

Article

Transparent, Adherent, and Photocatalytic SiO₂-TiO₂ Coatings on Polycarbonate for Self-Cleaning Applications

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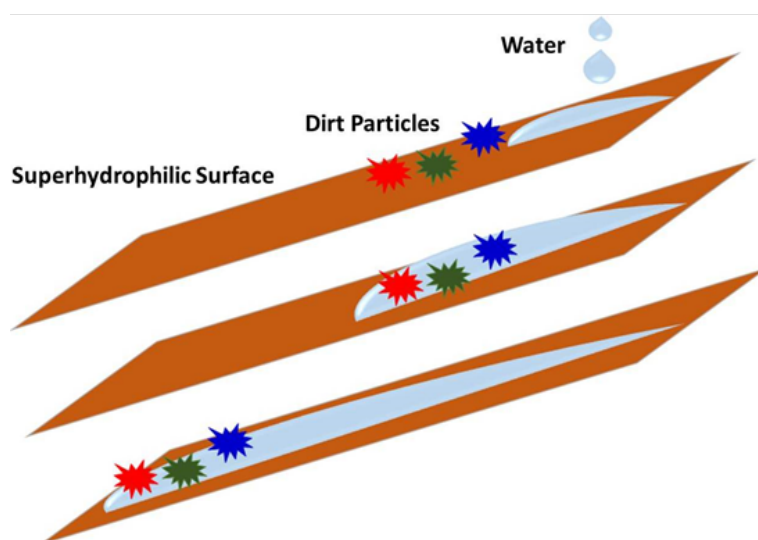
Abstract: Photocatalytic TiO₂ coatings are famously known for their excellent self-cleaning behavior, where very thin water layer formed on the superhydrophilic surface can easily wash-off the dirt particles while flowing. Here we report the preparation of the optically transparent, adherent, highly wettable towards water and photocatalytic SiO₂-TiO₂ coatings on polycarbonate (PC) substrate for self-cleaning applications. The silica barrier layer was applied on UV-treated PC substrate before spin coating the SiO₂-TiO₂ coatings. The effect of different vol% of SiO₂ in TiO₂ and its influence on the surface morphology, mechanical stability, wettability, and photocatalytic properties of the coatings were studied in detail. The coatings prepared from 7 vol% of SiO₂ in TiO₂ showed smooth, crack-free surface morphology and low surface roughness compared to the coatings prepared from the higher vol% of SiO₂ in TiO₂. The water drops on this coating acquires a contact angle less than 10° after UV irradiation for 30 min. All the coatings prepared from different vol% (7 to 20) of SiO₂ in TiO₂ showed high transparency in the visible range.

Keywords: photocatalytic; wettable; transparent; SiO₂-TiO₂ coatings; self-cleaning

1. Introduction

TiO₂ is one of the most widely researched photocatalytic semiconductor materials to date. When irradiated with UV light, TiO₂ can decompose the organic pollutants present on its surface, and in addition the surface turns to be highly hydrophilic [1]. Water spread out instantaneously by forming a thin layer on the superhydrophilic TiO₂ thin films and steadily carries away dust particles from the surface while flowing (Figure 1). Photocatalytic superhydrophilic thin films with excellent self-cleaning properties are receiving much research attention worldwide because such smart surfaces can save time and reduce maintenance costs [2]. Today, the optically transparent, superhydrophilic and photocatalytic TiO₂ thin films are finding increasing industrial applications. Many reports on application of self-cleaning TiO₂ thin films on glass substrates are available in the literature [3–6]. An attractive soft polymer material, polycarbonate (PC) has great demand in the optical industry. PC can replace heavy glass in the optical and electronic industries in the coming future due to its extremely low weight, durability, low-cost, and optical transparency [7]. Many attempts have been made to improve the scratch resistance and UV degradation property of the PC by coating the surface by numerous photocatalytic materials with suitable binders.

Figure 1. Schematic showing the self-cleaning phenomena on superhydrophilic surface.



Hwang and coworkers [8] have prepared mechanically durable and optically transparent organic-inorganic SiO₂-TiO₂ nanocomposite coatings on PC by simple spray coating. The coating solution was prepared by incorporating nanosized TiO₂ sol into the silica polymeric sol. This nanocomposite coating also protected PC from photo-degradation under UV illumination. Lam *et al.* [9] reported the comparative study on the influence of NaOH etching and UVC irradiation on the mechanical stability of the TiO₂ thin films prepared on PC. They observed adherent TiO₂ film on UVC irradiated PC than NaOH treated PC due to increase in –OH and –COOH groups on the UVC-treated PC. However, the strong hydrophilic, antifogging, photocatalytic and self-cleaning properties were observed on the TiO₂ film coated on NaOH treated PC. Recently, Razan Fateh *et al.* have prepared optically transparent, highly hydrophilic, mechanically stable and photocatalytic TiO₂/SiO₂ [7,10], and TiO₂/ZnO coating [11] on PC for self-cleaning applications. In the present research work, we prepared

transparent, adherent, highly wettable and self-cleaning $\text{SiO}_2\text{-TiO}_2$ coating on PC by simple spin coating. The coating showed faster wettability switching (hydrophilic to superhydrophilic) after 30 min. of UV irradiation. The effect of different vol% of SiO_2 sol in TiO_2 and its influence on the surface morphology, mechanical stability, wettability, and photocatalytic properties of the coatings were studied in detail.

2. Results and Discussion

2.1. Surface Microstructure, Roughness and Chemical Composition of the Coatings

The surface morphologies of the coatings prepared with different vol% of SiO_2 in TiO_2 are shown in Figure 2. The $\text{SiO}_2\text{-TiO}_2$ coating prepared with 7 vol% of SiO_2 in TiO_2 showed uniform, crack-free and smooth morphology (Figure 2a). However, significant cracks on the entire coating surface were observed with increase in SiO_2 concentration in TiO_2 (Figure 2b–d). Some small cracks were started to appear on the coating prepared from 10 vol% of SiO_2 in TiO_2 (Figure 2b), and these cracks goes bigger with increase in vol% of SiO_2 . For the coating prepared with 20 vol% of SiO_2 in TiO_2 , the cracks on the surface were abundant and coating material was popped out detaching from the substrate (Figure 2d). In the case of sol-gel coated films, during drying process, the capillary forces might have generated which provides cracks on the surface [12]. The surface roughness of the coatings were also studied (Figure 3). The $\text{SiO}_2\text{-TiO}_2$ coating prepared with 7 vol% of SiO_2 in TiO_2 showed the surface roughness of 67 nm (Figure 3a), whereas the surface roughness increases drastically to 98, 191 and 287 nm for the coating prepared from 10, 15 and 20 vol% of SiO_2 in TiO_2 (Figure 3b–d), respectively. This drastic increase in surface roughness may due to the increased density of cracks on the coating surface.

Figure 2. Field Emission Scanning Electron Microscope (FE-SEM) images of the coatings prepared from (a) 7; (b) 10; (c) 15; and (d) 20 vol% of SiO_2 in TiO_2 .

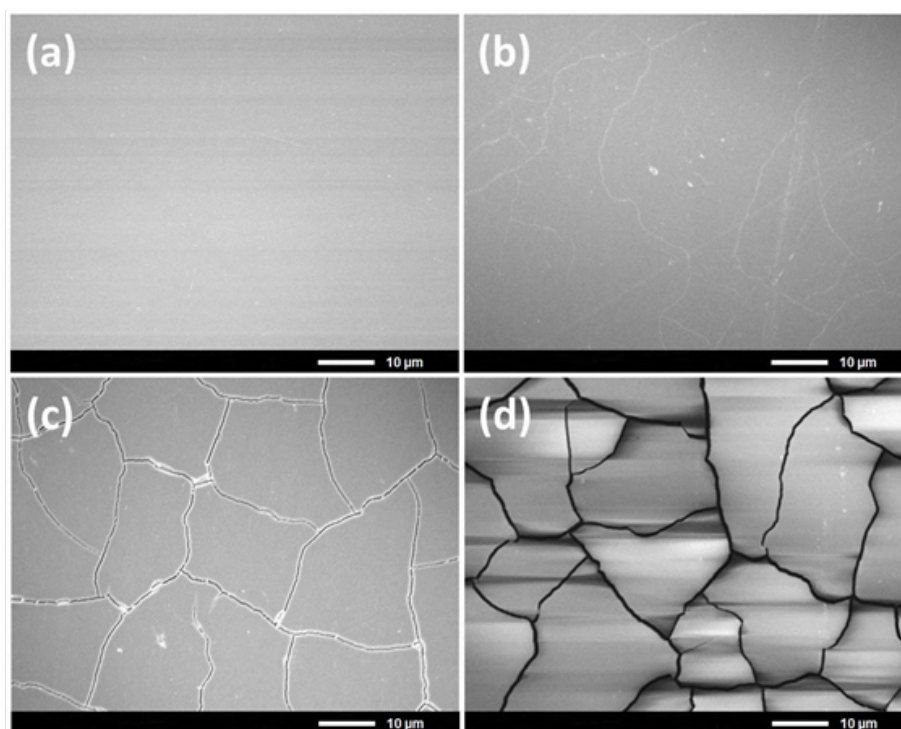


Figure 3. 3D Laser microscope images of the coatings prepared from (a) 7; (b) 10; (c) 15; and (d) 20 vol% of SiO₂ in TiO₂.

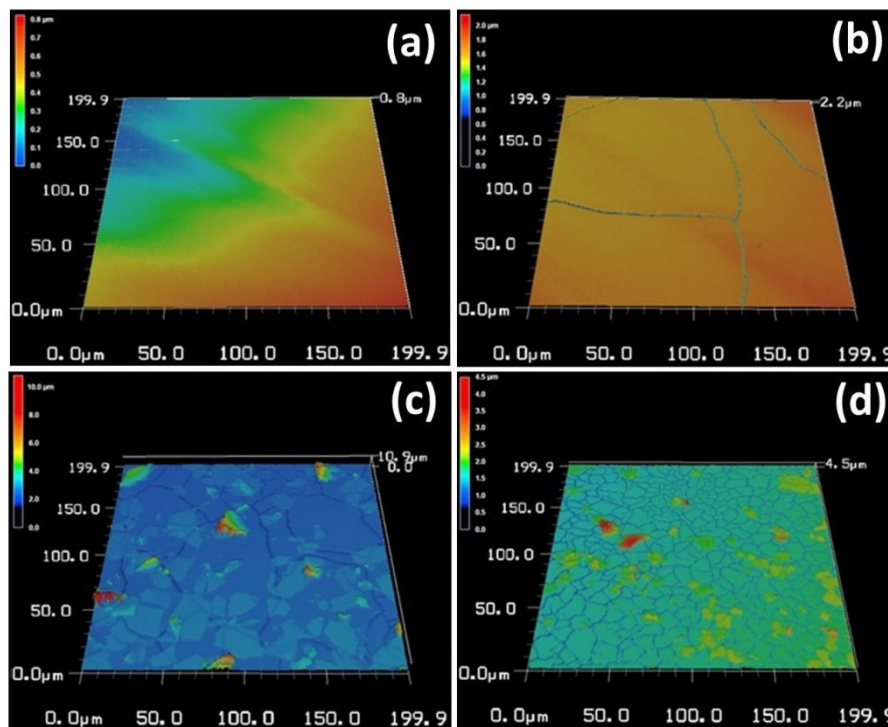
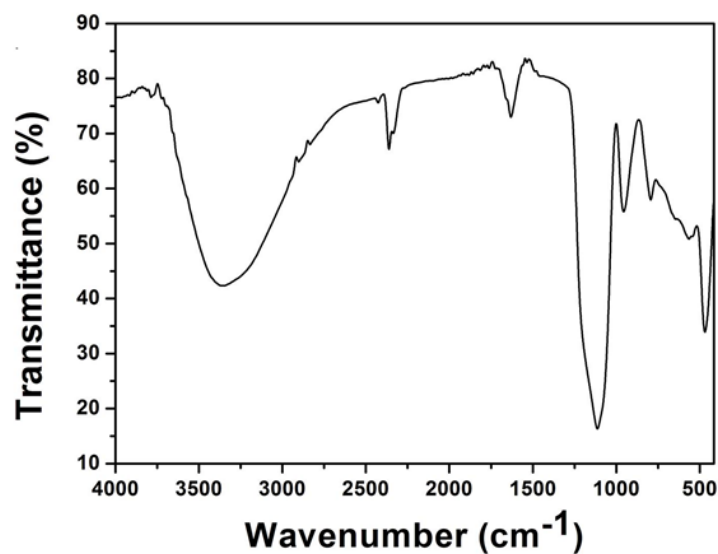


Figure 4 shows the FT-IR spectra of the coating prepared from 7 vol% of SiO₂ in TiO₂. The peaks observed in between 500 and 900 cm⁻¹ can be attributed to the characteristic vibrational modes of TiO₂ [13]. A peak observed near 954 cm⁻¹ is associated with Si-O-Ti vibration [14]. The absorption peak at 1118 cm⁻¹ confirms Si-O-Si linkage [14]. The absorption peaks near 3342 and 1630 cm⁻¹ can be attributed to the presence of stretching and bending vibrations of hydroxyl groups, respectively [15].

Figure 4. FT-IR spectra of the coatings prepared from 7 vol% of SiO₂ in TiO₂.



2.2. Superhydrophilic, Photocatalytic and Optical Properties of the Coatings

The wettability transition of the SiO₂-TiO₂ coating after UV illumination was studied. The prepared SiO₂-TiO₂ coatings were illuminated by UV light (365 nm, 2 mW/cm²). The UV illumination creates structural changes in TiO₂ (transformation of Ti⁴⁺ sites to Ti³⁺ sites) [16] and oxidizes the organic contaminants present on the surface of TiO₂, which effectively transforms the wettability of the TiO₂ surface towards more hydrophilic [17]. This is called as photo-induced hydrophilicity on TiO₂ surface [18]. The water contact angles (WCA) on the coatings before and after exposure to the UV light were measured. The water drop volume of 5 μ L was used to measure the water contact angles on the coating surface. The effect of UV exposure time on the wettability of the coatings was also studied. Figure 5 shows the wettability of the coatings prepared from 7 and 20 vol% of SiO₂ in TiO₂, before and after UV irradiation. Before UV illumination, the coating prepared from 7 and 20 vol% of SiO₂ in TiO₂ showed the WCA of 23° and 28°, respectively. After UV illumination of 30 min, the water drop immediately spread on the surface and the WCA drastically decreased to 8° on the coating prepared from 7 vol% of SiO₂ in TiO₂ and even for longer UV illumination time (5 h), the WCA remained in the range of 7°. The coating prepared from 20 vol% of SiO₂ in TiO₂ also showed decrease in WCA in the range of 10°, after longer UV illumination time. This slightly higher WCA in case of the coating prepared from 20 vol% of SiO₂ in TiO₂ is due to relatively high surface roughness provided by significant density of cracks present on the surface. Even after placing the UV irradiated coatings in dark for 3 months, the coatings showed stable wetting properties with WCA measured well below 10°. Figure 6 shows the optical photograph of water drops on bare PC substrate and the coating prepared from 7 vol% of SiO₂ in TiO₂ after 30 min. UV irradiation. Some of the water drops were colored blue using Methylene Blue for better visualization of water drops. The water drops on bare PC substrate maintain the contact angle of \sim 84°, whereas the water drops spreads on UV irradiated SiO₂-TiO₂ coating, confirming high affinity towards the water. In the case of SiO₂-TiO₂ coatings prepared by Fateh *et al.* [7], it needed more than 700 h of UV (A) irradiation to switch the wettability of the coatings in the superhydrophilic range.

Figure 5. Wetting properties of the coatings prepared from 7 and 20 vol% of SiO₂ in TiO₂ (Insets shows the shape of water drops on coatings).

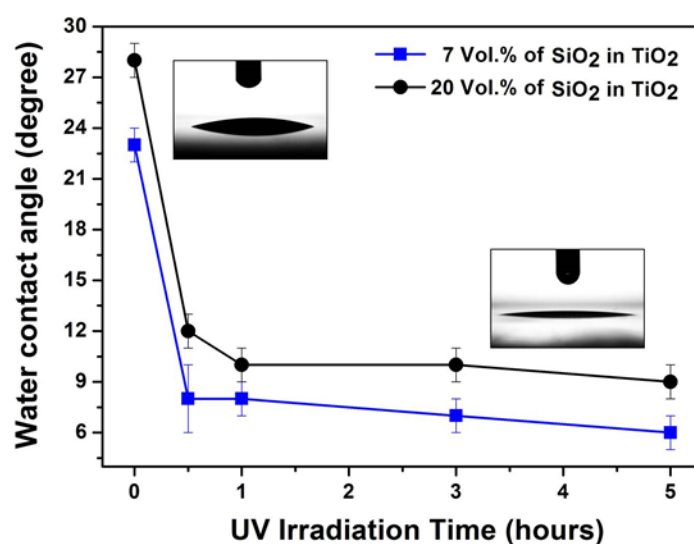
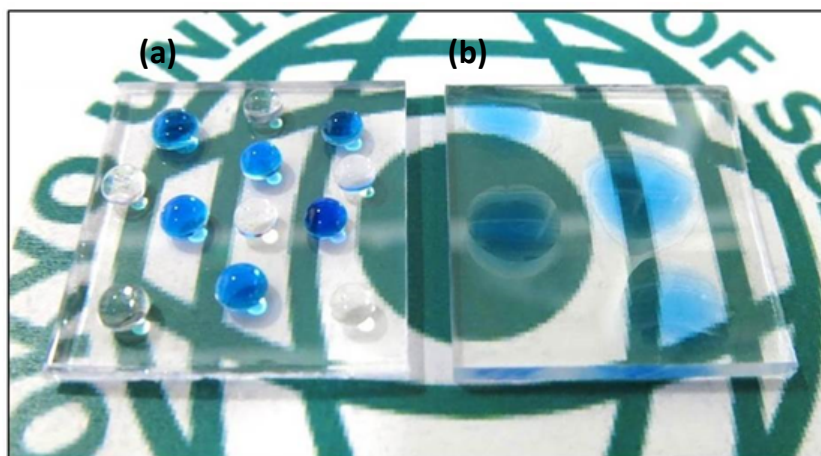
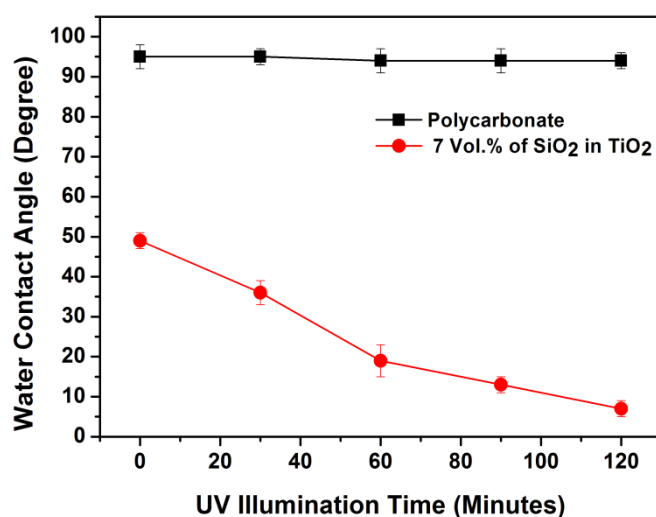


Figure 6. Optical photograph of water drops on bare PC substrate (a) and coating prepared from 7 vol% of SiO₂ in TiO₂ after 30 min. UV irradiation (b).



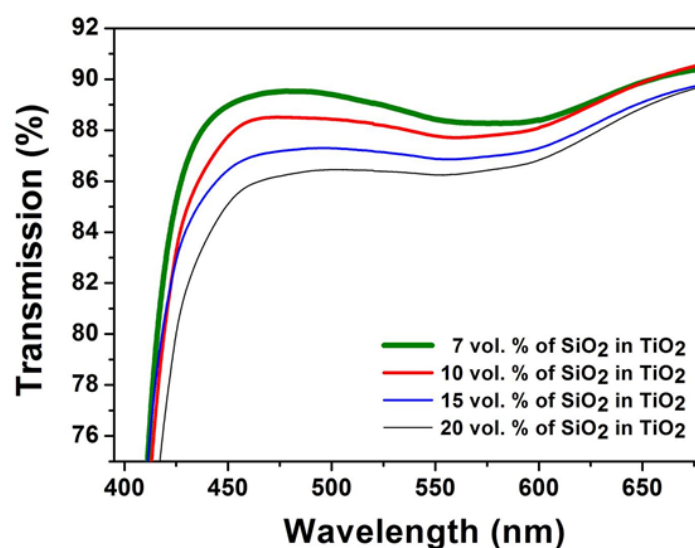
The TiO₂ is famously known for its excellent photocatalytic property, as it can degrade organic contamination under the illumination of UV light. We studied the photocatalytic degradation of the ODS monolayers after UV light illumination (365 nm, 2 mW/cm²) by means of water contact angle measurements. At first, the bare PC substrate and coating prepared from 7 vol% of SiO₂ in TiO₂ were irradiated with UV light (365 nm, 2 mW/cm²) for 1 h to make them superhydrophilic and hydrophobic ODS self-assembled monolayers (SAMs) were applied on them through vapor phase. To employ ODS SAMs on the surface, 2 mL of ODS in beaker was kept in the closed metal box containing the samples at 100 °C for 24 h. After application of ODS SAMs on the surface, the WCA on bare PC substrate and coating prepared from 7 vol% of SiO₂ in TiO₂ showed 95° and 50°, respectively (Figure 7). The ODS treated bare PC showed almost no change in WCA after 120 min of UV illumination, whereas the coating prepared from 7 vol% of SiO₂ in TiO₂ showed significant decrease in WCA as a function of UV illumination time and the surface becomes superhydrophilic after 120 min of UV illumination (Figure 7) confirming photocatalytic degradation of the ODS monolayers.

Figure 7. Wettability change on octadecyltrichlorosilane (ODS)-treated SiO₂-TiO₂ coatings under UV illumination.



Optical transparency is prerequisite for the application of self-cleaning coating on transparent glass or plastic surface. Figure 8 shows the optical transmission of SiO₂-TiO₂ coatings prepared on the PC substrate from different vol% of SiO₂ in TiO₂. All the coatings are highly transparent and showed the optical transmittance values above 85% over the entire visible wavelength range. The optical transmission was gradually decreased from 89% to 85% with an increase in SiO₂ concentration in TiO₂. The increased surface roughness is responsible for the slight loss in optical transmission in the visible range. The SiO₂-TiO₂ coatings prepared by Hwang *et al.* [8] showed an optical transmission of ~87%, whereas all the coatings prepared by Fateh *et al.* [7,10] showed an optical transmission of >92%.

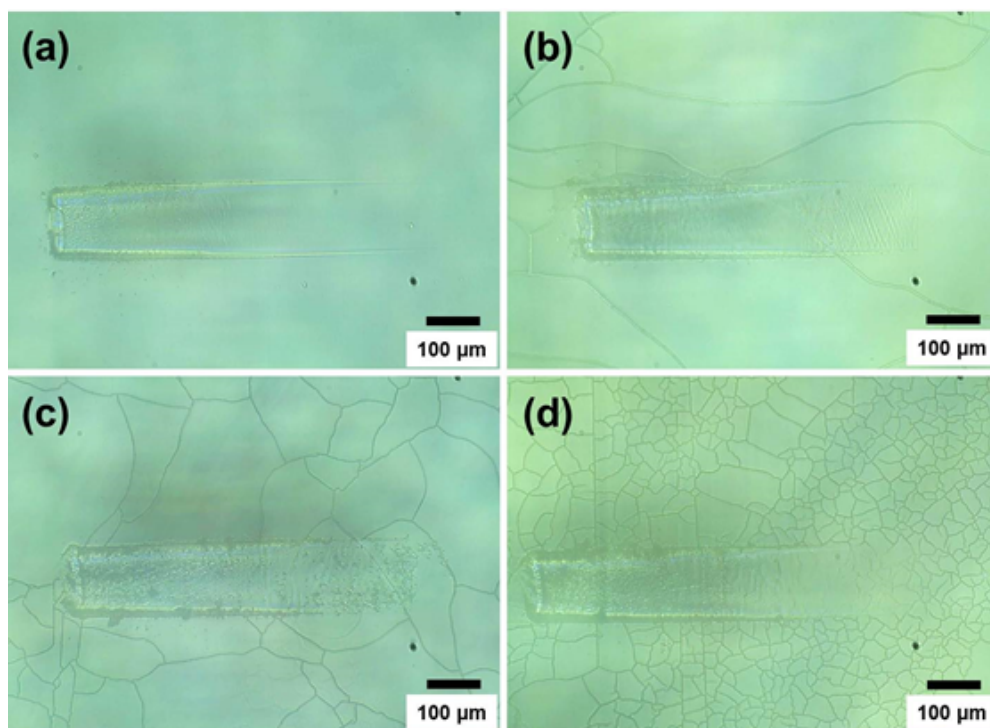
Figure 8. Optical transmission spectra of the SiO₂-TiO₂ coatings.



2.3. Mechanical Properties of the Coatings

The mechanical durability of the coatings is a very important criterion for industrial applications. The mechanical stability of the prepared SiO₂-TiO₂ coatings is depicted in Figure 9. The bare PC substrates get easily scratched at the applied force of less than 4.2 mN. For the coating prepared from 7 vol% of SiO₂ in TiO₂, the coating material was removed at the applied force of ~16.1 mN (Figure 9a), whereas this force was decreased to 12.2, 10.9 and 9.8 mN for the coating prepared from 10, 15 and 20 vol% of SiO₂ in TiO₂ (Figure 9b–d), respectively. The smooth, crack-free morphology and lower surface roughness on the coating resulted in the stable and adhesive coating on the PC substrate. Even rubbed by the fingers, the coating material was not easily removed. This is ascribed to the formation of an intermediate layer connecting the TiO₂ nanoparticles and the silica network. However, in the case of the coating prepared from higher concentration of SiO₂ in TiO₂, due to significant cracks and increased surface roughness, the coating material could be removed at relatively lower applied force.

Figure 9. Adhesion test performed on the coatings prepared from (a) 7; (b) 10; (c) 15; and (d) 20 vol% of SiO₂ in TiO₂.



3. Experimental Section

3.1. Materials

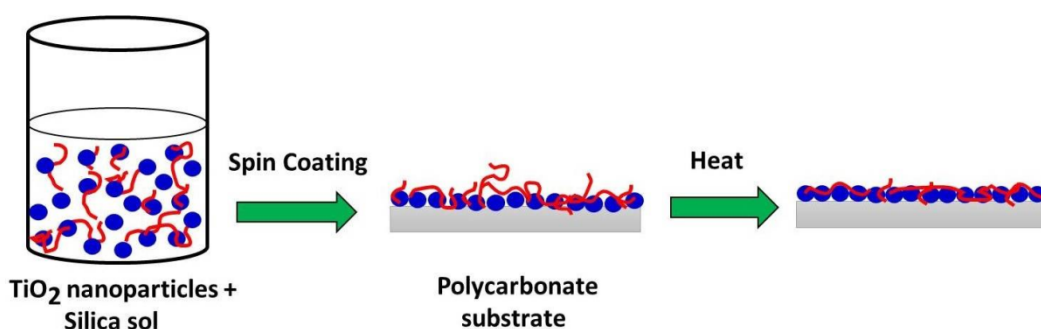
Tetraethylorthosilicate (TEOS) and Octadecyltrichlorosilane (ODS) were purchased from Sigma Aldrich (St. Louis, MO, USA). Ethanol (99.5%) and nitric acid (69%) were purchased from Wako Pure Chemical Industries Ltd. (Kanto region, Japan). PC substrates (ECK, 100UU) were bought from Sumitomo Bakelite Co. Ltd. (Akita, Japan). The commercially available TiO₂ nanoparticle solution (NRC-300C) was purchased from Nippon Soda Co. Ltd. (Tokyo, Japan).

3.2. Self-Cleaning Coating on PC Substrates

PC substrates are known to be hydrophobic in nature and so the adhesion is not strong between the coating material and the PC substrate [19]. The hydrophobic nature of PC substrates can be transformed to strongly hydrophilic by UV irradiation due to occurrence of photo-Fries reaction on the surface [20]. At first, PC substrates were gently cleaned by using detergent and water and kept for ultrasonication in double distilled water for 30 min. After drying at room temperature, the PC substrates were illuminated by UV light (365 nm, 2 mW/cm²) for 2 h. The PC substrates can photocatalytically degrade, if the TiO₂ coating is applied directly on the PC substrates. For this reason, the sol-gel processed silica layer was applied on the PC substrates prior to TiO₂ coating. A silica sol was prepared by adding 1.5 mL TEOS in 4 mL ethanol and this mixture was hydrolysed by adding 3 mL of double distilled water with 1 mL of nitric acid. This alcosol was stirred overnight and spin-coated on UV-treated PC substrates at 2000 rpm. This silica coating was annealed at 100 °C for 2 h. The

above prepared silica sol was mixed at different vol% (7, 10, 15 and 20 vol%) in commercially available TiO_2 nanoparticle solution and spin-coated on SiO_2 pre-coated PC substrates with 2000 rpm and annealed in oven at 110 °C for 6 h. No change in PC substrate was observed after annealing at 110 °C, however for annealing above 120 °C, PC substrate start to bend in irregular shape due to softening. The schematic of coating preparation steps are shown in Figure 10.

Figure 10. Schematic showing coating preparation steps.



3.3. Characterization Techniques

The surface morphology was studied by Field Emission Scanning Electron Microscope (FE-SEM, JEOL, JSM-7600F; Tokyo, Japan). The surface roughness of the prepared coatings was evaluated by laser microscopy (KEYENCE, VK-X200 series; Itasca, IL, USA). The chemical composition was studied by Fourier transform infrared spectroscopy (FT-IR, JASCO, FT/IR-6100; Tokyo, Japan). The water contact angles (WCA) were measured at six different locations on same sample by using contact angle meter (KYOWA, Drop Master; Saitama, Japan) and average value is reported as a final contact angle value. The optical transmission of the coatings was measured by UV-VIS spectrophotometer (JASCO, V-670; Tokyo, Japan). The coatings were illuminated by UV light (365 nm, 2 mW/cm²). The UV lamps were purchased from TOSHIBA (FL10BLB; Tokyo, Japan) and assembled with proper electric supply inside the wooden box covered by thick black cloth. The adhesion of the coating material on PC substrate was checked at five different spots by using Scratch tester (Nano-Layer Scratch Tester, CSR-2000; Rhesca, Tokyo, Japan). The adhesion of the coatings on PC substrate and the maximum force required to remove the coating material was calculated. The cantilever was moved from right to left side in contact with the coating surface. The force was gradually increased while moving towards left side. The maximum force at which the coating material was removed from the PC substrate was noted as critical force to damage the coating. The optical photographs were recorded using Canon Digital Camera (G 15 series).

4. Conclusions

The mechanically durable, optically transparent, photocatalytically active and superhydrophilic SiO_2 - TiO_2 coatings are successfully prepared on PC substrates for self-cleaning applications. The uniform, crack-free coatings prepared from 7 vol% of SiO_2 in TiO_2 showed higher optical transmission in the visible range, strong superhydrophilicity and good scratch resistance properties. Such coatings can be applied on light-weight window and door polycarbonates for excellent self-cleaning applications.

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Author Contributions

Sanjay S. Latthe conceived the idea and designed the structure of article. Sanjay S. Latthe and Shanhu Liu carried out the experiments and wrote the original manuscript and Chiaki Terashima, Kazuya Nakata and Akira Fujishima participated in the discussions and helped to revise it.

Conflicts of Interest

The authors declare no conflict of interest.

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