles with 2, 3, and 5 nm were conducted, with the results for the 2 nm particles selected to be presented because smaller particles have a greater tendency to sinter than larger ones do, due to larger surface tension forces. Two classic sintering modes are manifested. Fig. 9a shows that with initial low particle temperature, e.g., 573 K, the temperature increases sharply by ~60 K after 20 ps, due to decrease in surface energy. Subsequently, the two particles neck, but cannot completely sinter into one large particle, as seen in Fig. 9a. In this mode, the temperature fluctuation in the equilibrium state is ~120 K. The particles are aggregated mainly by van der Waals dispersion interactions (forming soft-agglomerates), as well as by slight sintering bonds (forming hard-agglomerates) [29]. In the other mode, Fig. 9b shows that with a particle initial temperature of 1473 K (e.g., for particles close to the flame zone), the two particles experience necking, and then sinter completely into one larger particle, with a final temporally-averaged temperature increment of 200 K. Large temperature fluctuations (~280 K) exist at the equilibrium state due to the high characteristic particle temperature.

Given that the temperature of the substrate surface is ~378 K (much less than the initial
573 K used in the MD simulations), it is unreasonable for the 4–5 nm TiO\textsubscript{2} nanoparticles, as shown in Fig. 9b, to sinter and grow after their deposition on the substrate. Therefore the results of the MD simulations fully support our experimental findings (Figs. 6 and 7). Of course, if cooling of the substrate is insufficient and the particles reach elevated temperatures, then considerable sintering and particle growth will result in particle aggregates on the substrate, as found by others and shown in the MD simulations (e.g., Fig. 9b).

5. Conclusions

The results of the work demonstrate that a novel premixed, stagnation swirl flame (SSF) can produce ultrafine, high-purity anatase TiO\textsubscript{2} nanoparticles, with sizes of 5–10 nm, suitable for photocatalytic applications. The main conclusions drawn from this work are given below:

1. Above the DBO limit using SSF, synthesis of anatase titania nanopowders can be accomplished for flames stabilized near the burner (b-SSF) or near the substrate (s-SSF).
2. With increasing substrate–burner distance, \(d_{\text{sub}}\), the BET diameters of the nanoparticles increase from 5.7 to 8.5 nm for the b-SSF cases, but remain nearly constant within the narrow ranges of 5.4–5.7 nm for the s-SSF cases.
3. By increasing TTIP precursor loading rate from 0.0125 to 0.05 g/min, the BET average diameters of collected particles linearly increases from 5.0 to 8.4 nm under the conditions of s-SSF with \(d_{\text{sub}} = 18\) mm. For \(d_{\text{sub}} = 18\) mm, the BET diameters of the nanoparticle increase from 5.7 to 8.5 nm for the s-SSF cases.
4. TEM imaging shows that the particles in the flow field, prior to deposition on the substrate, are non-agglomerated. The particle sizes before and after deposition are as close as 6.4 and 6.8 nm, respectively.
5. The nanopowders collected from the substrate are almost completely anatase, with negligible rutile content. Molecular dynamics simulation of the sintering behavior of two TiO\textsubscript{2} nanoparticles strongly supports the experimental findings that sintering and growth of TiO\textsubscript{2} nanoparticles do not occur on the cold substrate.

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