Preparation of High-Transparency, Superhydrophilic Visible Photo-Induced Photocatalytic Film via a Rapid Plasma-Modification Process

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Abstract: In this study, different amounts of SiO 2 nanoparticles (7 nm) were added to simultaneously reach high transmittance, high hardness, and high adhesion for TiO 2 film prepared by the sol–gel method and coated on glass through a dip-coating technique. For the film to achieve self-cleaning, anti-fogging, superhydrophilicity, and visible photo-induced photocatalysis, TiO 2-SiO 2 film was modified via a rapid microwave plasma-nitridation process for efficient N-doping by various N 2-containing gases (N 2, N 2/Ar/O 2, N 2/Ar). Through nitrogen plasma, the content of N atom reached 1.3% with the ratio of O/Ti atom being 2.04. The surface of the thin films was smooth, homogeneous, and did not crack, demonstrated by the root mean square (RMS) roughness of film surface being 3.29–3.94 nm. In addition, the films were composed of nanoparticles smaller than 10 nm, with a thickness of about 100 nm, as well as the crystal phase of the thin film being anatase. After the plasma-nitridation process, the visible-light transmittance of N-doped TiO 2-SiO 2 films was 89.7% (clean glass = 90.1%). Moreover, the anti-fogging ability was excellent (contact angle < 5°) even without light irradiation. The degradation of methylene blue showed that the photocatalytic performance of N-doped TiO 2-SiO 2 films was apparently superior to that of unmodified films under visible-light irradiation. Moreover, the pencil hardness and adhesion rating test of the thin films were 7H and 5B, respectively, indicating that the obtained coatings had great mechanical stability.

Keywords: plasma modification; self-cleaning; anti-fogging film; superhydrophilic photocatalyst; nitridation

1. Introduction

Titanium oxide (TiO 2 ) is a very important material due to its multifunctional application in photocatalysis, hydrophilic or hydrophobic material, gas sensors, biosensors, photovoltaic cells, photochromic/electrochromic/optical devices, corrosion protection, and bactericide [1–3]. Superhydrophilic and self-cleaning TiO 2 film on glass can be used to decompose oily stains or air pollutants, which could have promising potential applications in industry. Moreover, through the production and modification of light-sensitive TiO 2 thin films, mirrors or windows with high performance of self-cleaning and anti-fogging functions could be achieved [4–6].

TiO 2 has a high refractive index (n = 2.52 for anatase; 2.76 for rutile), resulting in poor transmittance, no adsorption bands in the visible wavelengths, and the formation of white surface coatings [7,8]. Hence, refractive index grading at the interface of two materials is required for reaching efficient transmission of a normal-incident wave for some particular wavelengths. Since SiO 2 provides a refractive index that is intermediate between that of air (index of refraction, n = 1) and that of glass (n = 1.55), SiO 2 (n = 1.46), it is generally used
in solar cells of silicon-based thin film [9]. A previous study proposed mixing TiO$_2$ and SiO$_2$ for the promotion of various unique purposes, including superhydrophilic and self-cleaning functions under UV-light illumination [10]. The results revealed that the surface oxygen vacancies are saturated by OH groups, leading to a superhydrophilic surface [11]. Hence, adding SiO$_2$ nanoparticles into TiO$_2$ sol–gel to elevate the transmittance of film was carried out in this study.

Modified TiO$_2$ photocatalysts can be produced by the deposition of metal (Cu, Ag, Pt, Au, Pd) or the doping of non-metal elements (N, P, S, C, F). The photocatalysis can be achieved under ultraviolet or visible-light irradiation, which highlights the demand for them as usable materials within the energy and environmental sectors [2,12–16]. The production of visible-light photocatalysts can lower the threshold energy of photoexcitation, and then apparently enhance the utilization of solar energy. The doping of various elements, particularly with N, has been carried out in several studies [17–19]. N-doped TiO$_2$ photocatalysts can be synthesized via gas-phase or liquid-phase reactions, including the sol–gel method, chemical treatment of bare oxide, or high-temperature oxidation [17,18,20,21]. However, the plasma N-doping technique provides a dry and rapid process.

The production of hydrophilic TiO$_2$ photocatalyst film has been demonstrated through numerous approaches: radio-frequency magnetron sputtering, electron beam evaporation, and the sol–gel method accompanied by spin-coating or dip-coating [22–25]. Furthermore, the photocatalytic activity of TiO$_2$ thin films doped with nitrogen can be utilized to form TiO$_2$–xN$_x$ photocatalysts via sputtering at low pressure, heating in an NH$_3$-contained atmosphere, oxidative annealing of TiN, and direct high-temperature nitridation [26]. As a result of plasma-nitridation, it is a relatively simple and rapid process. Ti-N bonds and oxygen vacancies in the TiO$_2$ films were formed by using a 13.56 MHz cathodic magnetron plasma at 30–100 W, 5 Pa for 5 min [26]. For an N-TiO$_2$/CNT electrode, nitrogen-doped TiO$_2$ was previously synthesized by plasma-enhanced atomic layer deposition on carbon nanotubes to enhance the specific capacity [27].

Simultaneously achieving high transparency/adhesion, superhydrophilicity, and visible photo-induced photocatalysis for the TiO$_2$-based catalysts is exceedingly difficult. Due to the refractive index of TiO$_2$ film/glass and the use of additives for modifying the catalyst, the combined interaction apparently decreases the transmittance of films. High-transparent, superhydrophilic, visible photo-induced photocatalytic N-doped TiO$_2$–SiO$_2$ nano film on glass has received scarce attention within the literature, and thus is one of the focal points of the current study.

2. Materials and Methods

2.1. Experimental Materials

Ti-containing gel was prepared by first mixing acetylacetone (AcAc, CH$_3$COCH$_2$COCH$_3$, 98%, Fluka®, Milwaukee, WI, USA) and tetraisopropoxide (TTIP, Ti[OCH(CH$_3$)$_2$]$_4$, 99.8%, Acros®, Rochester, NY, USA) and then adding ethanol (EtOH, C$_2$H$_5$OH, 99.5%, Shimakyu Pure Chemicals, Samut Sakhon, Thailand), hydrochloric acid (HCl, 37%, Nihon Shiyaku Reagent, Taipei, Taiwan), and H$_2$O with a TTIP/AcAc/EtOH/HCl/H$_2$O molar ratio of 1:5:1:10:0.02. The molar concentrations of AcAc, TTIP, EtOH, HCl, and H$_2$O were 0.123, 0.615, 13.53, 0.003, and 0.664 M, respectively. The solution was stirred for 3 h at 50 ℃. Then, varying amounts of silica gel (SiO$_2$) nanoparticles (7 nm, Sigma-Aldrich, St. Louis, MO, USA) (0, 0.1, 1, 3 wt.%) were added to the sol–gel solution and stirred for 1 h to adjust the refractive index, as well as to reach the highest transmittance of film on the glass.

2.2. Method

The cleaning procedure of glass substrate (1.1 mm thick, 76.2 by 25.4 mm) was carried out first. The processes are as follows: ultrasonic shock in detergent solution for 20 min by an ultrasonic cleaner (400 W, 40 kHz, Delta DC400H, Delta Ultrasonic Co. Ltd., New Taipei City, Taiwan); deionized (DI) water flushing; ultrasonic shock in DI water for 20 min; ultrasonic shock in methanol/HCl (v/v = 250:250 mL) solution for 20 min, followed by
DI water flushing. Then, the TiO$_2$/SiO$_2$ films on dry glass were applied via dip-coating technology at various withdrawal speeds (WS = 5, 8, 10, 20, 40 mm/s) to examine the effects on transmittance, adhesion, and hardness of the films on glass. Consequently, the prepared thin film was calcined by a furnace (in air, 2.3 kW, Tender F-12, TenDer Co. Ltd., Kaohsiung, Taiwan) at 500 °C for 1 h with a heating rate of 2 °C/min for transforming amorphous crystallization into the anatase phase.

To induce the self-cleaning ability of the film at visible light, the sensitive photocatalyst thin films with high transmittance and superhydrophilic attributes were modified by N-doping the film via the microwave (MW) plasma-nitridation procedure using different reaction gases, including N$_2$, N$_2$/Ar(4.7%)/O$_2$(2%), and N$_2$/Ar(6.7%) at a total flow rate of 12 L/min (N$_2$ is balanced gas) and an applied power of 900 W with a nitridation temperature of 500 °C for 1 min. The pressure used in the MW plasma system during plasma-nitridation process was at atmospheric pressure. Table 1 presents the parameters and conditions of sample preparation in this study.

Table 1. Parameters and conditions of sample preparation.

| Parameter                                      | Conditions                  |
|------------------------------------------------|----------------------------|
| Addition of SiO$_2$ nanoparticles (wt.%)       | 0, 0.1, 1, 3               |
| Withdrawal speed (mm/s)                        | 5, 8, 10, 20, 40           |
| Gas compositions for plasma-nitridation        | N$_2$, N$_2$/Ar(4.7%)/O$_2$(2%), N$_2$/Ar(6.7%) |

The 2.45 GHz microwave (MW) plasma apparatus was applied to modify the thin films. The general scheme of the system is similar to the previous study [28]. The plasma system was assembled with a commercially available magnetron (YJ-1600, National Electronics, La Fox, IL, USA), with a stationary power of 5 kW (maximum) and operated in continuous-wave mode by passing microwaves through a circulator and a waveguide with a three-stub tuner, then reaching a cavity. An arc was used to ignite the plasma. A quartz tube reactor with a diameter of 2.9 cm intersected the waveguide (ASTEX WR340, MKS, Wilmington, MA, USA), and a resonator was placed perpendicular to it.

A glass dish was used for the photocatalytic experiments. The dish was cleaned by using DI water and ethanol solution, separately, with an ultrasonic oscillator for 30 min at room temperature. Then, the SiO$_2$-TiO$_2$ film/glass was located at the bottom of dish. The photocatalytic performance of the samples was assessed by adding 15 mL methyl blue (MB) (15 ppm) solution to the dish under visible light (Philips, T5-6WA, max. peak at 610 nm, Amsterdam, The Netherlands). The effect of N-doping on the catalysis performance of methylene blue via visible photo-induced process was examined and discussed.

2.3. Analytical Methods

The transmittance of the produced TiO$_2$/SiO$_2$ thin film was measured by using a UV-Vis spectrophotometer between 400 and 800 nm (Perkin Elmer/Lambda 35, Waltham, MA, USA). The thickness, morphology, and topology of thin films were characterized by scanning with an electron microscope (SEM, S3000N, Hitachi, Krefeld, Germany). The crystal structure of the synthesized TiO$_2$-SiO$_2$ film was determined using X-ray diffraction (XRD, RINT-2000, Rigaku, Austin, TX, USA) with CuKα radiation in the scan range of 15° to 85° (2θ). The superhydrophilic capacity of films was examined by a contact-angle analyzer (Digidrop/R&D, GBX, Dublin, Ireland). The roughness of films was analyzed by an atomic force microspore (AFM, NanoMan NS4 + D3100, Digital Instruments, Bresso, Italy). In the glow discharge zone, an optical emission spectrometer (OES, Ocean Optics, HR 4000CG, Kent, UK) was used to detect the active species involved in the plasma-nitridation process.
3. Results and Discussion
3.1. The Effects of SiO₂ Addition and Withdrawal Speeds
3.1.1. Average Transmittance

After the cleaning procedure of glass substrate, the average transmittance of dry glass was 90.5% for the visible light region between 400 and 800 nm. Then, TiO₂ thin films were prepared by the gel prepared from the TTIP/AcAc/EtOH/HCl/H₂O solution via the dip-coating process. As a result, the average transmittance of double-sided TiO₂ film/glass (without SiO₂ addition) was apparently reduced. At a 5 mm/s withdrawal speed (WS), the average transmittance was only 68.3%. When WS was increased from 8 to 40 mm/s, the average transmittance was between 71.6% and 72.5% (Figure 1), significantly lower than that of original glass due to the high refractivity of TiO₂ (n = 2.52 for anatase; 2.76 for rutile) compared to that of glass (n = 1.55) with a low surface roughness, which led to a reduction in transmittance for visible light.

![Figure 1](image-url)

Figure 1. The transmittance of TiO₂ film/glass with the addition of various amounts of SiO₂ and different withdrawal speeds.

In order to elevate the transmittance of TiO₂-SiO₂ thin films, the nanoparticles of SiO₂ (0.1–3 wt.%) were added to the TiO₂ gel. It is a similar technique with the production of anti-reflection optical film by adding the material of a lower index of refraction [29]. When the additional amount of SiO₂ was in the range of 0.1–3 wt.%, the average transmittances were significantly higher than those lacking the additional SiO₂ (71.6%); a secondary result yielded a slight increase from increasing the withdrawal speed from 8 mm/s to 40 mm/s (Figure 1). The high visible-light transmittance (88.0% to 90.6%) of as-prepared film/glass could be achieved (90.5% for clear glass) when SiO₂ nanoparticles were added; this new value was higher than those without the addition of SiO₂ due to the reduction of the index of refraction. In addition, a higher withdrawal speed led to an increase of either film thickness or roughness, resulting in higher transmittance. Due to the higher transmittance for 0.1 wt.% added SiO₂ than that for other amounts of added SiO₂ at a withdrawal speed of 8–40 mm/s, an additional amount of SiO₂ was fixed at 0.1% for the subsequent experiments.
3.1.2. Superhydrophilic Characteristics

The angle of contact (θ) was about 10° for the glass substrate after cleaning procedures. However, it was easily dirtied when absorbing the air pollutants or organics which existed in the atmospheric environment. When the TiO$_2$ film was coated on the glass, θ decreased from 18° to 7° when the withdrawal speed was reduced from 40 to 5 mm/s due to the elevation of the roughness of the surface, leading to an increase in hydrophilicity [30]. After 20 min of UV radiation, the angle of contact could decrease to under 5°, producing a superhydrophilic property of the film. However, θ reverted to its original status after 24 h of storage time in the dark.

When factoring in the addition of SiO$_2$, θ decreased with the increase in the SiO$_2$ addition, the decrease in withdrawal speed, and the UV irradiation time. At 0.1% SiO$_2$, θ decreased from 10° to 5° by decreasing WS from 40 mm/s to 5 mm/s under the condition of no UV irradiation (Figure 2) due to the elevation of roughness. Moreover, after UV irradiation for 20 min, θ decreased to 1.5°–5° (Figure 2a), achieving superhydrophilic and anti-fogging properties, as well as reverting to its original status after 24 h of storage time in the dark (Figure 2b). Furthermore, when the addition of SiO$_2$ was increased from 0.1 wt.% to 3 wt.%, θ only decreased 1–3° due to similar roughness [31].

![Figure 2](image_url)

Figure 2. Surface contact angle of TiO$_2$-SiO$_2$ (0.1%) film (a) at various withdrawal speeds and UV irradiation times, and (b) the effect of storage time in the dark.

3.2. Thickness, Morphology, and Topography of TiO$_2$-SiO$_2$ Films

Figure 3 shows the profile and thickness of the TiO$_2$ film at SiO$_2 = 0.1$ wt.%. The faster withdrawal speed in the dip-coating process led to a thicker film [32]. The thickness of the thin film was only 70, 90, and 110 nm at withdrawal speeds of 5, 8, and 10 mm/s, respectively.
From the morphology analysis, SEM images (Figure 4) showed that the films comprised well-distributed nanoparticles and the primary particle size was uniform and smaller than 10 nm. As the various withdrawal speeds increased, the particle size and porosity gradually became smaller, resulting in the roughness being reduced (Figure 4). The surface of the films was exceptionally smooth, and the nanoparticles were arranged compactly. Moreover, there was no aggregation or agglomeration of particles found, even after sintering at 500 °C.

Figure 3. Thickness of TiO$_2$-SiO$_2$ (0.1%) films prepared at various withdrawal speeds (SEM ×100,000).

Figure 4. Morphology of TiO$_2$-SiO$_2$ (0.1%) films prepared at various withdrawal speeds (SEM ×100,000).
Based on the XRD patterns of TiO$_2$-SiO$_2$/glass substrate (Figure 5), the amorphous TiO$_2$ structure existed either in the as-prepared film/glass or after annealing at 200 °C. After annealing at 500 °C, characteristic peaks of main anatase TiO$_2$ (JCPDS No. 21-1272) without rutile crystal structures were observed.

![Figure 5. Features of the XRD pattern for glass and TiO$_2$-SiO$_2$ film annealing at 200 °C and 500 °C.](image-url)

The analysis of the atomic force microscope indicated that the root mean square roughness of the surface was only 0.25 nm for clean glass. After the coating of TiO$_2$ with 0.1 wt.% SiO$_2$, excluding the film thickness, the roughness was affected by withdrawal speed, reaching 5.73 nm at a WS of 5 mm/s, then decreasing to 0.61 nm at a WS of 40 mm/s (Table 2).

| Withdrawal Speed (mm/s) | 5   | 8   | 10  | 20  | 40  | Glass |
|-------------------------|-----|-----|-----|-----|-----|-------|
| RMS roughness (nm)      | 5.73| 3.94| 2.83| 1.01| 0.61| 0.25  |

In order to access the adhesion between the TiO$_2$-SiO$_2$ (0.1%) film and clean glass, the standard test method (ASTM D3359) [33] was used by applying and removing pressure-sensitive tape over cuts made in the film. The results showed that the adhesion forces of films prepared for all withdrawal speeds are ASTM class 5B, indicating no film pull-off and representing the highest level of adhesion.

3.3. Rapid Plasma-Nitridation of Films by Different N$_2$-Containing Gases

The superior experimental conditions when preparing the high-adhesion, transparent, and superhydrophilic TiO$_2$-SiO$_2$ film on glass were achieved by adding 0.1 wt.% of SiO$_2$ at a WS of 8 mm/s. However, the photocatalytic performance should be carried out under UV irradiation. To produce a visible photo-induced photocatalytic TiO$_2$-SiO$_2$ film,
the prepared films were modified by doping N atoms via the rapid microwave plasma-nitridation process in 1 min by inducing different N₂-containing gases (N₂, N₂/Ar/O₂, N₂/Ar).

3.3.1. Surface Composition Analyses

The surface compositions and functional groups of the modified films were measured by XPS analysis. The results of chemical composition analysis showed that the content of N atoms was 1.3, 0.9, and 0.1 wt.% in the TiO₂-SiO₂ film by using N₂, N₂/Ar/O₂, and N₂/Ar plasma gases, respectively, indicating that more N atoms could be doped by N₂ plasma.

In Figure 6, the N₁s peak regions were deconvoluted into surface functional group contributions. The peaks of N₁s observed with the chemical bonding energies around 398.2–399.3 eV, 400.6–401.7 eV, 402.7–403.7 eV, 407.1–407.3 eV, and 409.1 eV when using N₂ or N₂/Ar/O₂ gases indicate the possible presence of N-TiO₂ or N-O bonds (TiNₓOᵧ), adsorbed N₂, TiO-N, N₂O adsorption, and NO²⁻ (surface nitrate), respectively (Figure 6a,b) [34–37]. However, by using N₂/Ar as plasma gases (Figure 6c), it is similar to unmodified films (Figure 6d), lacking an apparent N peak region that can be deconvoluted into surface functional group contributions, which may be caused by the reduction in density of high energetic N-containing species due to easier energy transfer to Ar than to N₂ molecules in the discharge zone. The main functional groups for the plasma N-doped films showed that O can be substituted rapidly for the N in TiO₂ via the formation of oxygen vacancy [38] by using an atmospheric-pressure MW plasma coupled with plasma-nitridation gases.

![Figure 6. XPS spectra of N₁s for as-prepared SiO₂-TiO₂ films modified by different plasma gases: (a) N₂, (b) N₂/Ar/O₂, (c) N₂/Ar, and (d) without nitridation (dots: measured XPS data; dashed lines: fittings of binding energy spectra to XPS data; solid lines: sum of the fitted data).](image-url)
3.3.2. Photocatalytic Performance of As-Modified Films under Visible-Light Irradiation

Under the condition of UV-light irradiation, the TiO$_2$-SiO$_2$ films will be superhydrophilic ($\theta<5^\circ$). However, for utilization under a visible photo-induced environment, for example, indoors or a cloudy day, the superhydrophilic visible-induced TiO$_2$-SiO$_2$ (0.1 wt.%) films on glass with high adhesion, transparent, and anti-fogging ability are prepared via the rapid (1 min) plasma N-doping process by different plasma gases, including N$_2$, N$_2$/Ar/O$_2$, and N$_2$/Ar.

The analysis of UV-visible spectra of the non-doped and N-doped TiO$_2$-SiO$_2$ films (Figure 7) indicated that nitrogen plasma modification promoted visible-light absorption and red shift. The non-doped TiO$_2$-SiO$_2$ film shows the absorbance edge around 380 nm. A red shift in the absorption edge toward the visible-light region ($\lambda$ is about 410 nm) is evident in the N-doped TiO$_2$-SiO$_2$ film modified by N$_2$ plasma at 0.9 kW for 1 min due to the incorporation of nitrogen atoms into the lattice of TiO$_2$.

![Figure 7. UV-vis absorption spectra of the non-doped and N-doped films.](image)

The removal efficiency of methylene blue (MB) in a glass reactor was carried out using visible-light irradiation, to evaluate the performance of the individual N-doped films [39]. The results of degradation for the photocatalytic activity of the TiO$_2$-SiO$_2$ (0.1 wt.%) films modified by different plasma gases are compared in Figure 8. Under visible-light degradation, the orders of conversion of MB are the films modified by N$_2$ (84.3%) > N$_2$/Ar/O$_2$ > N$_2$/Ar >> without nitridation (14.8%) after a visible-light irradiation of 500 min, indicating that the photocatalytic performance of TiO$_2$-SiO$_2$ films modified by N$_2$ plasma was slightly higher than that of those by N$_2$/Ar/O$_2$ or N$_2$/Ar plasma; however, this was much higher than that of those without N-doped film.

The results revealed that a higher removal efficiency of methylene blue for visible-light induced degradation was found at a higher content of N atoms in TiO$_2$-SiO$_2$ film, because the red shift of N-doped films into the visible light absorption range was achieved. The results also indicate that the plasma-nitridation process can be used for rapid N-doped modification of films. Moreover, the photocatalytic reaction of MB is usually fitted with the pseudo-first-order reaction rate under visible light irradiation [28].
Figure 8. Photocatalytic conversion of methylene blue under visible-light irradiation for the TiO2-SiO2 (0.1 wt.%) films modified by different plasma gases (N2, N2/Ar/O2, N2/Ar, unmodified) (MB = 15 ppm, MB solution = 15 mL).

3.3.3. Characterization of Optical Emission Spectra

An MW plasma can be successfully used to rapidly dope N atoms into TiO2-SiO2 films in 1 min of residence time. Resulting from active or energetic N-containing species, including atomic N, excited N2, N ions, and N2 ions, are generated from nitrogen and ammonia gas in the glow discharge zone [40,41]. These energetic N-containing species can thermodynamically react with TiO2 more easily than N2 molecules, forming TiO2−xNx.

Figure 9 shows the optical emission intensity of intermediate species that were detected in the glow discharge zone at 0.9 kW. For nitrogen plasma, the active or energetic species can be produced via the complex plasma-chemical reactions, such as electron-impact processes, dissociative ionization, ionization, excitation reactions, and Penning ionization reaction. The characteristic emission lines of N2 from the first positive band (B3Πg → A3Σu+ transition, at 550–900 nm) and the second positive band (C3Πu → B3Πg transition, at 300–400 nm), and the emission lines of N2+ from the first negative band (B2Σu+ → X2Σg+ transition, at 381–470 nm) [40–42], and nearly all the peaks correspond to molecular nitrogen and ionic molecular nitrogen for N2 or N2/Ar plasma gases (Figure 9) can be identified. However, the atomic nitrogen metastable molecule and ionic atomic nitrogen can not to be observed in the discharge zone. Moreover, weak representative optical emission spectra of Ar in the range of 700–850 nm can also be identified. Except for N2 or N band, Figure 9 also shows that N–O bands (γ system, 226.9, 237.0, 247.9, 259.6, 272.2, 286.0 nm) and very weak O peaks (777.2, 777.4 nm) can be observed in the O2− containing (N2/Ar/O2) MW plasma [43,44].
3.4. Characteristics of TiO$_2$-SiO$_2$ Films after Plasma-Nitridation

θ was about 10° for the clean glass substrate, 7~18° for TiO$_2$ film/glass, 5~10° for TiO$_2$-SiO$_2$ (0.1 wt.%) film/glass, and lower than 5° after UV radiation of 20 min for TiO$_2$-SiO$_2$ (0.1 wt.%) film. The TiO$_2$-SiO$_2$ (0.1 wt.%) film was prepared via modification by a rapid (1 min) microwave plasma-nitridation process using different N$_2$-containing gases, resulting in θ being lower than 5° without visible-light irradiation, as shown in Table 2. After the plasma-nitridation process, the regular, porous, and smooth surface was formed, leading to an increase in hydrophilicity [45]. Moreover, θ was still decreased to about 3° after visible-light irradiation for 20 min, regardless of what kind of plasma gases were utilized (Table 3), revealing that the modified superhydrophilic and anti-fogging films could be used in a visible photo-induced environment.

Table 3. Contact angle (θ) for different N-containing gases after various visible-light irradiation times (min) by MW plasma for TiO$_2$-SiO$_2$ (0.1%) films.

| Irradiation Time (min) | 0    | 5    | 10   | 20   |
|------------------------|------|------|------|------|
| Plasma Gases           |      |      |      |      |
| N$_2$                  | 3.7  | 3.6  | 3.2  | 3.1  |
| N$_2$/Ar/O$_2$         | 3.8  | 3.6  | 3.4  | 3.5  |
| N$_2$/Ar               | 3.9  | 3.8  | 3.5  | 3.5  |

After the plasma-nitridation process, the RMS roughness of the film surface slightly decreased when compared to that without plasma-nitridation, from 3.94 nm (unmodified) to 3.54 nm (N$_2$ plasma), 3.50 nm (N$_2$/Ar/0$_2$ plasma), and 3.29 nm (N$_2$/Ar) (Table 3). Hence, the RMS roughness of films was not affected significantly by plasma-nitridation. Visible-light transmittance was also unchanged by the different plasma gases, more so than that of the unmodified TiO$_2$-SiO$_2$ film or clean glass, reaching a range of 89.8~90.1% (Table 3). Both the film being modified at low temperature (500 °C) and a short modification time (1 min) resulted in the roughness not being significantly changed, and the film surface was porous and smooth with a high visible-light transmittance.

In order to assess the hardness of the TiO$_2$-SiO$_2$ (0.1%) film on the glass, the standard test method (ASTM D3363-05) [46] was carried out by drawing with pencil leads of known
hardness. This ranges from 9H (hardest), 8H, 7H, . . . 7B, 8B to 9B (softest). The results showed that the pencil hardness of all prepared films for various plasma nitridation gases was 7H (Table 4), indicating good sol–gel coatings on glass (9H) due to the in situ prepared nanoparticles with only 0.1% SiO$_2$ nanoparticles due to the nature of networking [47].

Table 4. Characteristics of TiO$_2$-SiO$_2$ (0.1%) films after plasma-nitridation modified by various plasma gases (withdrawal speed = 8 mm/s).

| Plasma Gases | Unmodified | N$_2$ | N$_2$/Ar/O$_2$ | N$_2$/Ar | Clean Glass |
|--------------|------------|-------|----------------|----------|-------------|
| RMS roughness (nm) | 3.94 | 3.54 | 3.50 | 3.29 | 0.25 |
| Average | 89.7 | 90.1 | 89.8 | 90.0 | 90.5 |
| transmittance (%) | 7H | 7H | 7H | 7H | 9H |

4. Conclusions

This study successfully developed procedures to optimize the operational conditions for the sol–gel dip-coating method combined with a rapid plasma-nitridation technique to produce N-doped TiO$_2$-SiO$_2$ nano film on glass, while simultaneously achieving a high transmittance (~90%), high hardness (7H), superhydrophilicity (θ < 5°), and good adhesion (5B) for the applications of self-cleaning and anti-fogging. Moreover, the high photocatalytic performance of the film/glass can be easily accomplished under visible photo-induced irradiation after the rapid plasma-nitridation process.

Author Contributions: B.-J.L.: investigation, formal analysis, validation, writing—review and editing; K.-T.L.: conceptualization, formal analysis, writing—review and editing; Y.-M.K.: resources, supervision, project administration, writing—review and editing; C.-H.T.: investigation, visualization, data curation, methodology, writing—original draft. All authors have read and agreed to the published version of the manuscript.

Funding: We would like to thank the Ministry of Science and Technology of Taiwan for its financial support under grants MOST 107-2221-E-992-003 and MOST 107-2622-E-992-017-CC3.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors gratefully acknowledge the use of EM000600 and EM000600 of MOST 108-2731-M-006-001 belonging to the Core Facility Center of National Cheng Kung University.

Conflicts of Interest: The authors declare no conflict of interest.

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