Superhydrophilic Transparent Titania Films by Supersonic Aerosol Deposition

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Photocatalytic and hydrophilic TiO_2 thin-film applications include water purification, cancer therapy, solar energy conversion, self-cleaning devices, and antifogging windows. We demonstrate superhydrophilicity of aerosol-deposition (AD) TiO_2 films on a glass substrate without use of a carrier solvent, thereby removing the possibility of impurity contamination. AD films exhibit high visible light transmittance (greater than 80%) and superhydrophilicity (0° contact angle) with even minimal UV-light irradiation exposure. This AD method represents a significant step toward the realization of economically viable, functional thin films for the aforementioned applications.

I. Introduction

S INCE the discovery of the photocatalytic properties of TiO₂ by Fujishima and Honda in 1972,¹ the use of TiO₂ has revolutionized fundamental science and practical applications, which include air and water purification; sterilization and cancer therapy; solar energy conversion; transparent conducting oxides; and self-cleaning, antifogging, and antibeading windows, mirrors, and windshields.² Inexpensive, transparent, highly stable, and nontoxic properties make the use of TiO₂ even more attractive. In addition, TiO₂ films are durable, hard, and weather resistant. We are particularly interested in self-cleaning applications that rely on two distinct photo-induced phenomena: hydrophilicity and photocatalysis.

The photocatalytic effect promotes the decomposition of organic compounds. Upon UV-light exposure, electrons and holes are excited, which then react with oxygen to produce superoxide radical anions. Next, photogenerated holes combine with water to produce OH⁻ radicals, which lead to decomposition of organic compounds. TiO₂ hydrophilicity leads to high wettability of liquid droplets on UV-light exposed TiO₂ surfaces. Photogenerated holes can react with (absorb) water to produce OH^- radicals. This reaction also produces Ti³⁺ and oxygen vacancies, which in turn adsorb water molecules at defect sites and further promote hydrophilicity. In summary, photocatalysis decomposes organic compounds, which can be cleaned by rinsing with water due to the TiO₂'s high hydrophilicity; this synergistic effect of photocatalysis and hydrophilicity yields self-cleaning TiO₂ coatings and films. In addition, by increasing the surface structure (or roughness) of the film without UV light, even hydrophobic surfaces of water contact angle of 90° or greater, can be obtained.^{3,4} Interestingly, increased film roughness counterintuitively enhances hydrophilicity because a rougher TiO₂ film provides larger surface area that results in a larger concentration of Ti³⁺ when exposed to UV light. Overall, TiO₂ films may possess multifunctional characteristics suitable for various applications. The self-cleaning feature of the TiO₂ film is maintained through two pathways: First, photocatalysis directly decomposes organic compounds into H₂O and CO₂; second, the decomposition of soiled compounds adsorbed on the TiO₂ surface promotes the hydrophilicity of TiO₂; lastly, the hydrophilic surface can be easily cleaned with water that spreads on the surface with almost zero contact angle.⁵

In addition to photocatalysis and hydrophilicity, the transparency of TiO_2 is important in the use of the film for selfcleaning optical devices and products. Surface roughness is another property that must be controlled because it has moderate influence over both microscale hydrophilicity and macroscale hydrophobicity. While surface roughness can alter hydrophilicity, it also affects film transparency because the rougher the surface, the greater the light scattering, which decreases the transparency of the film. Film roughness, transparency, and hydrophilicity are investigated by experiments in this study.

Conventional methods of TiO₂ powder deposition can be either nonvacuum or vacuum based. Nonvacuum methods include doctor blading,⁶ dip coating,⁷ spin coating,⁸ screen printing,⁹ and sol–gel¹⁰ approaches whereas vacuum-based methods include chemical vapor deposition,¹¹ pulsed laser deposition,¹² and sputtering.¹³ All of these methods require a high-temperature postannealing process (sintering) to enhance the network or electrical contacts between TiO₂ powders to maximize the electrical or optical performance of devices. All of these methods have shortcomings, however. First, these methods require significant amounts of energy. Second, flexible polymer substrates cannot be readily used because of the high processing temperature requirement; this prohibits the use of roll-to-roll flexible substrates, which need to be used for low-cost mass production of functional materials. A low-temperature coating process that does not require postprocessing could facilitate energy-efficient, environmentally friendly, and low-cost production. Third, nonvacuum methods generally require the use of polymer carrier solvents whose residues can remain on the film even after annealing. These residues generally degrade the electrical, optical, and self-cleaning performance of the film; hence, motivating the use of a dry-powder process.

Aerosol deposition (AD) avoids the above-mentioned shortcomings by promoting^{14,15} adhesion and cohesion between TiO₂ powders and substrates through simple impacting of dry-powder particles onto the substrate, requiring neither a high-temperature process nor a liquid solvent. AD uses a high-velocity gas jet to accelerate feedstock powder to a sufficiently high velocity such that high-density coatings (or porous coating upon inclusion of organic binders or

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surfactants) are formed at low temperatures. AD is a lowcost process that yields dense nanocrystalline films under the proper conditions. AD has typically been used on smaller devices like microactuators, embedded passive components for high-frequency devices, and high-speed optical modulators even though it can be applied to large-scale substrates such as automobile and building components.

To our knowledge, we have, for the first time, aerosoldeposited TiO_2 powder (60% anatase and 40% rutile) directly onto glass substrates for self-cleaning applications. This study introduces the AD technique for dry powder coating that does not use a carrier solvent, thereby removing any possibility of this source of impurity contamination. Transparency to light, which is essential for optical applications, is investigated as a function of AD film thickness. Through measurement of the water contact angle, the hydrophilicity of our AD films is compared to those of films manufactured by the sol–gel method.¹⁶ The effects of annealing on surface morphology and light transmittance are also presented.

II. Experimental Setup

Figure 1 is a schematic of the AD experimental setup, consisted of a gas tank, fluidized-bed powder feeder, nozzle, vacuum chamber, 2-D x-y stage, booster pump, and vacuum pump. TiO₂ powder was premixed with dry-air in a fluidized bed and fed into the nozzle. Replacing dry-air with a lighter inert gas, such as helium, improves the overall coating quality because such a gas prevents oxidation and has a speed that is high enough to increase the particle impact speed. TiO₂ particles were accelerated through a supersonic nozzle. Particle-laden air was injected into a deposition chamber evacuated by vacuum and booster pumps. The deposition chamber was evacuated ($P_{amb} = 0.35 - 5.6$ Torr) to minimize TiO₂ particle deceleration before impact. This evacuation was ensured by mitigating excessively high flowrates through the nozzle (because there is a limit to how low the vacuum and booster pumps can maintain the pressure as flowrates increase). Experimental conditions are summarized in Table I. Schlieren images showing the presence of shock waves at the nozzle exit confirmed supersonic gas speed (not shown here).17,18

Figure 1(a) shows an SEM of a commercially available TiO_2 powder, consisting of a mixture of 60% anatase and 40% rutile by weight. Agglomeration is observed. To break up particle clusters, the powder was mixed with water and put into a rotary evaporator, calcined at 400°C, then ballmilled for 24 h. This breakup process resulted in particles



Fig. 1. Schematic of the experimental setup (a) SEM of the TiO_2 powder (b) side and (c) top views of an AD TiO_2 film.

Pressure in deposition chamber [Torr]	0.35~5.6
Propellant gas	Air
Nozzle exit area [mm ²]	10×35
Standoff distance [mm]	5
Gas temperature	RT (20°C)
Consumption of propellant gas [L/min]	10
Stage traverse speed [mm/s]	0.72
Number of passes	1-2

 Table II.
 The Crystal Phase, Structure, and Lattice Constant of TiO₂ Powder¹⁹

Crystal Phase	Structure	Lattice Constant	
Anatase	tetragonal	a = 3.784 c = 9.515	
Rutile	tetragonal	a = 4.5936 c = 2.9587	

having an average size of approximately 0.5 μ m. Such pre treated powders are expected to improve the deposition rate.¹⁴ Figures 1(b) and (c) are the side and top views of the TiO₂ deposited film, respectively. The highly accelerated TiO₂ particles of irregular shapes collide at supersonic speed with the substrate and their fragments are deposited. Table II provides information regarding the crystal phase, structure, and lattice constant of the raw TiO₂ powder.¹⁹

Mass flowrate of the supply air was set to 10 L/min. For the average particle size of $d_{50} = 0.5 \ \mu m$, $St_k < 0.2$, which implied that the particles attain in excess of 90% of the gas flow speed.¹⁸ The Stokes number, $St_k = \tau_p/\tau_g$, is the ratio of particle response time to the surrounding flow, $\tau_p = \rho_p d^2/$ (18 μ_g), to the characteristic time of the surrounding flow, $\tau_{\rm g} = D/u_{\rm g,exit}$ ($\rho_{\rm p}$ and d are the particle density and diameter, respectively; μ_g is the gas dynamic viscosity, and D and $u_{g,exit}$ are the nozzle exit diameter and gas speed, respectively). The substrate was situated 5 mm away from the nozzle, which was installed onto a maneuvering stage that could move up to 0.72 mm/s). The nozzle traversed the substrate only once (N = 1 pass) supplying varied amounts of TiO₂ powder to form an AD layer whose thickness varied from 60 to 300 nm. Although a uniform distribution of powder was desired across the nozzle exit, the particle number density at the nozzle center was likely to be greater than that at the periphery. The primary parameters influencing coating quality appeared to be: (1) nozzle geometry, (2) particle size and mass flowrate, (3) air mass flowrate, and (4) substrate standoff distance.

All TiO₂ films were manufactured at room temperature on soda-lime glass substrates with surface area and roughness of $1.0 \text{ cm}^2 \times 3.5 \text{ cm}^2$ and $R_a < 5 \text{ nm}$, respectively. Substrates were cleaned in an ultrasonic acetone bath for 10 min before use. The microstructures and crystallinity of the deposited TiO₂ films were characterized by both high-resolution scanning electron microscopy (HRSEM; XL30SFEG Phillips Co., Holland at 10 kV) and X-ray diffraction (XRD; D/MAX-2500, Rigaku, Tokyo, Japan), using CuK_{\alpha} radiation over a 2\theta range of 20°-50°. Atomic force microscopy (AFM; XE-100, Park Systems Corp., Suwon, Korea) was carried out to measure the surface roughness of the substrate. An optical microscope was used to measure the water contact angle after UV light ($\lambda = 365 \text{ nm}$) exposure.

III. Results and Discussion

(1) Film Transmittance

Figure 2 is an image of the TiO_2 film on the transparent glass substrate. The translucent rectangular region on the



Fig. 2. The AD-deposited TiO_2 film on a soda-lime glass. The TiO_2 layer thickness is L = 112 nm with surface roughness of 3.64 nm and average transmittance of 86% in the wavelength range of 400–800 nm. This is an as-deposited film.

glass corresponds to the AD TiO_2 film. This as-deposited film has a thickness of 112 nm; average transmittance is 77% in the wavelength range of 400–800 nm and the roughness is 3.6 nm.

Figure 3(a) shows the optical transmittance spectra (T) of the as-deposited AD TiO₂ films of various thicknesses (L) across a wavelength range of 250–850 nm, which includes the ultraviolet and visible wavelength. The transmittance, reflectance, and absorption spectra as well as the band gap energy and optical constants were obtained by UV-Vis spectrophotometers (JASCO V-650, JASCO, Analytical Instruments, Tokyo, Japan).

In Fig. 3(a), the solid curve shows the transmittance of the soda-lime glass; the absorption edge is at a wavelength of about 340 nm. These films retain high transparency (average transmittance greater than 89%) in the visible spectrum (400–800 nm). The high transmittance implies uniformity and

smoothness of the film. Of course, the thicker the film, L, the lower the transmittance. This trend is expected due to the increased scattering of light by grain boundaries and mesoscale pores in thicker films. It is also apparent that the annealed films have the lower transmittance for L = 65 and 112 nm. The reason is because the annealed films are subject to greater surface roughness which in turn scatters more lights, thereby reducing the transmittance. However, for L = 208 nm, the transmittance is higher for the annealed film than for the as-deposited film. When increasing film thickness, the roughness effect is reduced and crystallinity of the bulk film dominates. As a general rule, crystallinity improves with annealing and thus the annealed film has the better transmittance than the as-deposited film for the thick film, such as L = 208 nm, in the wavelength range of $\lambda > 650$ nm.

In theory, transmittance may be controlled by varying film thickness, pore size (or densification), and surface roughness, all of which contribute to the magnitude of light scattering. Note also that the absorption edge remains constant at 340 nm for L = 65 and 112 nm with the smaller crystallite size. However, the soda-lime glass adsorption edge is blunted upon increasing L = 208 nm, indicating that the larger crystallite size not only enhances reflection and absorption but also shifts the absorption edge. This reflectance and absorption enhancement with increasing L is shown in Figs. 3(b) and (c), respectively. In Fig. 3(b), the annealed films have the larger reflectance for L = 65 and 112 nm cases because of the larger scattering with greater surface roughness. However, for L = 208, the reflectance is lower for the annealed film. The reason is again that, for the thicker film, the roughness effect is diminished and crystallinity of the bulk film dominates for $\lambda > 475$ nm.

Figure 3(d) shows the absorption coefficient (α) as a function of photon energy (*hv*) for films of thickness L = 65, 112, and 208 nm. The absorption coefficient and photon energy are related by (αhv) = A_2 ($hv - E_g^2$)², where A_2 is a constant



Fig. 3. Optical (a) transmittance, (b) reflectance, and (c) absorption of the AD and annealed films according to thickness deposited at room temperature. (d) Indirect transition band gap energy.

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and E_g is the indirect band gap. In addition, transmittance (T) and reflectance (R) and α are related by $\alpha = -\ln [T/T]$ (1-R)]/L²⁰ The band gap energy of the film is identified by extrapolating a tangent line from the linear part of the curve. Extrapolated values are 3.78, 3.6, and 3.4 eV for L = 65, 112, and 208 nm, respectively. It is interesting that the band gap energy of the thickest film (208 nm) is close to the typical value of the indirect band gap energy of anatase TiO_2 thin films from the previous studies.^{13,21,22} Given that the band gap of the bulk anatase TiO_2 is 3.2 eV, the thickest TiO_2 film has the best crystalline state as its band gap energy is close to that of the bulk material. Thus, the 208-nm film yields the largest photocatalytic effect in the ultraviolet region of the spectrum ($\lambda < 380$ nm), even though its transparency is the lowest. It is worth it to note that neglecting reflectance does not alter the extrapolated values of the band gap (i.e., 3.78, 3.6, and 3.4 eV). We have taken R = 0 and used $\alpha = -\ln [T]/L^{21}$, which has yielded the same band gap values.

Figure 4 shows the average T from the UV-Vis spectrophotometer and the surface roughness, R_a , from the atomic force microscope as a function of film thickness. The film thickness error ranges 8–20 nm and the roughness error ranges 1–3 nm. As in Fig. 3(a), T decreases with increasing L. Also, R_a increases with film thickness. This increase has an influence on hydrophilicity as will be discussed later.

(2) Effect of Annealing

Figure 5 shows the XRD patterns of the AD TiO₂ films at various annealing temperatures. The XRD pattern of the raw powder corresponds to 60% anatase and 40% rutile by weight. The diffraction pattern of the as-deposited film shows peaks of minimal intensity; however, this minimal intensity increases as the film undergoes annealing. The formation of these peaks (indicating anatase and rutile structures) suggests that there has been no phase transformation during either the AD coating process or the annealing process. The peaks of the AD film are broader than those of the raw powder, indicating smaller grains for the film than for the powder. This is in line with material deposited by AD. As a function of annealing temperature the peak intensity increases, which indicates crystallization of the film. The Debye-Scherrer relation states that broad XRD peaks imply the production of nano-sized grains from the disintegration of the impacting particles,²³ consistent with what is expected from AD; see Table III. The AD coating process disintegrates the original TiO₂ powder, resulting in a notable reduction in grain size. Residual stresses in the nano-sized grains would cause shifts in the position of the XRD peaks, but no significant shifts in the peak positions were observed.

Figure 3(a) shows the effect of annealing on T. The solid and dashed curves indicate the as-deposited and annealed



Fig. 4. Transmittance and surface roughness of AD films deposited on glass substrates as a function of thickness.



Fig. 5. XRD patterns of TiO₂ films.

 Table III.
 Crystal Size of TiO2 Lattice After Heat

 Treatment at Various Temperatures

	Heat-treatment temperature [°C]			
TiO ₂ lattice	100	200	300	400
Anatase (101) Rutile (110)	14.6 nm 16.1 nm	15.6 nm 17.0 nm	15.9 nm 17.6 nm	17.2 nm 17.9 nm

films, respectively; annealing reduces T by 1%-8%. Gao *et al.*²¹ also showed decreased T for TiO₂ films after the annealing process. This T reduction upon annealing may be related to increased variance in surface morphology (or roughness).

Figure 6 compares the surface morphologies of TiO₂ films (as-deposited and annealed at 400°C); the change in R_a between as-deposited and annealed films is minimal, but R_a increases with L. The surface roughens with increasing the film thickness, producing a highly cross-linked and selfassembled structure, known as "3D honeycomb," appears. However, because most of our AD films reported herein are fairly thin (i.e., $L < 1 \mu m$), these honeycomb structures do not develop. During film development, TiO2 particles are more likely to adhere to previously deposited TiO₂ particles to yield a highly roughened morphology. Surface roughness plays an important role in hydrophilicity and hydrophobicity. Increased surface area of a rougher surface allows greater photocatalystic activities on the surface, which in turn, promote both hydrophilicity and hydrophobicity. This feature gives the switchable function of the TiO_2 film. If the surface becomes exceedingly roughened, hydrophilicity may be hindered by the rough surface. Therefore, there is a limit on the



Fig. 6. AFM images of the surfaces of both as-deposited and annealed TiO₂ films by AD. The AFM image is 10 mm² \times 10 mm².

roughness for realization of the switchable function. The roughness should be limited to 100 nm³, if both hydrophilicity and hydrophobicity are to be promoted. Nakajima et al.³ reported that TiO₂ films switch from being hydrophilic to hydrophobic around $R_a = 100$ nm, above which the protrusions begin to physically block the spread of water (despite increased photocatalytic activity due to the increased surface area). Hence, if the roughness is greater than 100 nm, hydrophobicity dominates. On overroughened surfaces, light scattering will increase, undesirably reducing T, as shown in Figs. 5 and 3(a). For this reason, hydrophobicity and transparency should be recognized as competing properties. Because a roughened surface also slows the state conversion rate from hydrophilic to hydrophobic,²⁴ one may purposely control the switchable rate of hydrophilicity and hydrophobicity by adjusting the surface roughness. Our AD method can realize the hydrophilic/hydrophobic switchable function of TiO₂ films because it can control the surface roughness of the films. The AD operating conditions (such as powder feeding rate, number of passes, particle size, etc.) as well as the annealing process can be used to control R_a to produce functional TiO2 films.

(3) Contact Angle

All TiO₂ films were kept inside a dark box for two days prior to the contact angle measurement. Then, each film was irradiated inside a UV light box for various durations. As a next step, the film was taken outside the UV box and then an ultra-pure water droplet (20 M Ω resistivity at 20°C) of 2 mm diam was placed on the film for a snapshot. The interval between the films being taken outside the UV box and photo-snapshot was less than 1 min so that the effect of the surrounding indoor lights is minimized. For reliable data, each contact angle value represents an average of three repeatable tests.

Figure 7 qualitatively shows the effect of film thickness on water contact angle according to UV-light exposure time (t). All films were kept inside a dark box for 2-3 days prior to measurement to create an unaffected baseline. The contact angle of a water droplet decreased after 5 h of UV-light exposure. With increasing film thickness, the contact angle decreased, indicating the effect of thickness on the water contact angle for the thickness range we considered herein 65 nm $\leq L \leq$ 208 nm. This effect might seem contradictory to the conventional belief that hydrophilicity is an interfacial (and not a bulk) property.²⁵ However, the reason as to why film thickness affects hydrophilicity was briefly mentioned in the discussion of Fig. 3 above. When L = 208 nm, the band gap of the film is 3.2 eV, which is the typical value of the band gap of the bulk anatase TiO₂, at which the photocatalystic effect in the ultraviolet region of the spectrum is maximized. Any thickness greater than L = 208 nm, we found that the band gap energy of the films did not change and remained at 3.2 eV (not shown here). Thus, hydrophilicity or



Fig. 7. Photographs of water wetting test (i.e., static contact angles) after UV light (365 nm) exposure for 0 and 5 h. The 2.1 mm diam water droplet was immediately placed on the substrate after UV-light exposure.

the contact angle was not affected by the film thickness beyond a certain thickness, which confirms that hydrophilicity is inherently an interfacial property, not a bulk property. However, as shown in Fig. 7, if film thickness is below 200 nm bulk characteristics do play a role in affecting hydrophilicity and, in turn, the water contact angle. We also note that AD films annealed at 400°C showed superhydrophilic behavior; the contact angle neared zero. This superhydrophilic behavior of the AD TiO₂ film was achieved without any UV-light illumination. The reason for this superhydrophilicity of the annealed films may be attributed to the rise of the brookite phase, which begins to appear with increasing the annealing temperature; see XRD results from Fig. 5. Shibata et al.²⁶ also observed a better hydrophilic behavior of the film consisting of the brookite phase than the film consisting of the anatase phase. They reasoned that the main face of the brookite particles used for their film fabrication, (010), had twofold oxygen atoms with high surface concentration. This high oxygen content might have contributed to the better hydrophilic behavior of the brookite phase than the anatase phase. To summarize, for hydrophilicity, the AD films were superior to films produced by conventional deposition methods, such as sol-gel²⁴ and dip coating.⁷

Figure 8 quantitatively compares the contact angles of various films as a function of UV-light exposure time. For comparison, the contact angle data of Wang et al.¹⁶ are also included in Fig. 8. Wang et al. prepared their TiO₂ films by the dip-coating technique. The thickness of their films was 150 vs. 153 nm for ours. Figure 8 compares the contact angles between as-deposited films and annealed films as a function of UV exposure time. The final measurement was taken after the films were placed inside a dark box for 24 h. For as-deposited films (triangles), the contact angle of the AD film was lower than that of the dip-coated film, except at 5 h and after storage in the dark box. The slower conversion rate of the dip-coated films after 24 h in a dark box was probably due to 100% anatase composition of TiO₂ powders of Wang et al. When comparing 300°C annealed films (circles), the AD film always has a contact angle lower than that of the dip-coated film. The AD film annealed at 400°C was superhydrophilic, consistent with Fig. 7.

Nam *et al.*²⁴ also compared the contact angles of the films produced by both sol–gel and magnetron sputtering deposition methods. The film thickness produced by sol–gel and sputtering was 200 and 1500 nm, respectively. They concluded that the sol–gel method could produce a film with better hydrophilic performance than the sputtering method, if additional treatments by argon/oxygen plasmas in a microwave discharge were implemented. Their sol–gel-deposited TiO₂ films retained the apparent contact angle of 5°–7° with oxygen and argon treatments, respectively, which is not considered superhydrophilic. This less hydrophilicity is due to



Fig. 8. Comparison contact angle between AD films and dip-coated films of Wang *et al.* (2000).¹⁶ The film thickness was 150 nm for Wang *et al.* and 153 nm for ours.

less crystallinity as a result of their low annealing temperature of 80°C. Ye et al.²⁵ produced TiO₂ films by sputtering and studied the effect of annealing temperature on the apparent contact angle. They showed that superhydrophilicity could be achieved at annealing temperature of 650°C. We demonstrated superhydrophilicity of AD films at 400°C, even without UV illumination. At relatively low annealing temperature, conditions which reduce the energy requirement in production of thin films of about 200 nm.

IV. Conclusions

Superhydrophilic, high-transmittance TiO₂ films were produced using a low-temperature AD technique. These AD films showed a significantly (factor 2) lower contact angle than those produced by conventional deposition methods, indicating that the AD films were more hydrophilic. The AD technique, with its low energy consumption and the overall rapid coating process, provides an important route to the realization of low-cost, high-performance, functional TiO2 films for self-cleaning applications.

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