Synthesis of nano-phase TiO$_2$ crystalline films over premixed stagnation flames

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Abstract

A new method is proposed to fabricate nanocrystalline titania (TiO$_2$) films of controlled crystalline size and film thickness. The method uses the laminar, premixed, stagnation flame approach, combining particle synthesis and film deposition in a single step. A rotating disc serves as a combination of substrate-holder and stagnation-surface that stabilizes the flame. Disc rotation repetitively passes the substrates over a thin-sheet, fuel-lean ethylene–oxygen–argon flame doped with titanium tetraisopropoxide. Convective cooling of the back side of the disc keeps the substrate well below the flame temperature, allowing thermophoretic forces to deposit a uniform film of particles that are nucleated and grown via the flame stabilized just below the surface. The particle film grows typically at $\sim$1 $\mu$m/s. The film is made of narrowly distributed, crystalline TiO$_2$ several nanometers in diameter and forms with a 90% porosity. Analysis shows that the rotation of the stagnation-surface does not reduce the stability of a stagnation flame, nor does it affect the fundamental chemistry of particle nucleation and growth that occurs between the flame and the stagnation surface.

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1. Introduction

Thin-films of titanium oxide (titania, TiO$_2$) nanoparticles have many applications including dye sensitized solar cells (DSSC) [1,2] and gas-sensors [3,4]. In DSSC, a thin film of porous nanocrystalline TiO$_2$ several micrometers in thickness serves to immobilize a photosensitive dye containing ruthenium atoms in a complex of molecular ligands and anchoring groups [5]. Photoexcitation of the dye leads to charge separation and metal-to-ligand charge transfer, that injects electrons into the conduction band in TiO$_2$. For gas-sensors the film acts as an atmosphere-dependent resistor, whereby the conductance across the particle film changes by the surface adsorption of an atmospheric trace species [3]. Thin films of TiO$_2$ nanoparticles may be fabricated by sol-gel spin coating [6,7], screen printing [8], spray deposition [9], and doctor blading [7]. Sol-gel can combine nanoparticle synthesis and film deposition in a single step, but the nanoparticles are generally amorphous and flame aerosol deposition processes can deposit crack free films [10]. Both processes involve high temperature.
treatment (∼450 °C) not suitable for low temperature substrates. All other methods either are indirect, requiring several separate steps, in which pre-synthesized TiO$_2$ nanoparticles are suspended in a surfactant solution and then coated onto a suitable substrate, or involve a direct one-step flame deposition but the resulting size distributions are usually very wide. Again, high temperature film sintering is used to oxidize the solvent and surfactant to achieve reasonably good electric conductance. The need to sinter the nanocrystalline film eliminates any possibility of using low-temperature substrates and permits reel-to-reel operation, thus complicating the production process and hindering development of thin-film DSSCs.

Here we explore a new single-step method to fabricate a nanocrystalline TiO$_2$ film. The work builds on previous studies of flame synthesis of TiO$_2$ nanoparticles [11–13] using a premixed-flame technique in which particles are produced from a nearly one-dimensional stagnation flame stabilized at a small distance beneath a stationary cooled surface [11]. Unlike sprays or gas-jet diffusion flames, particle nucleation and growth in premixed stagnation flames occurs with a controlled residence time in an environment that is spatially uniform. Because of the large flame-to-substrate temperature gradient and the small flame thickness, the residence times are short, limiting particle size growth and creating tunable, ultra-narrow size distributions of phase-pure, single-crystal anatase particles that are resistant to sintering up to 700 °C [12].

The objective of the current work is to demonstrate that porous, nanocrystalline particle films may be fabricated by combining particle synthesis and film deposition in a single step, by rotating the disc that serves as a combination of stagnation-surface/substrate-holder. The rotation repetitively passes the substrates over the flame while convective cooling of the back side of the disc keeps the substrate well below the flame temperature, allowing film deposition by thermophoretic forces.

There are obvious concerns that the rotation of the stagnation-surface will affect the flame, and with it affect the synthesis conditions and particle/film properties. To determine these effects, we experimentally and computationally examined the underlying flames. In addition, we used a transmission electron microscopy (TEM) and scanning mobility particle sizing (SMPS) to characterize particles, high resolution HRTEM to examine the crystallinity of the particle, and scanning electron microscopy (SEM) to examine film properties.

2. Experimental details

The burner assembly is shown schematically in Fig. 1. It consists of an aerodynamically shaped nozzle with a 1-cm exit diameter to generate a stagnation gas jet against a circular titanium disc 12 in. in diameter, placed 3.4 cm from the nozzle exit. The rotating disc is multifunctional. First, it acts as a stagnation-surface to stabilize the flame by flow stretch. Second, it serves as the surface for mounting substrates for film deposition. Lastly, its rotational motion convectively cools the substrate, allowing the substrate temperature to be controlled through its rotation speed. This temperature may be further tuned by four equally spaced gas jets placed above the disc. We have used air and nitrogen at a total volumetric flow rate $V_c = 40$ L/min (STP). The entire assembly is placed in a glove box vented through a fume hood to prevent the loss of the particles to the surrounding air. The pressure in the glove box is held at 35 Pa below the ambient pressure which did not noticeably increase when operational flows were introduced.

A laminar jet of unburned mixture (3.96%C$_2$H$_4$–26.53%O$_2$–Ar, $\phi = 0.45$) is issued from the nozzle exit at a velocity of $v_0 = 429$ cm/s. Flow divergence and flame stretch stabilize the flame below the disc [14]. The gas jet and the flame are isolated from the surrounding air by a shroud of argon issued through a concentric tube at a rate of 11 LPM (STP). Gases are individually metered with mass flow meters (Omega FMA 1700–1800) and mixed before entering the burner nozzle. A rotometer controls the flow of shroud argon. Driven by a syringe pump (Genie Plus, Kent Scientific), a hypodermic needle injects the titanium precursor, titanium tetraisopropoxide (TTIP, Aldrich, 97%) into the unburned mixture. The maximum volumetric flow rate of TTIP was 11.2 mL/h, which corresponds to 1070 PPM of TTIP in the reactant mixture at 1 atm. As the saturation pressure of TTIP is ∼0.025 atm at 100 °C, the gas lines and the burner are maintained at 150 °C, ensuring the liquid TTIP vaporizes.

The titanium disc is mounted on a precision stepper motor (Aerotech BM250_UF), having a positional accuracy of 1 arc s. The motor speed

![Fig. 1. Schematic of the synthesis burner setup.](Image)
is controlled by a BAI Intellidrive controller. The center-to-center distance between the motor axis and the gas jet is 12.1 cm. Deposition substrates are mounted into a series of flat slots machined into the titanium disc. As the disc rotates, the substrates repetitively pass over the flame and particles deposit thermophoretically onto the substrates, allowing for growth of continuous nanocrystalline TiO$_2$ films. The gas temperature was measured along the centerline of the gas jet impinging against a stationary disc with a 125 μm Type-S thermocouple coated with a Y/Be/O mixture to minimize surface reaction and corrected for radiation [18]. In measuring the plate temperature, the process was run for 15 min to ensure steady temperature was established. The cooling jet, flame, and disc motor were simultaneously stopped and a K-type thermocouple was immediately put in contact to the plate for measurement.

Particles were sampled for TEM analysis by rapid insertion of copper-supported grids (200 mesh) fastened onto the spinning disc, 12.1 cm from the axis, over the flame centerline with a typical insertion time of several milliseconds. An Akashi 002B TEM imaged particles and collected size statistics and a 300 kV Tecnai F30 field emission TEM examines particle structure and morphology. Particle size distribution functions (PSDF) were measured by an SMPS with gas samples gathered online through a pinhole drilled into a tube [13,15–17]. Unfortunately, this measurement could only be performed for a stationary stagnation surface, since the probe is mounted inside the stagnation plate to achieve flame conditions comparable to that of a rotating surface. The SMPS incorporates a TSI 3080 Electrostatic Classifier and a TSI 3025a Ultrafine Condensation Particle Counter.

3. Computational method

The flame chemistry was simulated using the reaction model of [19]. The stagnation flame structure was calculated with the one-dimensional OPPDIF code [20], using windward differencing and a mixture-averaged transport formula. The laminar flame speed was computed with PREMIX [21], using a multicomponent transport formula and including thermal diffusion.

4. Results and discussion

Typical synthesis flame conditions are summarized in Table 1. The ethylene/oxygen/argon mixture ($\phi = 0.45$) has an adiabatic flame temperature of 2250 K. No corrections to equivalence ratio need be made given the small loadings of the TTIP precursor. The laminar flame speed was calculated to be 96 cm/s for an unburned gas temperature of 150 °C.

With the disc held stationary, the flame is stabilized as a thin sheet about 3 cm in diameter and located 0.29 ± 0.03 cm beneath the disc (see the left most panel of Fig. 2). The spatial precision of the temperature measurement was hampered by flow disruption around and flame anchoring to the thermocouple, collectively limiting the determination of axial flame position to ±0.1 cm. This prevented reliable temperature measurement in the post flame region. Nonetheless, the temperature measured along the centerline of the gas jet in Fig. 3 shows the expected behavior. There, the temperature first remains constant and equal to the inlet temperature (150 °C) up to ~0.2 cm below the flame, and then rises sharply reaching a maximum value of $T_f = 2124 ± 50$ K—about 100 K below the adiabatic flame temperature. This temperature is more than sufficient to keep nascent particles molten as it is greater than the melting point of bulk TiO$_2$ (m.p. 1913 K) and one expects the melting point for nanoparticles to be substantially lower.

The temperature of the flame stabilization disc was measured as a function of its rotation speed $\omega$ and the volumetric flow rate of the cooling jets above the rotating disc. Figure 4 shows that the disc is progressively cooled by increasing rotation speed. For disc rotation $\geq 300$ RPM, or an equivalent local linear translating velocity of 380 cm/s, the disc temperature becomes independent of the flow rate of the cooling jets, indicating that the rotationally induced convection dominates the heat transfer. At or below 150 RPM, however, forced convection by the cooling jets is necessary to keep the disc cool. Figure 4 shows at 40 L/min of flow rate, the disc temperature is maintained below 420 K regardless of rotation rate. As a result, this flow velocity was used for all results presented here.

Figure 3 also shows the flame structure computed assuming a one-dimensional stagnation flow—a case which applies to a stationary disc only. The computed temperature profile shown in the top figure agrees with experiment within the position error in the temperature measurement. The minimum velocity ahead of the thermal

Table 1

<table>
<thead>
<tr>
<th>TTIP loading (PPM)</th>
<th>Disc speed (RPM)</th>
<th>Deposition time (ms/insertion)</th>
<th>$\delta^s$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>306</td>
<td>300</td>
<td>8</td>
<td>0.1</td>
</tr>
<tr>
<td>1070</td>
<td>100</td>
<td>24</td>
<td>0.2</td>
</tr>
<tr>
<td>1070</td>
<td>300</td>
<td>8</td>
<td>0.1</td>
</tr>
<tr>
<td>1270</td>
<td>600</td>
<td>4</td>
<td>0.07</td>
</tr>
</tbody>
</table>

* Boundary layer scale estimated for air at 150 °C.
the H atom concentration, occurs at about 0.3 cm below the stagnation-surface (roughly 3.05 cm from the nozzle). This is in agreement with the measured value of 0.29 ± 0.03 cm obtained from the photographs of Fig. 2. There, the temperature increases to 1850 K, causing the TTIP to undergo rapid decomposition into vapor Ti atoms. These Ti atoms are immediately oxidized to form TiO₂(v) which nucleates to form particles. As the axial component of the convective velocity exceeds 100 cm/s up to a distance of 0.08 cm from the stagnation-surface, the characteristic time for growth of these particles is quite short. As the axial component of the convective velocity decreases, the temperature gradient increases to dT/dx ∼ 5 × 10⁸ K/cm within that distance, leading to a fairly large thermophoretic velocity. The time history from the point of view of the particles may be determined by integrating the reciprocal “particle” velocity \( v_p \) with respect to the axial distance, \( t = \int_0^x v_p \, dx \). Here, \( v_p \) is the sum of the convective velocity along the centerline of the gas jet (as shown in the middle panel of Fig. 3) and the thermophoretic velocity, \( v_T = v + v_r \). The latter may be calculated from [22] as:

\[
v_T = \left( 1 - \frac{6 \Omega_{1.2}^{avg}}{5 \Omega_{avg}^{1.1}} \right) \frac{\kappa}{NkT} \frac{dT}{dx}
\]

where \( \Omega_{avg} \) is the reduced collision integral, \( \kappa \) the thermal conductivity of the gas, \( N \) the gas number density, \( k \) the Boltzmann constant, \( T \) is the temperature. Assuming hard-sphere elastic scattering, \( \Omega_{avg}^{1.1} = \Omega_{avg}^{1.2} = 1 \), the thermophoretic velocity is calculated to be 30 cm/s immediately adjacent to the stagnation-surface. We may now piece together the particle time history, as shown in Fig. 5. Assuming that all particles nucleate within the flame sheet, their growth is limited to a time of about 2 ms. To estimate the particle size, we integrate the second order rate equation to yield:

\[
[\text{TiO}_2]_t = \frac{[\text{TiO}_2(v)]_0}{1 + 2\beta [\text{TiO}_2(v)]_0 t}
\]

Inserting values of 1070 PPM TTIP ([TiO₂(v)]₀ = \( \sim 2 \times 10^{16} \text{ cm}^{-3} \)) and assuming \( \beta \) to be a constant and equal to \( \sim 8 \times 10^{-16} \text{ cm} \text{s}^{-1} \), typical in flame particle processes, the particle number

Fig. 2. Images of undoped flames. The disc rotates counterclockwise when viewed from the bottom. The apparent, fainter flame luminosity towards high rotation speed is caused by faster camera shutter speed. The distance from the middle of the flame to the bottom of the disc is 0.29 ± 0.03 cm.

Fig. 3. Flame structure. The symbols in the top panel are experimental data and the lines are simulation results.

Fig. 4. Effect of the disc rotation speed and flow rate of the cooling jets \( V_c \) on the disc temperature.

mixing layer was calculated to be 118 cm/s, which is 23% greater than the laminar flame speed, indicating that flame stretch is the dominant mechanism of flame stabilization.

The bottom panel of Fig. 3 shows that the most intense reaction, indicated by the peak in
density immediately adjacent to the stagnation-surface is about $3 \times 10^{11} \text{ cm}^{-3}$. Assuming a mass density of $3.87 \text{ g/cm}^3$, corresponding to pure anatase, this predicts particle diameters of $\approx 15 \text{ nm}$ after 2 ms growth. A more accurate model for particle growth would require a population balance, this predicts particle diameters of 15 nm after 2 ms growth. For example, this predicts particle diameters of $\approx 15 \text{ nm}$ after 2 ms growth. A more accurate model for particle growth would require a population balance, this predicts particle diameters of 15 nm after 2 ms growth.

Next we examine the effect of disc rotation on the flame. Figure 2 shows little or no apparent change in flame characteristics, even when the rotation speed is as high as 600 RPM, which corresponds to a local, linear velocity of 760 cm/s. The flame-to-disc distances are fixed at $\approx 0.3 \text{ cm}$ and the flame sheet remains approximately 3 cm in diameter. Only minor flame perturbations, caused by a slight wobble of the rotating disc perpendicular to the flame, were observed. Also, at high RPM the flame sheet tilts slightly in the direction of motion of the rotating disc surface, but at an insignificant angle of about 1 degree. The relatively limited changes can be understood by considering the characteristic scales of the boundary layer as a function of the rotation speed. As long as the boundary layer is thinner than the flame standoff, one would expect the rotation to have little effect on the flame. In the absence of the impinging jet, the characteristic scale is $\delta = (v/\omega_{\text{rad}})^{1/2}$ [23], the boundary layer induced by the shear of a moving plate (for $\omega_{\text{rad}} > 0$), where $v$ is the kinematic viscosity and $\omega_{\text{rad}}$ is the plate’s angular velocity. These values for $\delta$ are listed in Table 1 for various rotation speeds. For example, $\delta = 0$ for zero rotation, 0.2 cm at 100 RPM, decreasing to 0.07 cm at 600 RPM. As the jet will act to thin the boundary layer, $\delta$ is an over-estimate of the true boundary layer scale and indeed, the demonstrated lack of flame response to the rotation indicates that the actual boundary layer must be somewhat thinner.

Thus, the fact that they are of the same order or smaller than the flame-to-surface distance explains fundamental cause for the observed flame stability.

As demonstrated in previous studies, the particle size may be tuned by varying the precursor loading [10,11]. Figure 6 shows the variation of the PSDFs with respect to TTIP loading, ranging from 10 to 1070 PPM. These PSDFs, observed by SMPS, correspond to particles produced and collected at zero disc rotation. The PSDFs are clearly log-normal, with the median diameter $\langle D_p \rangle$ varying from 4.6 to 13 nm. Particles grown from TTIP concentrations up to 306 PPM are quite monodisperse. The geometric standard deviation is below that of a self-preserving size distribution having $\sigma \approx 1.45$ [24], indicating that coalescence growth is limited. At 1070 PPM, the median diameter is 13 nm, in close agreement with the 15 nm estimate made earlier. The PSDF approach a self-preserving size distribution, characteristic of coagulation dominated growth. Coagulation becomes important at higher TTIP concentrations because the characteristic time for growth decreases with increasing nuclei concentration [25].

TEM analyses show that particles are single crystalline particles or as aggregates of crystalline particles (see Fig. 7). The lattice spacing in some well defined crystal structures corresponds to that of anatase, as expected. Larger, primary particles as observed, appear to attach to each other due to van der Waals forces, while the smaller, primary particles are often aggregated as evidenced by sintered necks [26]. This is expected since small particles have a greater tendency to sinter than larger particles because of larger surface tension forces that draw the particles together [27]. Regardless aggregation and sintering is most likely to occur on the substrate when the particles are collected, forming necks and blurring boundaries, as concluded in [11,13] based on a comparison.
of the primary particle/crystalline sizes observed by three separate methods (SMPS, TEM, and X-ray diffraction).

The particle size distribution is, however influenced by disc rotation. Figure 8 shows the size distributions of particles grown from two TTIP loadings and collected at several disc rotation speeds. The PSDFs for the stationary surface were measured by SMPS, and those for rotating disc were observed by TEM. At 1070 PPM doping, the median diameter \( D_p \) drops from 13 nm at zero disc speed to around 9 nm at finite rotation speeds. However, from 100 to 600 RPM, however, the variation of the PSDFs is too small to discern within the uncertainty of the data. Previously, we have shown that with a stationary surface the mobility diameter observed by SMPS and apparent diameter measured by TEM are essentially the same [13] in the particle size range of interest. Hence, this observed shift in particle size cannot be attributed to the different measurement techniques employed. Rather the shift is caused by the change in disc temperature which is related to the disc rotation rate. Without rotation, the absence of convective cooling allows the local temperature of the disc to reach \( \sim 1000 \) K. Consequently, the temperature gradient and resulting thermophoretic velocities decrease resulting in longer particle growth times. Hence the rotation of the disc controls its surface temperature and, subsequently, through the thermophoretic force, indirectly controls the particle growth time and properties.

SEM analysis of the films confirms that uniform porous films can be generated in a short period of time on both glass and alumina, the substrate of choice for low cost gas-sensors. Films were successfully grown on alumina and on pre-cleaned microscope glass. For cross section analysis by SEM, these samples were broken along their centerline. Figure 9 shows a typical SEM image for a particle film deposited for 15 min at 300 RPM spin rate with a TTIP loading of 1070 ppm. Under these conditions, the film grows 45 \( \mu \)m over a period of 10–15 min. Typical film thicknesses are 50–100 \( \mu \)m for gas sensor applications and 10–20 \( \mu \)m for DSSC. Hence the current technique is expected to be suitable for both applications. Moreover, film thickness can be easily and reliably controlled over a wide range of deposition conditions. Recall that the deposition is intermittent, since the flame is 3 cm in diameter, but the perimeter of the disc is 76 cm. For this reason, the total growth time is only 2.4 seconds per minute of operation; and we estimate the net film growth rate to be about 1.5 \( \mu \)m/s.

There were some concerns whether already deposited particles would sinter into each other inside the film during film deposition. We tested this for a film grown at 300 RPM for 30 min with 1070 ppm TTIP loading. A sample of the resulting film was scraped off, sonicated in an ethanol solution, and deposited onto a grid. TEM analysis shows no noticeable increase in particle size or
sintering than the in-situ deposited sample, indicating the films are agglomerates.

Figure 9 also shows that the film is highly porous. The porosity may be estimated by assuming 100% Ti precursor recovery over a 3 cm deposition area. Combining with the net growth rate of 1.5 μm/s, we estimate the porosity is 90%. There is experimental evidence that continued heating of an already deposited film at 450 °C without the presence of the TTIP precursor results in better packing, reduced porosity and better structural integrity of the film.

5. Conclusions

TiO$_2$ nanoparticle films have been synthesized in a one-step, continuous process through the use of a premixed, stagnation flame, doped with a titanium precursor and stabilized under an air-cooled rotating disc. By altering the precursor concentration, we are able to produce particles having a desired size, similar to those reported earlier [11–13]. Rotating the disc over the flame not only allows for uniform thermophoretic capture of the particles and film growth, but it also shortens the growth span of the particle, allowing for greater tunability and monodispersity. Low concentrations of precursor ($\lesssim$ 300 ppm) favor smaller, more narrowly distributed particle sizes. The resulting films are uniform and porous, and their thickness can be controlled by the deposition duration. Experiments show that the flame characteristics and particle size properties are nearly constant over a range of rotation speeds from 100 to 600 RPM. Without rotation, the particle size increases and the size distribution widens. We attribute the increase in particle size to the increase in particle residence time in the growth region for a stationary disc.

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