



Double layer SiO₂-TiO₂ sol-gel thin films on glass for antireflection, antifogging, and UV recoverable self-cleaning

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Double layer thin films, mechanically stable and adhering to glass, were produced through the sol-gel process, using tetraethyl orthosilicate and titanium butoxide as precursors. The refractive index of the titania and silica-titania composite layers were typically 2.1 and 1.7, and their physical thicknesses were approximately 65 nm and 81 nm, respectively, as determined by ellipsometry. These optical constants allowed attainment of quarter-wave optical thicknesses at the center of the visible spectrum (550 nm) as designed, with an increase of 3.4% in transmittance. The nanometric surface roughness, measured by optical profilometry, was effective to decrease light scattering and water contact angles to below 10°. As novelty in dip-coated sol-gel films, superhydrophilicity for self-cleaning, antifogging, and antireflection in the mid-visible spectrum were simultaneously attained with durability of 9 weeks in the dark. Further application of UV light allowed regeneration of contact angles for self-cleaning. © 2020 Optical Society of America

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1. INTRODUCTION

The development of self-cleaning photocatalytic materials through the sol-gel route has been of great interest recently and presents a vast area of applications, such as for windows of buildings, automobiles, sensors, and thermo-solar and photovoltaic panels [1–3].

On the other hand, metal-oxide films have been extensively studied due to their electric and optical properties. Titania thin films (TiO₂) are used for the photodissociation of organic materials in water and sewage treatments [4], in the fabrication of solar cells [5], as well as in photocatalysis and antireflection [6,7]. Moreover, titania displays an ultraviolet (UV) photo-induced hydrophilicity that allows self-cleaning to self-heal [8,9]. Silica coatings (SiO₂) have been used where light transmission is an essential factor, as in windows and solar panels, besides presenting good adherence and additional mechanical resistance to glass [10].

There are numerous methods for producing metal-oxide films, including physical vapor deposition [11], chemical vapor deposition (CVD) [12,13], sputtering [14], ultrasonic spray pyrolysis [15], pulsed laser deposition [16] and e-beams [17,18]. Recent reports on titania thin films used as hydrophilic material include: Chemin *et al.* [19] produced them by plasma-enhanced chemical vapor deposition, Khan *et al.* [11]

by glancing angle deposition (GLAD), Liu *et al.* [20] by *in situ* growth of nanospheres, Latthe *et al.* [21] by spray coating, Lin *et al.* [22], İközler [23], and Zhang *et al.* [24] by sol-gel dip coating, and Tao and Zhang [25] by sol-gel dip-coated nanospheres and CVD. Each of these studies presents one or more of the properties attained in this work, but not all of them simultaneously, as discussed in Section 3.

The sol-gel process appears to be a good method due to its rapidity, great variety of precursors, low synthesis temperature compared to the melting point of the materials involved, and structural and morphological controllability [14,26]. Furthermore, the materials and processing involved are relatively low cost, a chief factor for wide industrial use [27].

This research aims at producing a silica-titania double layer coating on glass, through the sol-gel process, with simultaneous and durable properties of self-cleaning, antifogging, and antireflection in the mid-visible spectrum.

2. EXPERIMENTAL

Materials: Tetraethyl orthosilicate 99.0% and titanium (IV) butoxide 97% were purchased from Sigma-Aldrich. Ethanol (EtOH) 99.8% was purchased from NEON. Hydrochloric acid

37% was purchased from Êxodo. Acetic acid PA-ACS was purchased from Dinâmica. The water was deionized. All chemicals were used without further purification.

Preparation of acid-catalyzed SiO_2 sol: Tetraethyl orthosilicate (TEOS) was mixed with deionized water (H_2O), ethanol (EtOH), and hydrochloric acid (HCl). The final molar ratio of TEOS: H_2O :EtOH:HCl was 1:15.4:31.2:6.8. This mix, in a sealed flask, was stirred for 3 h and aged in a refrigerator for 24 h.

Preparation of acid-catalyzed TiO_2 sol: Titanium (IV) butoxide (TNBT) was mixed with deionized water, ethanol, and acetic acid (CH_3COOH). The final molar ratio of TNBT: H_2O :EtOH: CH_3COOH was 1:0.03:49.92:0.03. This mix, in a sealed flask, was stirred for 3 h and aged in a refrigerator for 24 h.

Preparation of $\text{SiO}_2 - \text{TiO}_2$ blend sols: The silica sol and the titania sol were mixed together in another stirrer, for 2 h, in a 55:45 wt% proportion. This new mix was aged in a refrigerator for 24 h.

All samples were fabricated on VWR Micro Slides PLAIN 3 in \times 1 in, 1 mm thick glass substrates. The titania sol for the first layer was deposited by dip coating (ambient temperature 25°C , air humidity 30%) with withdrawal speeds of 0.5, 2.0, 3.3, 4.0, 4.5, and 5.0 mm/s. After natural drying for five minutes, the sample was heated in a muffle furnace at 90°C for one hour to fully evaporate the solvent and at 400°C for one hour to form the titania layer. Using the same process parameters, the second layer was fabricated from the silica–titania blend sol.

Characterization: Water contact angles were measured by the sessile drop method using home-built equipment, which employed a digital camera connected to a computer to capture the drop image and to run a software (Surftens) analysis. Surface roughness was measured with an optical Contour GT-K profilometer (Bruker). Film thickness was determined with a spectral ellipsometer, SOPRA GE-5SE. Optical transmittance was measured with a spectrophotometer, CARY 5000 (Agilent), in the 400 to 700 nm wavelength range.

3. RESULTS AND DISCUSSION

The silica–titania sol–gel coatings consist of hard ceramic layers that adhere well to glass and whose mechanical stability is not affected by scratching with an HB pencil, for example.

Figures 1(a) and 1(b) show typical results of optical profilometry performed on titania, which forms the first layer of the coatings. On different days, two sets of samples were produced using the same process and under the same general conditions with a dip-coater withdrawal speed of 4.0 mm/s. For the titania sample surfaces, measured values of root-mean-square roughness (R_q) ranged between 127.0 and 67.6 nm.

Figures 2(a) and 2(b) show the typical results of the optical profilometry measurement on the silica–titania that formed the second layer of the coatings. On different days, both samples were fabricated using the same process and under the same general conditions with a dip-coater withdrawal speed of 5 mm/s.

A comprehensive measurement was obtained, considering that experimental data were registered from all the silica–titania surfaces. Their nanometric rms roughness (R_q), ranging

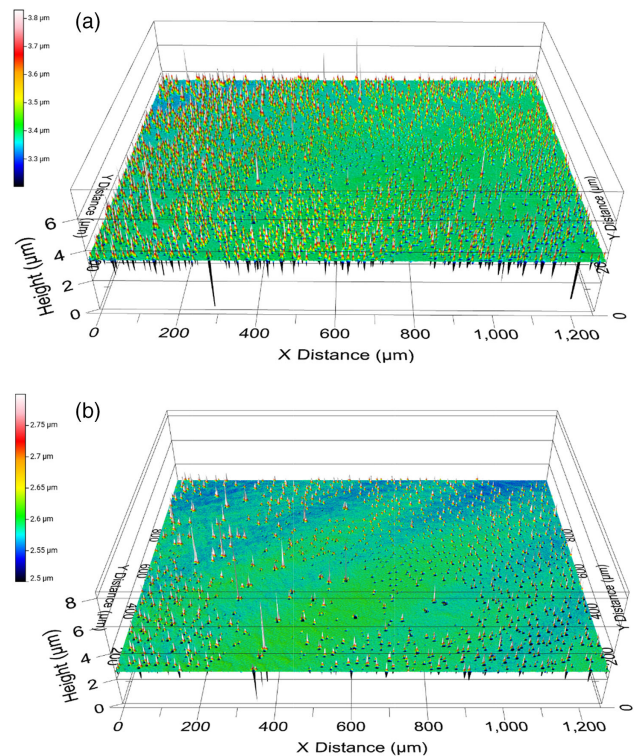


Fig. 1. Topology images of the titania film surfaces, prepared through the sol–gel route described in the experimental section, obtained by optical profilometry in white light interference mode. The uncertainty in the rms roughness R_q is ± 0.1 nm.

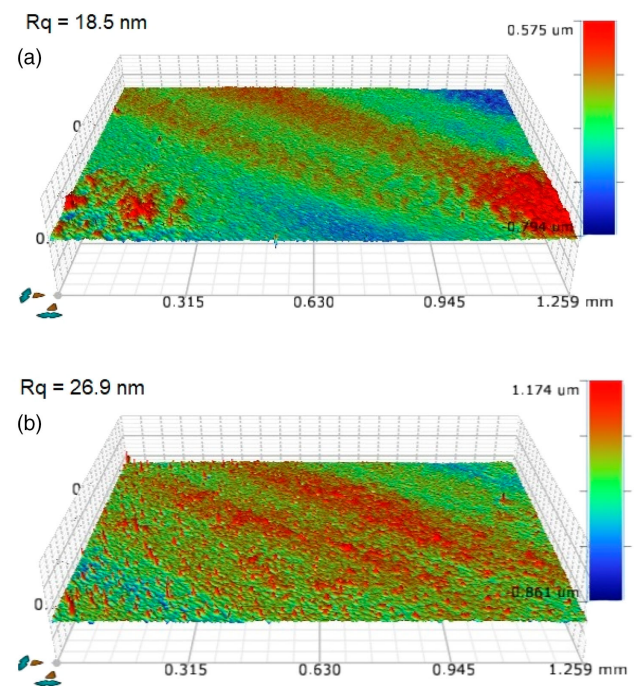


Fig. 2. Optical profilometry images in white light interference mode of sol–gel silica–titania films, whose process parameters are described in the experimental section (surface rms roughness R_q uncertainty: ± 0.1 nm).

between 18.5 and 26.9 nm, shows reasonable surface uniformity and reproducibility.

Moreover, comparison between these optical profilometry results (Fig. 2) with those from the titania film surfaces (Fig. 1) leads to evidence that the addition of silica precursors to the sol produces smoothing of the surface.

A. Antireflection Double Layer

For antireflection by interference with a double quarter-wave layer at normal incidence, the following expressions apply [28]:

$$\left(\frac{n_2}{n_1}\right)^2 = \frac{n_s}{n_0}, \quad n_i d_i = \lambda/4; \quad i = 1, 2,$$

where n_s is the substrate refractive index (1.5 for soda–lime glass), n_0 is the refractive index of the incident medium (1.0 for air), n_2 is the refractive index of the titania layer, and n_1 is the index of the silica–titania layer; d_1 and d_2 are their corresponding physical thicknesses, and λ is the wavelength of light in a vacuum.

The resulting configuration is shown in Fig. 3.

The dependence of the layer thicknesses, measured by ellipsometry, on the dip-coating withdrawal speeds are shown in Fig. 4.

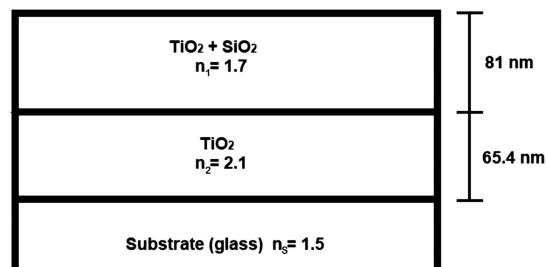


Fig. 3. Illustrative scheme showing the distribution of quarter-wave layers at normal incidence, their refractive indices, and calculated thicknesses for the mid-visible wavelength (550 nm).

Interestingly, in Fig. 4, a nonlinear influence of dip-coating speed on layer thickness is observed, which is peculiar to each sol material.

B. Transmittance

Four batches of samples with double layer coatings were fabricated. Their average optical constants and optical thicknesses are shown in Tables 1 and 2, respectively.

Three of the four curves display a transmittance peak raise of around 3.4% in comparison to that of the bare glass substrate in the central part of the visible spectrum. During dip coating, one of the glass substrate sides was masked with a tape, which was

Table 1. Titania and Silica–Titania Average Layer Thicknesses and Refractive Indices at 550 nm, Produced at Constant Temperature of 25°C and Air Humidity of 30%, Except for the Silica–Titania Film of Batch TS2 (28°C and 50% Air Humidity)

Sample Batch	TS1	TS2	TS3	TS4
Silica–Titania:				
Thickness (± 0.1 nm)	94.2	114.0	90.9	91.1
Refractive index (± 0.01)	1.63	1.65	1.63	1.58
Titania:				
Thickness (± 0.1 nm)	65.2	62.1	65.7	66.5
Refractive index (± 0.01)	2.09	2.10	2.10	2.10

Table 2. Optical Thickness (OT) Values of the Titania and Silica–Titania Layers at 550 nm, Calculated for the Four Batches from Table 1, and Their Respective Averages

OT (± 0.1 nm)/Batch	TS1	TS2	TS3	TS4
Silica–Titania	153.5	188.1	148.2	143.9
Titania	136.3	130.4	138.0	139.6
Average	144.9	159.2	143.1	141.7

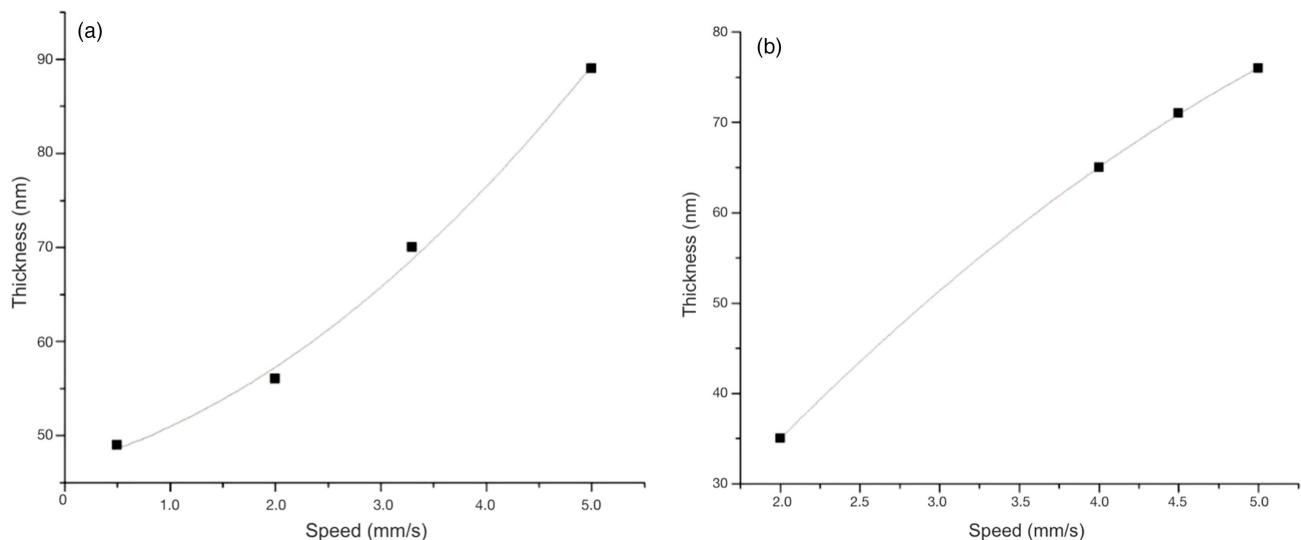


Fig. 4. Measured data of layer average thickness (± 1 nm, typically) versus dip-coating withdrawal speed (± 0.1 mm/s): (a) for the silica–titania sol and (b) for the titania sol. The continuous interpolation curves are an aid to the eye.

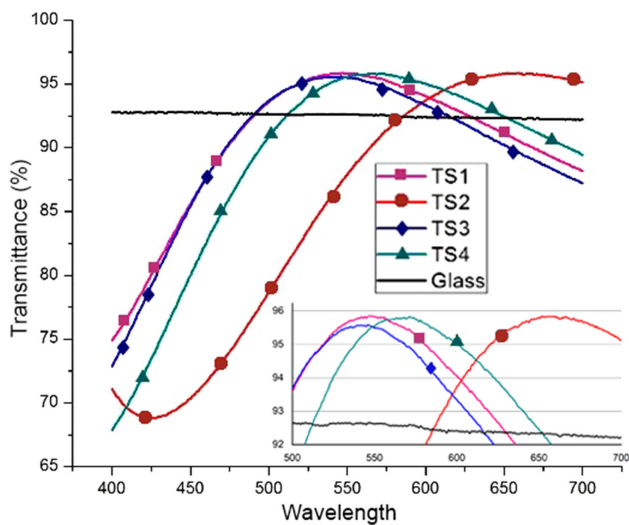


Fig. 5. Typical transmittance ($\pm 0.1\%$ uncertainty) of samples from the four batches (coated on one side only) in the visible spectrum (see Tables 1 and 2). At the inset, a close-up of the peak region is shown. Most of the transmittance loss is due to the uncoated side of the glass substrate ($\sim 4\%$).

later removed, producing a reflectance of around 4%. Table 2 and Fig. 5 can be analyzed according to the ideal optical thickness ($550 \text{ nm}/4 = 137.5 \text{ nm}$). Its nearest average match, from batch TS4, has its peak at almost 550 nm. The two typical batch samples with the most similar transmittance curves are also those with the closest average optical thicknesses.

The typical sample from batch TS2 shows the biggest discrepancy, both in optical thickness (see Table 2) and in the transmittance curve. This difference is due to temperature and air humidity deviations during dip coating, showing the importance of these sol-gel process parameters. Dependency on those deviations does not allow control of refractive indices and thicknesses as precisely as through physical vapor deposition techniques in a vacuum, which thus presents small differences from the designed configuration in Fig. 3. Their ultimate impact, shown in Fig. 5, is the slight departure of the transmittance maxima from the design wavelength at 550 nm.

C. Superhydrophilicity and Self-Healing

Besides the antireflection aspect, the silica-titania composition is extremely relevant to self-cleaning.

In this sense, the titania photocatalytic activity is important, since it breaks down the contaminant molecules on the surface, so that the water passing by can carry what remains there. However, this is only sustained when frequently illuminated by UV light. If the material is maintained in a dark place for a short period of time (a few days) the self-cleaning property is lost [29]. This phenomenon can be seen through the contact angle in Fig. 6.

In samples B and C, UV light was able to completely recover the titania surface's superhydrophilic property (contact angle $< 10^\circ$), which only lasted for about a week when stored in dark places. The water contact angle of Sample A, which initially increased at almost the same rate as those of the other samples

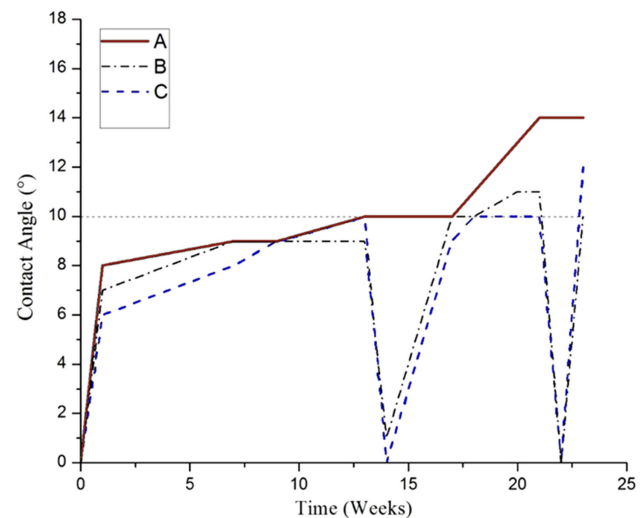


Fig. 6. Water contact angle variation of three samples (A, B, and C) prepared in the same batch of the titania thin films over 23 weeks. Samples B and C were exposed to 125 W UV light for 1.5 h in weeks 14 and 22. The measurement uncertainty is $\pm 2^\circ$.

Table 3. Water Contact Angles on Three Silica-Titania 55:45 wt% Coatings on Glass (Dip-Coating Batches at Constant Temperature of 25°C and Air Humidity of 30%) Over the First and Ninth Weeks Stored in the Dark^a

Samples \ Weeks	1	9
A	0°	3°
B	0°	4°
C	0°	3°

^aMeasurement uncertainty is $\pm 2^\circ$.

before they were exposed to UV, kept increasing during the 23 weeks of observation.

As reported in the literature [29–31], the blend of silica and titania is a good solution to improve superhydrophilicity and photocatalysis durability. Table 3 and Fig. 7 refer to three silica-titania coatings on glass, whose surfaces remained superhydrophilic for 9 weeks after storage in the dark. The superhydrophilicity also keeps the glass from fogging, since water droplets induce scattering of light (Fig. 8). Figure 7 shows that the water spreads as a continuous film, granting to glass the antifogging property [32,33].

The silica-titania surfaces maintain their superhydrophilicity much longer than monolayer titania samples (see Table 3 and Fig. 6).

Explanations for this behavior are reported by Houmard *et al.* [34] and Guan [35]. Silica forms on the film surface more OH groups, which are essential to the photocatalytic activity. The silica cations, Ti-Si, capture the OH⁻ of the water molecule, and so the surface adsorbs more hydroxyl radicals than pure titania. The OH groups existent on the film surface can be oxidized by the photocatalytic process of the titania, forming OH radicals that are responsible for decomposing the organic contaminants. The addition of silica to the titania also increases the acidity of the film surface, and thus water (OH⁻ groups) is

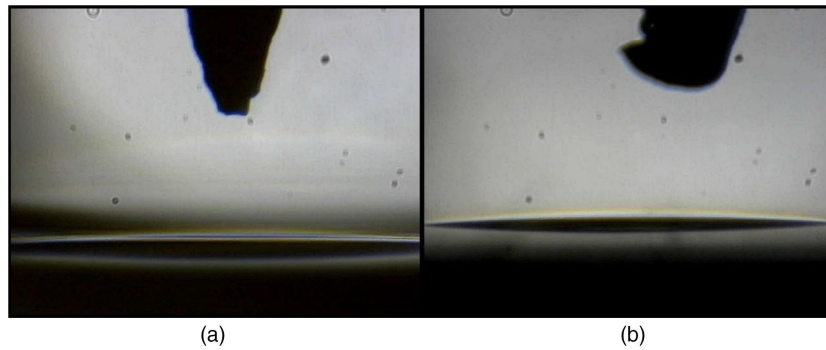


Fig. 7. Water contact angles on a silica–titania coating on glass: (a) first week and (b) after 9 weeks in the dark.



Fig. 8. Subjected to water vapor, from left to right, bare glass and coated samples show the antifogging property of the latter.

preferentially adsorbed, so that photocatalysis is improved and superhydrophilicity is maintained, decreasing contamination.

Therefore, the silica–titania layer composition contributes not only to antireflection by refractive index adjustment and to antiscattering by surface nanometric structuring, but also to self-cleaning by UV-recoverable photocatalytic activity.

A comparison follows with similar recent reports that use titania thin films.

Chemin *et al.* [19] achieved photocatalysis/self-cleaning, superhydrophilicity/antifogging but without antireflection, with a transmittance of $\sim 80\%$ in the visible spectrum. Khan *et al.* [11], using only titania thin films, obtained antireflection, good adherence, and mechanical stability, but not superhydrophilicity (contact angles: 17° , 23°). Liu *et al.* [20] reached superhydrophilicity with antifogging, but without antireflection and without mentioning durability. Lathe *et al.* [21] attained superhydrophilicity and scratch resistance but no antireflection property, with a transmittance of $\sim 89\%$ in the visible spectrum. Lin *et al.* Ref. [22], similarly to this work, used $\text{SiO}_2/\text{TiO}_2$ double layers, with two-sided antireflection reaching 98.8% transmittance, but without presenting superhydrophilicity or durability tests. İkizler [23] reached chemical and mechanical durability with double-layer antireflective thin films, but the superhydrophilicity lasted for only 7 days. Zhang *et al.* [24] present 95% transmittance, but did not mention the durability of superhydrophilicity or the film stability. Lastly, Tao *et al.* [25] reported up to 95.8% transmittance

with photocatalytic activity and mechanical robustness, but superhydrophilicity lasted for only 20 days.

4. CONCLUSIONS

In this work, silica–titania sol–gel coatings were deposited on glass by dip coating and subjected to 400°C calcination to present, besides antifogging, antireflection and self-cleaning properties simultaneously.

From optical profilometry measurements, the sample surfaces present a nanometric and uniform roughness, which allows low scattering losses in the visible spectrum. In the double layer configuration, silica–titania/titania/glass, refractive indices and thicknesses close to those calculated for antireflection were attained on one sample side, and thus peak transmittances up to 3.4% higher than that of the bare substrate around the visible central wavelength (550 nm) could be reached.

Superhydrophilicity for self-cleaning, antifogging, and antireflection in the mid-visible spectrum were, as novelty in dip-coated sol–gel films, simultaneously attained with 9-week durability in the dark, much more than that of titania alone and of previous reports.

The results of this work might be extended to a larger number of layers for a wider antireflection range in the visible or to other regions of the light spectrum.

In addition, it was observed that exposure to UV light produces self-healing with recovery of contact angles. Extension of this and catalytic action to the visible range, by decreasing the titania band gap through intermediate energy levels, such

as produced by doping or by defects, might be considered with regard to solar applications.

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REFERENCES

1. P. Nostell, A. Roos, and B. Karlsson, "Optical and mechanical properties of sol-gel antireflective films for solar energy applications," *Thin Solid Films*, **351**, 170–175 (1999).
2. S. Y. Lien, D. S. Wu, W. C. Yeh, and J. C. Liu, "Tri-layer antireflection coatings ($\text{SiO}_2/\text{SiO}_2\text{-TiO}_2/\text{TiO}_2$) for silicon solar cells using a sol-gel technique," *Sol. Energy Mater. Sol. Cells* **90**, 2710–2719 (2006).
3. T. Morimoto, Y. Sanada, and H. Tomonaga, "Wet chemical functional coatings for automotive glasses and cathode ray tubes," *Thin Solid Films* **392**, 214–222 (2001).
4. H. K. Pulker, "Characterization of optical thin films," *Appl. Opt.* **18**, 1969–1977 (1979).
5. B. Kraeutler and A. J. Bard, "Heterogeneous photocatalytic decomposition of saturated carboxylic acids on titanium dioxide powder. Decarboxylative route to alkanes," *J. Am. Chem. Soc.* **100**, 5985–5992 (1978).
6. H. Köstlin, G. Frank, G. Hebbinghaus, H. Auding, and K. Denissen, "Optical filters on linear halogen-lamps prepared by dip-coating," *J. Non-Cryst. Solids* **218**, 347–353 (1997).
7. A. Corma, "From microporous to mesoporous molecular sieve materials and their use in catalysis," *Chem. Rev.* **97**, 2373–2420 (1997).
8. R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, and T. Watanabe, "Light-induced amphiphilic surfaces," *Nature* **388**, 431–432 (1997).
9. J. Liu, X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, and M. Gong, "Hybrid mesoporous materials with functionalized monolayers," *Adv. Mater.* **10**, 161–165 (1998).
10. H. Nagel, A. Metz, and R. Hezel, "Porous SiO_2 films prepared by remote plasma-enhanced chemical vapour deposition—a novel antireflection coating technology for photovoltaic modules," *Sol. Energy Mater. Sol. Cells* **65**, 71–77 (2001).
11. S. B. Khan, Z. Zhang, and S. L. Lee, "Single component: bilayer TiO_2 as a durable antireflective coating," *J. Alloys Comp.* **834**, 155137 (2020).
12. T. Tölke, A. Heft, and A. Pfuch, "Photocatalytically active multi-layer systems with enhanced transmission," *Thin Solid Films* **516**, 4578–4580 (2008).
13. J. Yun, T. S. Bae, J. D. Kwon, S. Lee, and G. H. Lee, "Antireflective silica nanoparticle array directly deposited on flexible polymer substrates by chemical vapor deposition," *Nanoscale* **4**, 7221–7230 (2012).
14. K. Koc, F. Z. Tepehan, and G. G. Tepehan, "Antireflecting coating from Ta_2O_5 and SiO_2 multilayer films," *J. Mater. Sci.* **40**, 1363–1366 (2005).
15. P. H. Wöbkenberg, T. Ishwara, J. Nelson, D. D. Bradley, S. A. Haque, and T. D. Anthopoulos, " TiO_2 thin-film transistors fabricated by spray pyrolysis," *Appl. Phys. Lett.* **96**, 082116 (2010).
16. C. Deng and H. Ki, "Pulsed laser deposition of refractive-index-graded broadband antireflection coatings for silicon solar cells," *Sol. Energy Mater. Sol. Cells* **147**, 37–45 (2016).
17. A. F. Michels, P. A. Soave, J. Nardi, P. L. G. Jardim, S. R. Teixeira, D. E. Weibel, and F. Horowitz, "Adjustable, (super)hydrophobicity by e-beam deposition of nanostructured PTFE on textured silicon surfaces," *J. Mater. Sci.* **51**, 1316–1323 (2016).
18. S. B. Khan, H. Wu, Z. Xie, W. Wang, and Z. Zhang, " Al_2O_3 encapsulated Teflon nanostructures with high thermal stability and efficient antireflective performance," *ACS Appl. Mater. Interfaces* **9**, 36327–36337 (2017).
19. J. B. Chemin, S. Bulou, K. Baba, C. Fontaine, T. Sindzingre, N. D. Boscher, and P. Choquet, "Transparent anti-fogging and self-cleaning $\text{TiO}_2/\text{SiO}_2$ thin films on polymer substrates using atmospheric plasma," *Sci. Rep.* **8**, 9603 (2018).
20. F. Liu, J. Shen, W. Zhou, S. Zhang, and L. Wan, "In situ growth of $\text{TiO}_2/\text{SiO}_2$ nanospheres on glass substrates via solution impregnation for antifogging," *RSC Adv.* **7**, 15992–15996 (2017).
21. S. S. Latthe, S. Liu, C. Terashima, K. Nakata, and A. Fujishima, "Transparent, adherent, and photocatalytic $\text{SiO}_2\text{-TiO}_2$ coatings on polycarbonate for self-cleaning applications," *Coatings* **4**, 497–507 (2014).
22. W. Lin, J. Zheng, L. Yan, and X. Zhang, "Sol-gel preparation of self-cleaning $\text{SiO}_2\text{-TiO}_2/\text{SiO}_2\text{-TiO}_2$ double-layer antireflective coating for solar glass," *Results Phys.* **8**, 532–536 (2018).
23. B. İkizler, "Preparation of single- and double-layer antireflective coatings by sol-gel method," *Res. Eng. Struct. Mater.* **6**, 1–21 (2019).
24. H. Zhang, D. W. Fan, T. Z. Yu, and C. L. Wang, "Antireflective and self-cleaning properties of $\text{SiO}_2/\text{TiO}_2$ double-layer films prepared by cost-effective sol-gel process," *Chin. J. Chem. Phys.* **28**, 777–780 (2016).
25. C. Tao and L. Zhang, "Fabrication of multifunctional closed-surface $\text{SiO}_2/\text{TiO}_2$ antireflective thin films," *Colloids Surf. A* **585**, 124045 (2020).
26. D. S. Hinczewski, M. Hinczewski, F. Z. Tepehan, and G. G. Tepehan, "Optical filters from SiO_2 and TiO_2 multi-layers using sol-gel spin coating method," *Sol. Energy Mater. Sol. Cells* **87**, 181–196 (2005).
27. S. Haghighi, "Preparation of $\text{TiO}_2/\text{SiO}_2$ double layer nanofilm using sol-gel spin coating technique on quartz substrate for self-cleaning applications," *J. Sci. Today's world* **2**, 423–430 (2013).
28. E. Hecht, *Optics*, 5th ed. (Pearson Education, 2017), pp. 441–444.
29. R. Wang, N. Sakai, A. Fujishima, T. Watanabe, and K. Hashimoto, "Studies of surface wettability conversion on TiO_2 single-crystal surfaces," *J. Phys. Chem. B* **103**, 2188–2194 (1999).
30. C. J. R. Gonzalez-Oliver, P. F. James, and H. Rawson, "Silica and silica-titania glasses prepared by the sol-gel process," *J. Non-Cryst. Solids* **48**, 129–152 (1982).
31. N. Seriani, C. Pinilla, S. Cereda, A. De Vita, and S. Scandolo, "Titania-silica interfaces," *J. Phys. Chem. C* **116**, 11062–11067 (2012).
32. A. S. T. Kaya and U. Cengiz, "Fabrication and application of superhydrophilic antifog surface by sol-gel method," *Prog. Organ. Coat.* **126**, 75–82 (2019).
33. M. Nie, P. Patel, K. Sun, and D. D. Meng, "Superhydrophilic anti-fog polyester film by oxygen plasma treatment," in *4th IEEE International Conference on Nano/Micro Engineered and Molecular Systems* (2009), pp. 1017–1020.
34. M. Houmard, D. Riassetto, F. Roussel, A. Bourgeois, G. Berthome, J. C. Joud, and M. Langlet, "Morphology and natural wettability properties of sol-gel derived $\text{TiO}_2\text{-SiO}_2$ composite thin films," *Appl. Surf. Sci.* **254**, 1405–1414 (2007).
35. K. Guan, "Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of $\text{TiO}_2/\text{SiO}_2$ films," *Surf. Coat. Technol.* **191**, 155–160 (2005).