



Full Length Article

Photocatalytic, superhydrophilic, self-cleaning TiO₂ coating on cheap, light-weight, flexible polycarbonate substrates

Takahiro Adachi^a, Sanjay S. Latthe^b, Suresh W. Gosavi^c, Nitish Roy^a, Norihiro Suzuki^a, Hiroshi Ikari^a, Kazuki Kato^a, Ken-ichi Katsumata^a, Kazuya Nakata^a, Manabu Furudate^d, Tomohiro Inoue^d, Takeshi Kondo^a, Makoto Yuasa^a, Akira Fujishima^a, Chiaki Terashima^{a,*}

^a Photocatalysis International Research Center, Research Institute for Science & Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

^b Self-cleaning Research Laboratory, Department of Physics, Raje Ramrao College, Jath 416 404, Maharashtra, India

^c Centre for Advanced Studies in Material Science and Solid State Physics, Department of Physics, Savitribai Phule Pune University (formerly University of Pune), Ganeshkhind, Pune 411 007, India

^d PVC & Polymer Materials Research Center, Shin-Etsu Chemical Co., Ltd., Kamisu-shi, Ibaraki 314-0102, Japan

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ABSTRACT

Photocatalytic TiO₂/SiO₂ coatings with excellent superhydrophilic wettability were prepared on light-weight polycarbonate substrates for self-cleaning applications. The effect of distinct SiO₂ concentrations (0–40%) in TiO₂ on the morphology, wettability, UV–Vis transmittance, haze, and durability of the coatings was studied in detail. TiO₂/SiO₂ coatings prepared with 20% silica in TiO₂ showed superhydrophilic wetting properties with a smooth and uniform morphology with more than 85% transmittance. The lower haze value of TiO₂/SiO₂ coatings confirms their clear optical appearance. A low-friction layer of fluoroalkylsilane was applied to the coatings to improve their mechanical durability. In addition, the hydrophobic-hydrophilic patterns of different areas were prepared to check their effect on the haze and wetting properties.

1. Introduction

Over two decades ago, Fujishima and his research group showed the light-induced wettability change on a TiO₂ thin film surface for the first time [1]. It was reported that the water contact angle (WCA) behaves differently after exposure of the TiO₂ surface to UV light [2]. The hydrophilic TiO₂ film changed to superhydrophilic upon UV irradiation. The reason behind this partial to complete wetting of water on the TiO₂ surface after UV irradiation is that the UV light induces surface oxygen vacancies at the bridging sections of TiO₂ and, hence, radical species can form at the surface, aiding complete water wetting. In addition, the organic pollutants adsorbed on the TiO₂ surface undergo oxidative decomposition after UV irradiation. Total water wetting on the TiO₂ surface forms a continuous, thin water film that carries away dirt particles. This phenomenon is known as the superhydrophilic self-cleaning effect and has been found to be useful for various industrial applications [3]. To date, TiO₂ is one of the few low-cost materials known to show this change in wettability under light illumination.

Optically transparent glass materials have been used in many applications, including automobile windshields, window glass,

skyscrapers, microscopes, eyeglasses, solar cell panel covers, kitchen appliances, screens of many electronic devices, and optical instruments [4,5]. Apart from their many uses as forms of glass, they are heavy and, thus, increase the overall weight of a device. Moreover, they are fragile and ultimately prone to break under minimal mechanical force. Hence, extreme care has to be taken to protect them. In addition, much effort is required to keep them clean. However, a light-weight, highly durable surface with good mechanical strength is essential for the aforementioned uses. Expensive, heavy, and fragile glass can be perfectly substituted by inexpensive/low cost, lightweight, and flexible polycarbonate (PC) because of the similar optical transmission of both glass and PC [6]. However, the main issues with PC are its low glass transition temperature (< 145 °C) and poor scratch and photocorrosion resistance [7]. Few reports are available on the progress in increasing the transition temperature [8] and scratch resistance properties of PC [9]. Consequently, detailed and systematic studies still need to be carried out to address this challenge.

An abundance of literature is available on the preparation of self-cleaning TiO₂ coatings on glass substrates [10–13]. Development of photocatalytic, superhydrophilic, and self-cleaning TiO₂ coating on low

* Corresponding author.

E-mail address: terashima@rs.tus.ac.jp (C. Terashima).

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cost, light-weight, and flexible PC substrates is crucial for multifunctional self-cleaning devices to be useful [14]. Commonly, aqueous TiO_2 can be coated on the PC substrates at room temperature in three steps. First, ozone, plasma, or chemical pretreatment is required to render hydroxyl groups onto the PC surface. Next, a barrier layer (mostly SiO_2) is applied to the PC because applying the TiO_2 directly could degrade the PC under UV light. Last, the TiO_2 is coated onto the barrier layer [15]. Lam and colleagues [16] pretreated the PC with chemical NaOH-etching and UVC-irradiation separately and confirmed that the TiO_2 film was more adherent on the UVC-treated PC compared with NaOH-treated PC. However, dip coated TiO_2 films on NaOH-treated PC showed much better photocatalytic properties (methylene blue degradation) than on UVC treated PC. Langlet et al. [17] used an acid-catalyzed sol-gel process to spin-coat TiO_2 alcosol on different polymeric substrates. After ambient drying, the sol-gel-processed TiO_2 coatings were autoclaved (90–140 °C) in a water-ethanol atmosphere. The improvement in photocatalytic activity was confirmed with the increase in the thickness of the TiO_2 films. Fateh et al. successfully dip coated continuous mesoporous TiO_2 films on SiO_2 pre-coated PC substrates at low temperature for self-cleaning applications [18]. Complete superhydrophilic wettability was achieved by 24 h of UV irradiation and the films remained superhydrophilic for 3 months, confirming its efficient photocatalytic activity. The same research group [19] has prepared optically transparent, adherent, and photocatalytic $\text{TiO}_2/\text{SiO}_2$ coatings on a PC at room temperature through the dip coating method. However, the coatings did not begin to exhibit the superhydrophilic wetting state until continuous UV irradiation was applied for almost 1 month. This long UV exposure time is a main drawback and somewhat limits its usage for self-cleaning applications.

Herein, we prepared $\text{TiO}_2/\text{SiO}_2$ coatings on SiO_2 pre-coated PC substrates using a simple dip coating technique. The effect of specific SiO_2 concentrations (0–40%) in TiO_2 on morphology, wettability, UV-Vis transmittance, haze, and durability of the coatings was studied in detail. Attempts have been made to improve the mechanical durability of the coatings by applying a low-friction layer of fluoroalkylsilane (FAS). The haze and wetting properties of the hydrophobic-hydrophilic patterned and nonpatterned coating surface were then analyzed.

2. Experimental section

2.1. Materials

Silica aqueous solution (Shin-Etsu Japan), TiO_2 aqueous solution (Shin-Etsu Japan), PC substrates (C. I. Takiron Corporation, Japan), and trimethoxy(1H,1H,2H,2H-nonafluorohexyl)silane (Tokyo Chemical Industry Co. Ltd., Japan) were used. Oleic acid, liquid paraffin, and heptane were purchased from Fujifilm Wako Pure Chemical Corporation, Japan.

2.2. Coating preparation method

Polycarbonate substrates were thoroughly washed with deionized water and ultrasonicated for 10 min to remove contaminants. PC substrates were pretreated by exposing them to oxygen plasma for 1 min to render anchoring hydroxyl groups onto the surface. The oxygen plasma was created at a pressure = 20 Pa, gas flow = 10 sccm, and RF power = 100 W. The pretreated PC substrates were first coated with a SiO_2 barrier layer by the dip coating method. After drying at ambient temperature for 1 h, the SiO_2 pre-coated PC substrates were dip coated with TiO_2 - SiO_2 mixtures. The TiO_2 - SiO_2 mixture composition (v/v) was varied from 10:0, 9:1, 8:2, 7:3, and 6:4 and denoted as TS-1, TS-2, TS-3, TS-4, and TS-5 samples, respectively. The dip coating conditions were fixed for all depositions with a dipping speed of ca. 2 mm/s, deposition time of ca. 60 s, and withdrawal speed of ca. 1 mm/s. After dip coating, all of the coatings were dried in air at 100 °C for 1 h with the

temperature raised at a rate of 2 °C/min.

A low-friction layer of FAS was coated onto the $\text{TiO}_2/\text{SiO}_2$ coatings using a simple chemical vapor deposition method to improve the mechanical stability of the coatings. The $\text{TiO}_2/\text{SiO}_2$ coating and FAS (ca. 300 μL) were placed separately in small beakers in a closed stainless-steel box. This box was kept in an oven at 120 °C for 3 h for chemical vapor deposition of a thin FAS layer on the coating surface.

2.3. Characterization

The surface microstructure was observed by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7600F; Tokyo, Japan). A UV-Vis spectrophotometer (JASCO, V-670; Tokyo, Japan) was used to quantify transmittance of the coatings. The optical appearance of the coatings was analyzed by haze measurement using a haze meter (Nippon Denshoku, NDH 2000). The ratio of diffuse to total reflectance is known as the haze. Haze mainly arises from light scattering from the surface of the coatings. The lower the haze, the better the clear optical appearance of the coatings [20]. The chemical properties of the coatings were investigated using XPS (Kratos Co. Axis Nova, UK). A laser microscope (KEYENCE, VK-X200 series) was used to measure the surface roughness of the coatings. A closed wooden box with one open side covered by black napkin was fabricated and UV lamps (Intensity = 1 mW/cm^2) were fitted onto the ceiling of the box. Toshiba (FL10BLB; Tokyo, Japan) supplied the UV lamps. The photocatalytic property of the coating was confirmed by degradation of oleic acid on the coating surface under UV light as well as the decrease in WCA with UV illumination time. The wetting properties of the coating surface before and after UV irradiation were confirmed by WCA measurements. A contact angle meter (Kyowa, Drop Master; Saitama, Japan) was used to measure the WCAs. A 5- μL volume water droplet was produced using a microsyringe and was gently placed on the surface using a needle. Three locations on the coatings were chosen to measure the contact angle and these were then averaged to report the equilibrium contact angle. The durability of the coatings under mechanical abrasion was investigated using the Taber abrasion test (Taber Industries, 5130 Abraser, USA). During the Taber abrasion test, CS-10F abrasion wheels loaded with a force of 4.9 N were used with a rotation speed of 60 rpm. The extent of abrasion on the coating was confirmed using haze measurements.

3. Results and discussion

3.1. Surface morphology and chemical properties

The amount of SiO_2 incorporated into TiO_2 affects the surface morphology of the prepared coatings. Fig. 1 depicts FE-SEM images of the TS-1, TS-2, TS-3, TS-4, and TS-5 samples. The pristine TiO_2 coating (TS-1) shows a dense and compact microstructure (Fig. 1a). A change in morphology from dense to porous is observed when there is a higher composition of SiO_2 in the coating (Fig. 1b–e). A similar change in surface microstructure was also reported by Fateh et al. [19], Machida et al. [21], and Kumar et al. [22], wherein a porous microstructure was obtained by adding SiO_2 in TiO_2 . This also resulted in an increase in surface area of the composite coatings.

Fig. 2 shows X-ray photoelectron spectroscopy (XPS) images of the FAS-deposited TS-3 sample. A survey scan of the composite SiO_2 - TiO_2 , indicating the presence of Si 2p and Si 2s, Ti 2p, O 1s, and C 1s is shown in Fig. 2a, suggesting formation of the composite material. The formation of the composite can be further explained by the O 1s peak. The O 1s photoelectron peak split into two peaks, see Fig. 2b. The XPS photoelectron peak at 532.7 eV indicates the O 1s originating from SiO_2 . However, the O 1s peak at 529.60 eV is due to the photoelectron peak that originates from TiO_2 . This is because Si(IV) has a higher electronegativity and smaller ionic radius than Ti(IV). A smaller O 1s peak at 530.75 eV results from Ti-O-Si bonding. The Si 2p photoelectron

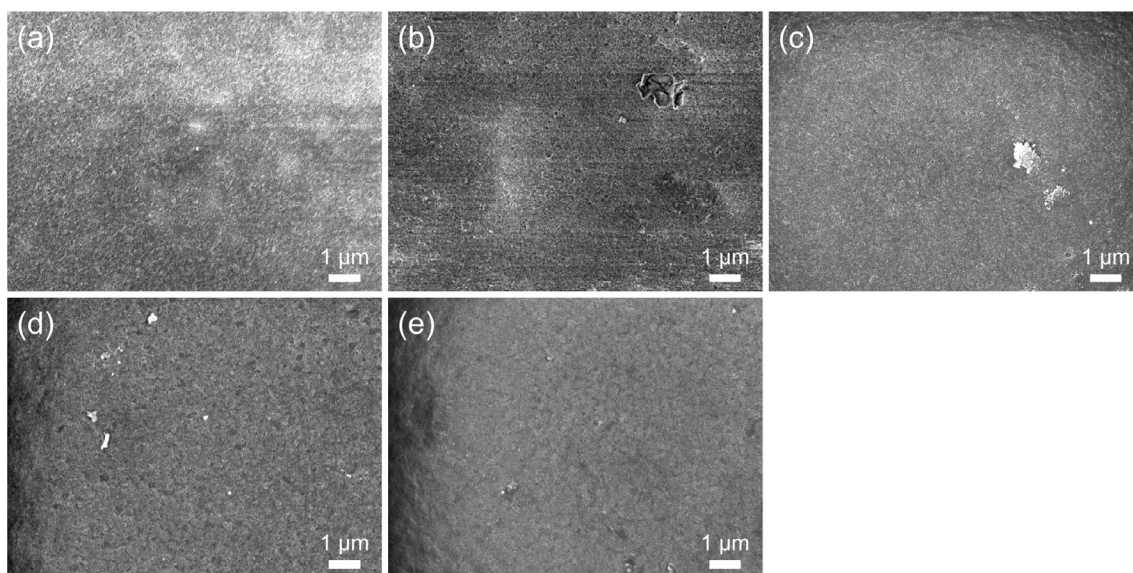


Fig. 1. FE-SEM images of (a) TS-1, (b) TS-2, (c) TS-3, (d) TS-4, and (e) TS-5 samples.

peak is located at 103.35 eV (Fig. 2c), which matches well to reported values for Si(IV). Similarly, the Ti 2p_{3/2} and 2p_{1/2} photoelectron peaks (Fig. 2d) are located at 458.25 and 464.15 eV, respectively, indicating the Ti(IV) state [23,24].

3.2. Photocatalytic, wetting, optical, and self-cleaning properties

The photocatalytic activity of the TiO₂/SiO₂ coating was confirmed by detecting the degradation of oleic acid (organic pollutant) on the coating surface under UV light, along with the decrease in WCA after UV irradiation time [25]. A 0.5 wt% oleic acid solution in heptane was

prepared and dip coated on the TS-3 sample with a dipping and lifting rate of 60 cm/min. A WCA of 33° was observed on the TS-3 sample surface; however, after oleic acid deposition, the WCA changed to 45° (Fig. 3). The oleic acid treated TS-3 sample was exposed to UV light and, as a result, the WCA decreased slowly from 45° to 10° during 32 h of irradiation time. The decrease in WCA after UV irradiation confirms the photodegradation of oleic acid by TiO₂.

Fig. 4 illustrates the effect of UV irradiation on the wettability of the coatings. The TS-1 sample is a pure TiO₂ coating, whereas in the TS-5 sample we used the highest percentage of SiO₂ in the TiO₂. The WCA for both the TS-1 and TS-5 samples was close to 48° before UV irradiation.

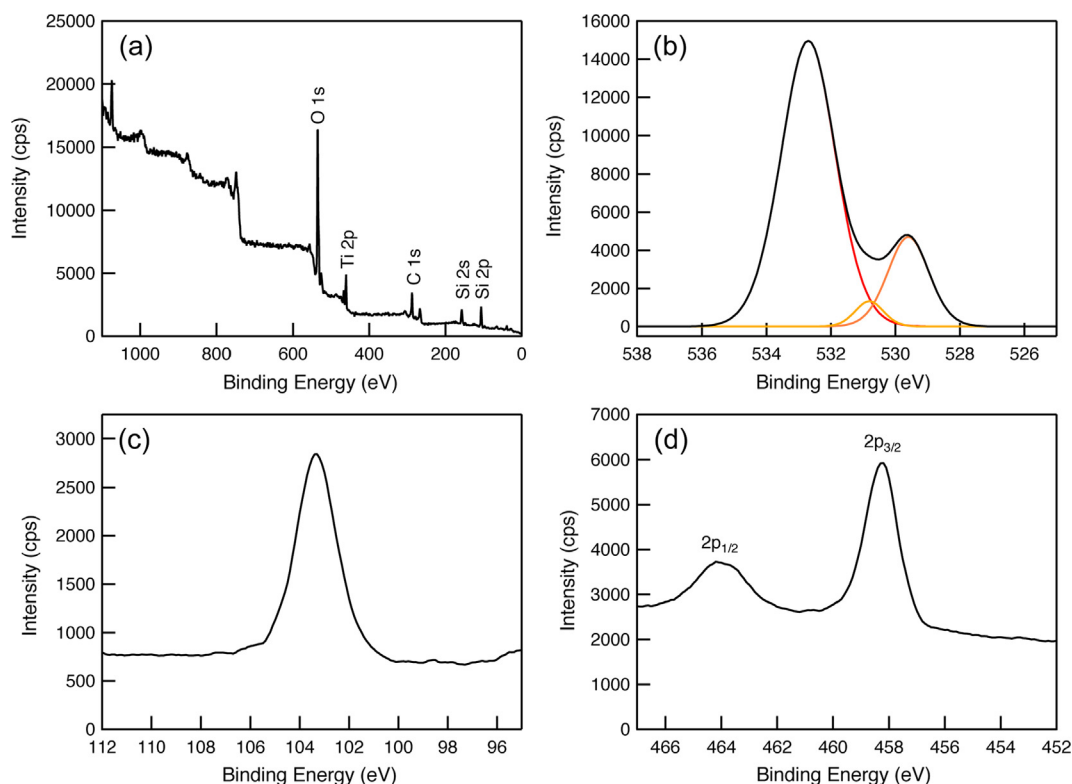


Fig. 2. (a) XPS surface survey of the SiO₂/TiO₂ composite showing Si 2p, Si 2s, Ti 2p, O 1s, and C 1s. (b) The O 1s peak split into two distinct peaks, as shown by the deconvolution, indicating two different O 1s from TiO₂ and SiO₂. (c, d) Si 2p and Ti 2p XPS peaks, respectively.

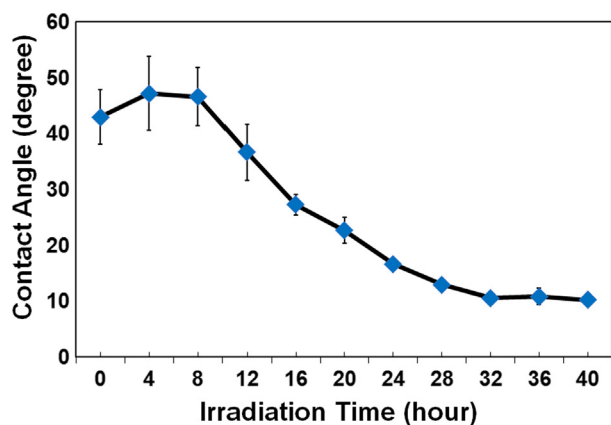


Fig. 3. Oleic acid degradation on the TS-3 coating surface after UV irradiation.

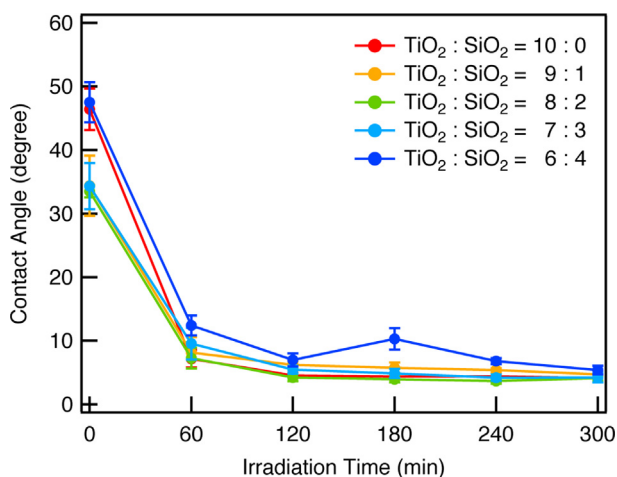


Fig. 4. Wettability of the TiO₂/SiO₂ coatings after UV illumination.

Generally, for the dip coated TiO₂ coatings, the WCAs before UV irradiation have been reported as being 40–50° [18,19,25]. The TS-2 to TS-4 samples revealed a WCA of approximately 34° because of the addition of the inherently hydrophilic silica in the coating solution. As the wettability is in the hydrophilic state for all TiO₂-SiO₂ coatings before UV irradiation, water droplets showed strong affinity towards the surface. The water droplets adhered strongly to the coating surface and could not slide off, even after extreme tilting of more than 90°.

The coatings were kept under UV light for 5 h and the distance from the UV lamp to the coating was fixed at 5 cm. The WCAs were checked after every hour of UV irradiation. All coatings showed a similar trend of decrease in WCA after UV irradiation. After 1 h of UV irradiation, all the samples showed a remarkable change in wettability with WCAs less than 10°. After more than 2 h of UV irradiation, the WCA decreased to less than 5° for the TS-1 to TS-5 samples. The coatings showed a quick response to UV light within 2 h, achieving a superhydrophilic state. This contrasts to some reports where superhydrophilicity was only achieved after UV irradiation for a prolonged period of time [19]. Our wettability results of the TiO₂/SiO₂ coatings after UV irradiation match well with the results of Guan et al. [26]. Water droplets placed on the coatings in our study eventually spread out on the surface and exhibit complete or perfect wetting. After spraying a few water droplets on the coating surface, the droplets ultimately spread, making a continuous thin film that flows according to the direction of tilt. This phenomenon is very useful for self-cleaning applications where organic compounds chemically degraded by TiO₂ can be washed off by running water over the film. Wetting stability in the dark is also an important parameter for self-cleaning applications. The prepared coatings showed no change in

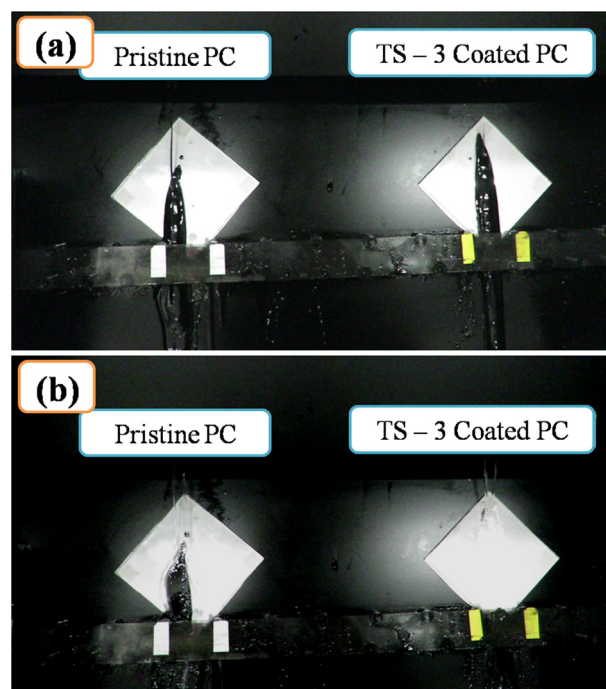


Fig. 5. Self-cleaning ability of the pristine PC and TS-3 coating (a) splashing of pseudo dirt on the surfaces and (b) cleaning by water flow.

wettability (superhydrophilic) after being kept in the dark for more than 1 month.

The self-cleaning ability of the TS-3 sample was checked. Fig. 5 shows the optical images of the superhydrophilic self-cleaning process on the coating. Furthermore, a video of the self-cleaning process on the coating is shown in the [electronic supporting information \(ESI\)](#). A viscous pseudo dirt was prepared by adding 1 wt% of carbon black in liquid paraffin. The pristine PC and TS-3 samples (after 5 h UV irradiation) were mounted on the aluminum holder and then placed on the platform. A viscous pseudo dirt was splashed onto it from atop through the nozzles (Fig. 5a). From Fig. 5b, it is observed that the water flow could easily take away all the pseudo dirt from the superhydrophilic TS-3 sample, whereas the dirt remained adhered to the pristine PC. The photocatalytic and superhydrophilic TS-3 sample showed good self-cleaning ability.

To evaluate the transparency of the coatings, UV-Vis spectra of the coatings were recorded (spectral range = 400–800 nm). Fig. 6 depicts the optical transmittance of the TiO₂/SiO₂ coatings. All coatings

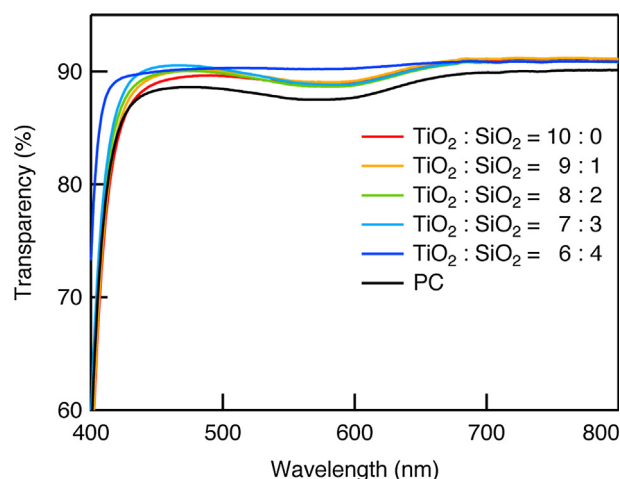


Fig. 6. Optical transmittance of the TiO₂/SiO₂ coatings.

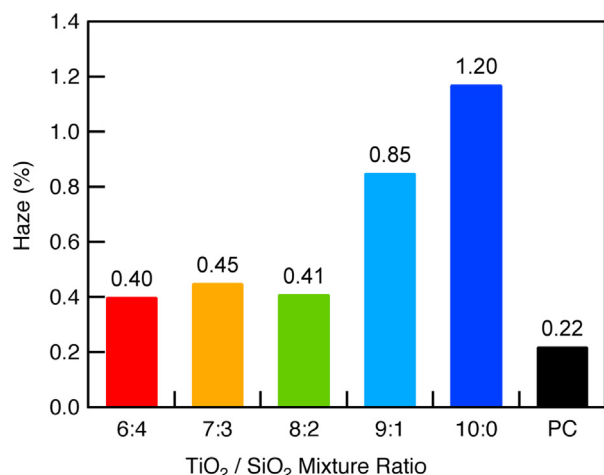


Fig. 7. Haze measurement of TiO₂/SiO₂ coatings and PC.

showed a nearly identical transmittance of more than 87%. Fateh et al. [19] reported more than 94% optical transmittance for dip coated TiO₂/SiO₂ coatings on PC. Guan et al. [26] prepared TiO₂/SiO₂ coatings on glass substrates using dip coating, providing a transmittance of approximately 80%.

Fig. 7 illustrates the haze measurement for all TiO₂-SiO₂ coatings and the PC. The PC shows 0.22% haze, whereas the TS-3 to TS-5 samples showed less than 0.45% haze. However, for the TS-1 and TS-2 samples, a higher haze percentage (1.2% and 0.85%, respectively) was observed because of the scattering of light from the dense and compact microstructures [20]. For a higher composition of silica in the coating, the porosity increased and hence the haze percentage was effectively reduced. Hegmann et al. smoothed the rough SiO₂/TiO₂ scattering layers by depositing an acid-catalyzed TEOS layer, which eventually resulted in lowering the haze of the coatings [27]. In the present case, mixing silica and TiO₂ formed a stable and homogeneous solution and, after deposition on the PC, a smooth porous surface was attained, which reduced the haze. Microstructure analysis using SEM shows a denser film with higher surface roughness for the TS-1 and TS-2 samples. The measured surface roughness using laser microscopy and its corresponding haze for various ratios of SiO₂:TiO₂ are given in Table S1 (ESI). As can be seen from Table S1, the increase in haze is associated with an increase in surface roughness of the coatings.

3.3. Taber abrasion test

The C1s and F1s peaks by XPS confirm the deposition of FAS (~300 μL) on the coating surface (ESI, Fig. S1). The deposition of the FAS layer was further confirmed by WCA measurements. The WCA of ca. 115° was achieved after FAS deposition. The mechanical durability

of the pristine and FAS deposited coating was examined by the Taber abrasion test (Fig. 8). After the test, haze measurement was performed on both of the coatings. For pristine and FAS-deposited coatings, haze percentages of, respectively, 0.41% and 0.33% were observed before the Taber abrasion test. After the Taber abrasion test, the pristine coatings showed a remarkable increase in haze percentage to about 43%, whereas the FAS-deposited coating showed ca. 35% haze. This confirms that FAS deposition adequately helps to improve the mechanical stability of the coatings. The increase in haze percentage after the Taber abrasion test is due to the severe scratches, which affect the optical appearance of the coating [28]. Because of abrasion, the surface of the coatings might get damaged with an uneven surface structure, which promotes light scattering.

3.4. Hydrophobic-hydrophilic patterned surface

A hydrophobic-hydrophilic patterned surface was created by masking the TS-3 sample with two sizes (0.3 × 0.3 cm² and 1 × 1 cm²) of square spaces on the coating surface (Fig. 9a). The exposed square surfaces after masking were subjected to chemical vapor deposition of FAS (300 μL) to render them hydrophobic (CA = 122°). The mask was removed after deposition of the FAS layer, which created a hydrophobic-hydrophilic patterned surface. Haze measurement was carried out on both patterned and non-patterned FAS-coated TS-3 samples after the Taber abrasion test. As shown in Fig. 9b, a haze percentage of ca. 35% was observed for both surfaces. However, as shown in Fig. 9c, after 72 h of UV irradiation, the WCA on a small area of the patterned surface (0.3 × 0.3 cm²) decreased to less than 10°, whereas the WCA decreased to nearly 68° for a large area of the patterned surface (1 × 1 cm²). However, for the non-patterned FAS-deposited coating, the WCA decreased gradually from 115° to about 89°.

4. Conclusion

We fabricated a photocatalytic, superhydrophilic, and self-cleaning TiO₂ coating on PC substrates. The incorporation of SiO₂ into TiO₂ dramatically altered the physicochemical properties of the resulting TiO₂/SiO₂ coatings. Haze was found to decrease significantly from 1.2% to 0.45% after appropriate SiO₂ addition into the TiO₂ coating. The surface morphology was also altered by silica addition from dense and compact to porous. The TiO₂/SiO₂ coatings were optically transparent and achieved a superhydrophilic state after UV irradiation for almost 2 h. Superhydrophilicity is a building block to self-cleaning ability and crucial for reliability. An attempt was made to improve the mechanical stability of the coating by applying a low-friction FAS layer and the improved stability was tested by Taber abrasion tests. The hydrophilic-hydrophobic patterned surface was also prepared with the aid of FAS layer deposition.

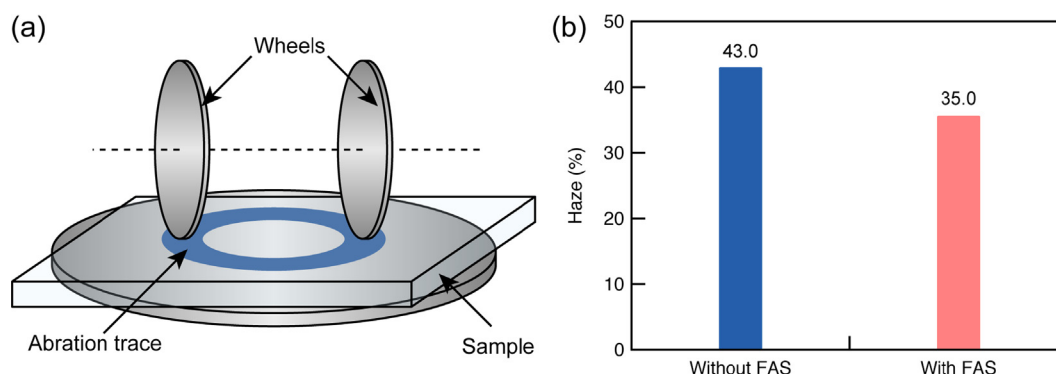


Fig. 8. (a) Schematic of the Taber abrasion test and (b) haze measurement after the Taber abrasion test on TS-3 coatings with and without FAS deposition.

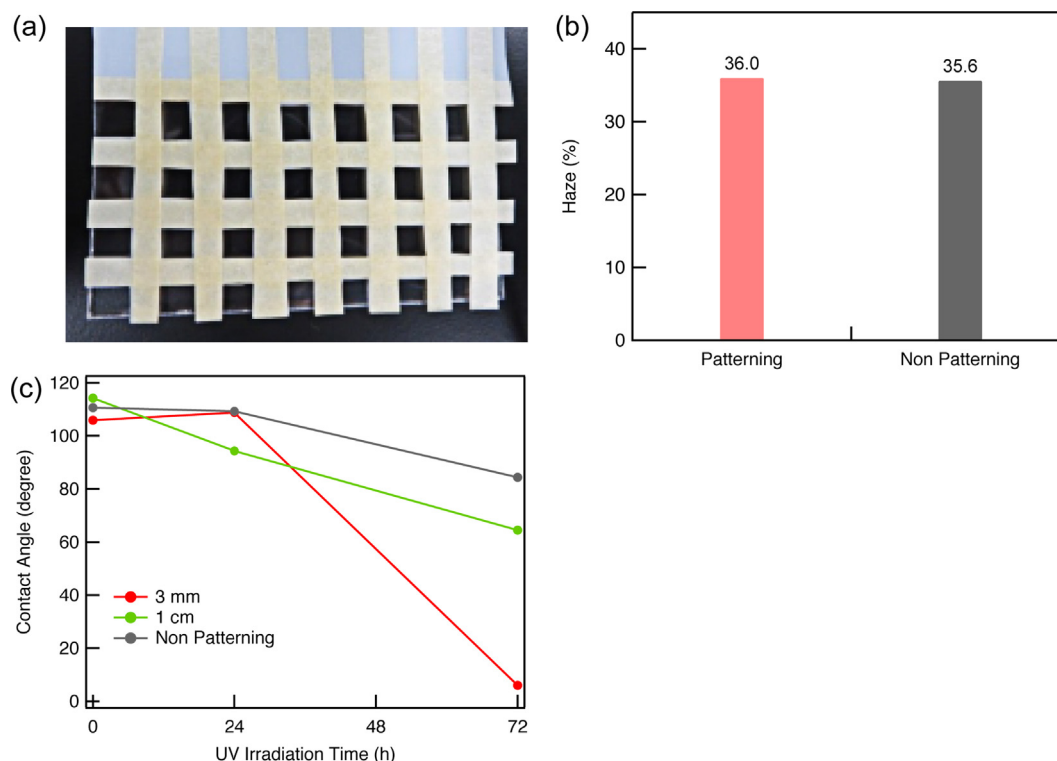


Fig. 9. (a) Patterning on the TS-3 coating, (b) Haze measurement on the patterned and non-patterned coating after the Taber abrasion test, and (c) Wettability of the patterned surface after UV illumination.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apusc.2018.07.172>.

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