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Research Article

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Design of SiO_2/TiO_2 that Synergistically Increases The Hydrophobicity of Methyltrimethoxysilane Coated Glass

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Abstract: This research work presents the design of a mixture of SiO_2/TiO_2 that increases the surface roughness and hydrophobicity of methyltrimethoxysilane (MTMS) coated glass. The deposition of SiO_2, TiO_2, and MTMS were conducted using a layer by layer dip coating technique. The SiO_2/TiO_2 coating was derived from complete hydrolysis of tetraethylorthsilicate and titanium tetraisopropoxide. In order to evaluate and compare the performance of SiO_2/TiO_2/MTMS coated glass, the SiO_2/SiO_2/MTMS and TiO_2/TiO_2/MTMS were also fabricated. SiO_2/TiO_2/MTMS samples displayed the highest water contact angle. The topography of surfaces showed that SiO_2/TiO_2/MTMS exposed higher surface roughness with micro-nanoscale structures. The sequence of SiO_2 and TiO_2 influenced the water contact angle and the stability of the coatings. SiO_2/TiO_2/MTMS produced higher contact angle and stability than TiO_2/SiO_2/MTMS.

Keywords: SiO_2/TiO_2; MTMS; surface roughness; stable; hydrophobic glass.

1 Introduction

The degree of water repellency depends on the surface energy and surface roughness. Several studies reported that surface roughness is a key factor for creating hydrophobic surfaces. Surface roughness can be increased by etching, chemical grafting, and the sol–gel process [1-2]. The sol–gel process is a wet chemical technique, also referred to as chemical solution deposition, which produces particles that are dispersed and aggregated on the surfaces. The clustered particles subsequently afford a highly hierarchical rough surface. Air bubbles are trapped in the grooves between aggregated particles which makes it difficult for water droplets to penetrate the gaps between the surfaces. Hence, surfaces with high roughness tend to follow heterogeneous wetting as the water easily rolls off from the surfaces [3].

The water contact angle depends on the surface roughness, which can be explained by two models: Cassie–Baxter and Wenzel models. Wenzel proposed a model in which water droplets penetrate into surface cavities, while Cassie–Baxter proposed a model in which water in the surface cavities is entrapped in air. Both these models explain the effect of the surface roughness on the water contact angle [2-4]. The correlation between the contact angle and surface roughness based on the Wenzel and Cassie–Baxter models is shown in equations 1 and 2, respectively.

$$cos\ \theta_w = r\ cos\ \theta \tag{1}$$

$$cos\ \theta_{CB} = f_1\ cos\ \theta - f_2 \tag{2}$$

where $cos\ \theta w$ and $cos\ \theta CB$ are the Wenzel and Cassie–Baxter contact angles respectively. r is the roughness factor, which is defined as the ratio of the actual area of the rough surface to the geometric projected area. $f1$ and $f2$ are the fractions of the surface occupied by solid/liquid

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and air /liquid respectively. *cos θ* is the contact angle of the flat surface.

Various metal oxides, such as SiO_2, TiO_2, Al_2O_3, and ZnO, were reportedly used to produce a rough surface [5-9]. SiO_2 and TiO_2 are typically used to modify the surface roughness. Currently, several studies reported the effect of dual size on the surface roughness [10-11]. However, only few studies reported the effect of a bimetallic oxide, especially SiO_2 and TiO_2, on wettability. The combination of crystalline/amorphous SiO_2 and crystalline TiO_2 was reported to enhance the photocatalytic performance of coatings [12-14]. Moreover, crystalline TiO_2 is not suitable to prepare hydrophobic surfaces. Under light conditions, crystalline TiO_2 absorbs UV irradiation from sunlight and performs photocatalysis. During photocatalysis, the photocatalyst TiO_2 produces hydrophilic hydroxyl groups which decrease the surface hydrophobicity [15].

Ramirez-Garcia et al. reported the use of amorphous SiO_2 and amorphous TiO_2 on surface coatings [16]. The SiO_2/TiO_2 layer enhances the durability and adhesion of coatings. Nevertheless, limited studies reported the effects of SiO_2/TiO_2 on the hydrophobicity of coatings. In this study, the effects of amorphous SiO_2 and amorphous TiO_2 on the hydrophobicity of coated glasses were comprehensively investigated. For this purpose, SiO_2 and TiO_2 were prepared by a sol–gel method using tetraethylorthosilicate and titanium isopropoxide as the precursors and ethanol as the solvent. MTMS was used as a hydrophobic agent to lower the surface energy. SiO_2, TiO_2, and MTMS were deposited on glass by the layer-by-layer dip-coating technique. For comparison, SiO_2/SiO_2/MTMS and TiO_2/TiO_2/MTMS layers were also fabricated. In addition, the effect of the sequences SiO_2/TiO_2/MTMS and TiO_2/SiO_2/MTMS was investigated. By this design, data regarding the effect of the SiO_2 and TiO_2 layers on coated glasses were obtained.

2 Methods

2.1 Materials

Tetraethylorthosilicate (TEOS, 99%) and ethanol (EtOH, 99%) were supplied by Merck. Titanium tetraisopropoxide (TTIP, 97%), methyltrimethoxysilane (MTMS, 95%), and hydrochloric acid (HCl, were purchased from Sigma Aldrich. All chemicals were used as received without any further purification. Glass slides (38 x 12 x 1 mm) were used as substrates.

2.2 Preparation of SiO_2, TiO_2, and MTMS Sols

In this experiment, SiO_2, TiO_2, and MTMS sols were prepared in different containers. SiO_2 sol was prepared from the hydrolysis of TEOS in ethanol and HCl. An acidic solution was prepared by mixing 0.2 mL of 0.1 M HCl into 8 mL of ethanol. Then, 3.35 mL of TEOS (15 mmol) was added to the acidic alcohol solution. The sol was stirred for 1.5 hours at 60°C. Then 2 mL of concentrated HCl (37%) was added into the sol under vigorous stirring. The total volume of sol was adjusted with ethanol until a volume of 20 mL was reached. Using a similar procedure, 15 mmol of TiO_2 sol was prepared by adding 4.44 mL of TTIP in acidic alcohol solution. A 2 mmol MTMS sol was made by mixing 0.28 mL of MTMS into the acidic alcohol solution.

2.3 Coating Preparation

Prior to film deposition, the glass was cleaned in ethanol using an ultrasonic bath for 30 minutes. The film was obtained by the layer-by-layer dip coating of the sols on the glass substrate at a withdrawal rate of 3 cm/min.

Firstly, the cleaned glass substrates were immersed in the SiO_2 sol for 1 minute and withdrawn at a rate of 3 cm/min. Secondly, the treated glasses were dried at room temperature for 10 minutes and subsequently at 70°C for 30 minutes. Then the TiO_2 sol was deposited on SiO_2-coated glasses. Finally, the as-obtained SiO_2/TiO_2-coated glass was immersed into the MTMS sol to fabricate SiO_2/TiO_2/MTMS-coated glasses. At each deposition step of TiO_2 and MTMS, a procedure similar to that described above for the preparation of SiO_2-coated glasses was employed. To investigate the effects of SiO_2 and TiO_2, SiO_2/SiO_2/MTMS and TiO_2/TiO_2/MTMS were also prepared. Table 1 summarizes the three coating designs.

To examine the effect of the layer sequence, two films (SiO_2/TiO_2/MTMS and TiO_2/SiO_2/MTMS) were fabricated. The films were different with respect to the positions of SiO_2 and TiO_2 as the bottom or middle layer. SiO_2/TiO_2/MTMS-coated glass was prepared by the procedure discussed in the previous paragraph. The amounts of SiO_2, TiO_2, and MTMS were 75, 30, and 2 mmol, respectively. Moreover, TiO_2/SiO_2/MTMS-coated glass was prepared by the immersion of the cleaned glasses into the TiO_2 sol as the first (bottom) layer. After 1 minute, the coated glasses were withdrawn at 3 cm/min. The coatings were cured under ambient conditions and then at 70°C for 30 minutes. Next, TiO_2-coated glasses were immersed into the SiO_2 sol. The top layer of MTMS was introduced by the deposition

Table 1: The composition and schematic design of SiO_2 and TiO_2 layer on MTMS coated glass.

Sample	First (bottom) layer	Second (middle) layer	Third (top) layer	Illustration of coatings
SSM	15 mmol of SiO_2	15 mmol of TiO_2	2 mmol of MTMS	
TTM	15 mmol of TiO_2	15 mmol of SiO_2	2 mmol of MTMS	
STM	15 mmol of SiO_2	15 mmol of TiO_2	2 mmol of MTMS	

of MTMS on the TiO_2/SiO_2-coated glass making the TiO_2/SiO_2/MTMS. Table 2 summarizes the coating illustration of SiO_2/TiO_2/MTMS and TiO_2/SiO_2/MTMS.

2.4 Characterizations

TiO_2 diffractogram was measured by XRD Pan Analytical using Cu Kα radiation as the X ray source. Surface roughness was determined by AFM N8 Neos Bruker. The water contact angle of samples was measured by ImageJ software.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 The Crystallinity of SiO_2 and TiO_2

Prior to analysis the sol was heated at 70°C, ground into a powder, and then was ready to use in XRD analysis. Heating the sol at 70°C did not change the crystallinity of the SiO_2 and TiO_2. Figure 1 shows the diffractogram of the prepared TiO_2 and SiO_2. The diffractogram of SiO_2 displayed a broad peak at 15-35° which is related to amorphous SiO_2 [17]. The XRD pattern of TiO_2 also revealed the amorphous phase. Under light or dark conditions, amorphous TiO_2 kept the same water contact angle. This is because amorphous TiO_2 does not exhibit the photocatalytic process which produces the hydrophilic OH groups. Previous research also reported that amorphous SiO_2-TiO_2 increased the adhesion of coatings compared to crystalline SiO_2-TiO_2 [12].

3.2 The Role of SiO_2 and TiO_2 Layer on the Coated Glass

The role of SiO_2 and TiO_2 on the coating was investigated by comparingthe water contact angles of three samples: (i) SiO_2 in the first and second layers (SSM), (ii) TiO_2 in the first and second layers (TTM), and (iii) SiO_2 in the first layer, followed by TiO_2 in the second layer (STM). All these samples were coated with MTMS as the third (top layer). To examine the effects of SiO_2 and TiO_2 on coatings, it is crucial that their amounts are the same. In this study, the amount of SiO_2 and TiO_2 was 0.015 mol. The estimated contact angles of SSM, TTM, and STM were 81.94 ± 0.50°, 80.94 ± 1.04°, and 93.75 ± 1.27°, respectively (Fig. 2). The STM sample was more hydrophobic than SSM and TTM. The higher contact angle value corresponded to the increased roughness of glass surfaces. The deposition of dual particles, i.e., SiO_2 and TiO_2, considerably affects the surface roughness which was confirmed by AFM measurements.

Figure 3 showed the AFM images of SSM, STM, and TTM. The surface roughness values for SSM, TTM, and STM were 67.7, 7.13, and 115 nm, respectively. The topography of STM exhibited higher roughness than the others. This result was supported by the estimated contact angle values. Surfaces with high roughness exhibit increased hydrophobicity. Notably, the different surface roughness values for SSM and TTM did not affect the water contact angles of the coated glasses.

The topography of the SSM images revealed the dispersion of large-sized silica particles on the surfaces. Furthermore, even though SSM exhibited high roughness, pores (wide distance) between these larger particles were clearly visible. When the water droplets reach the surface, there is a high probability that the water droplets penetrate into the large pores, thereby contributing to homogenous

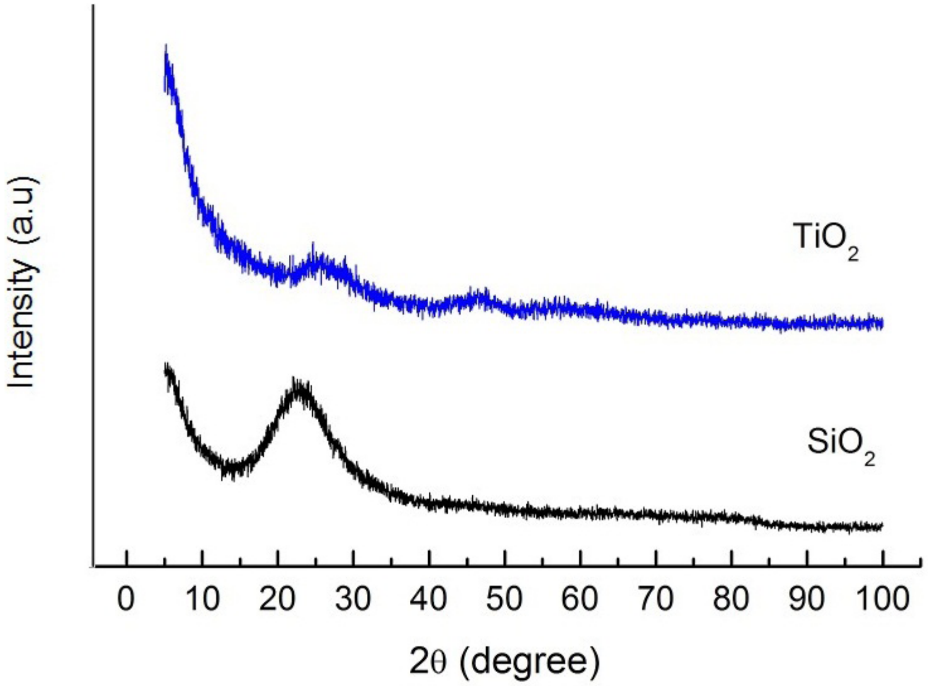


Figure 1: The diffractogram of prepared TiO2 and SiO2.

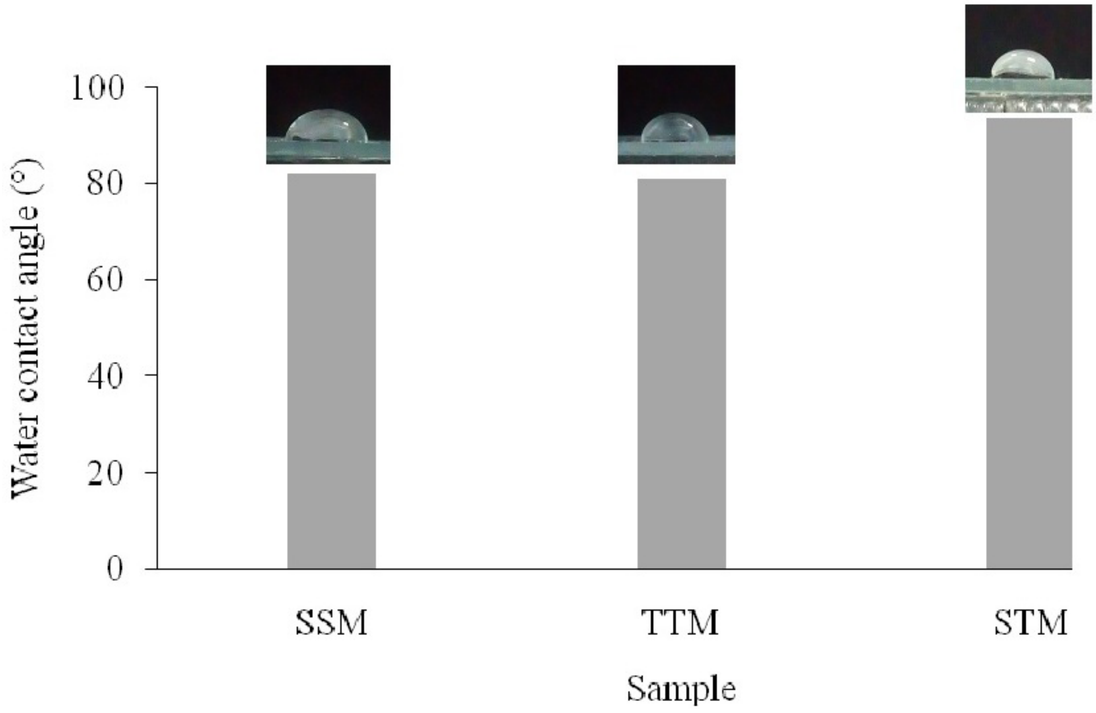


Figure 2: The water contact angle of SSM, TTM, and STM samples.

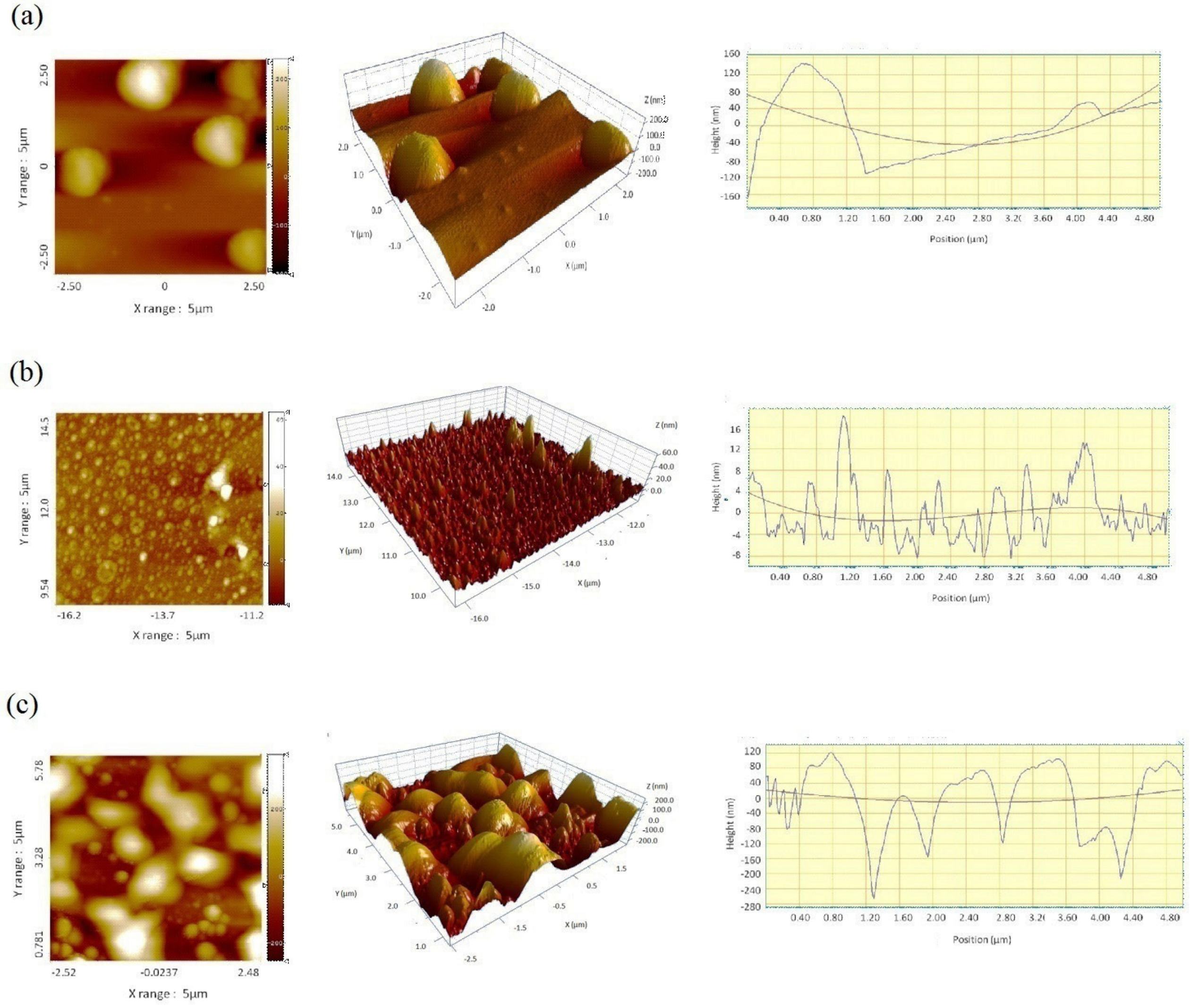


Figure 3: The AFM images of (a) SSM, (b) TTM, and (c) STM samples.

wetting [18]. Air was not trapped in the grooves; hence, water can easily penetrate into the surfaces. This result was supported by the estimated contact angles.

In contrast, TTM exhibited a lower roughness than STM, possibly related to the difference in the particle sizes between TiO_2 and SiO_2. The particle size of TiO_2 was less than that of SiO_2 under similar preparation conditions [19]. A uniform TTM surface without clear TiO_2 particle clusters was observed, affording smooth surfaces.

Table 3 summarized the height surface of samples based on two-dimensional AFM images. From the data obtained from the height curve, the roughness heights of SSM and TTM were 60–140 and 2–18 nm, respectively. The STM sample exhibited a roughness height in the range of 10–120 nm. According to the range of the roughness height, the STM sample exhibited a higher hierarchical roughness than SSM and TTM, revealing that the SiO_2 and TiO_2 layers exhibit a hierarchical structure with nano-micro roughness. The different sizes of SiO_2 and TiO_2 particles led to the production of micro-nanoscale surfaces. The data revealed that the combination of SiO_2 and TiO_2 exhibits a synergistic effect to create rougher surfaces.

3.3 The influence of coating sequence on wettability and stability coatings

The two types of coating, STM and TSM, were investigated. Figure 4 showed the water contact angles of STM and TSM. TSM-coated glass exhibited a lower hydrophobicity than STM. STM and TSM exhibited different types of chemical

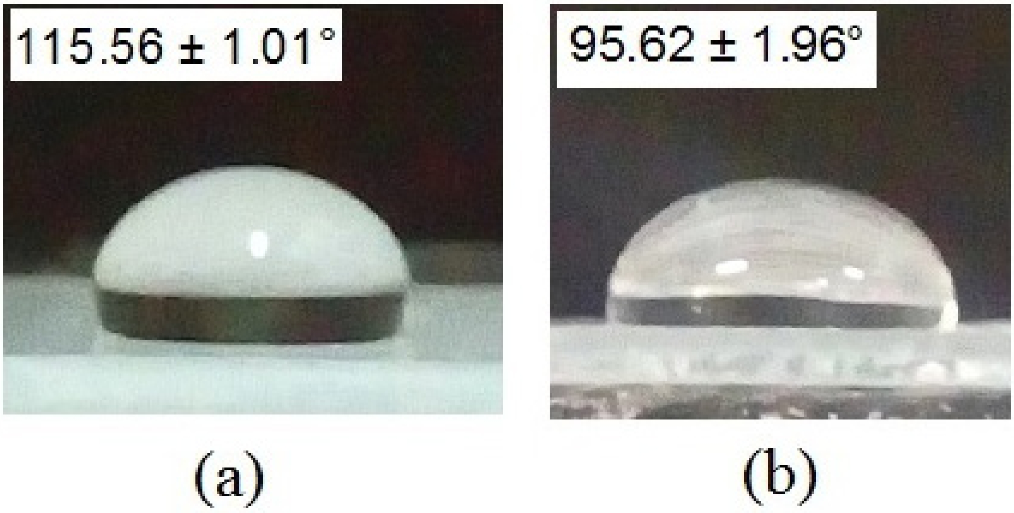


Figure 4: The image of water droplet on (a) STM and (b) TMS coated glass.

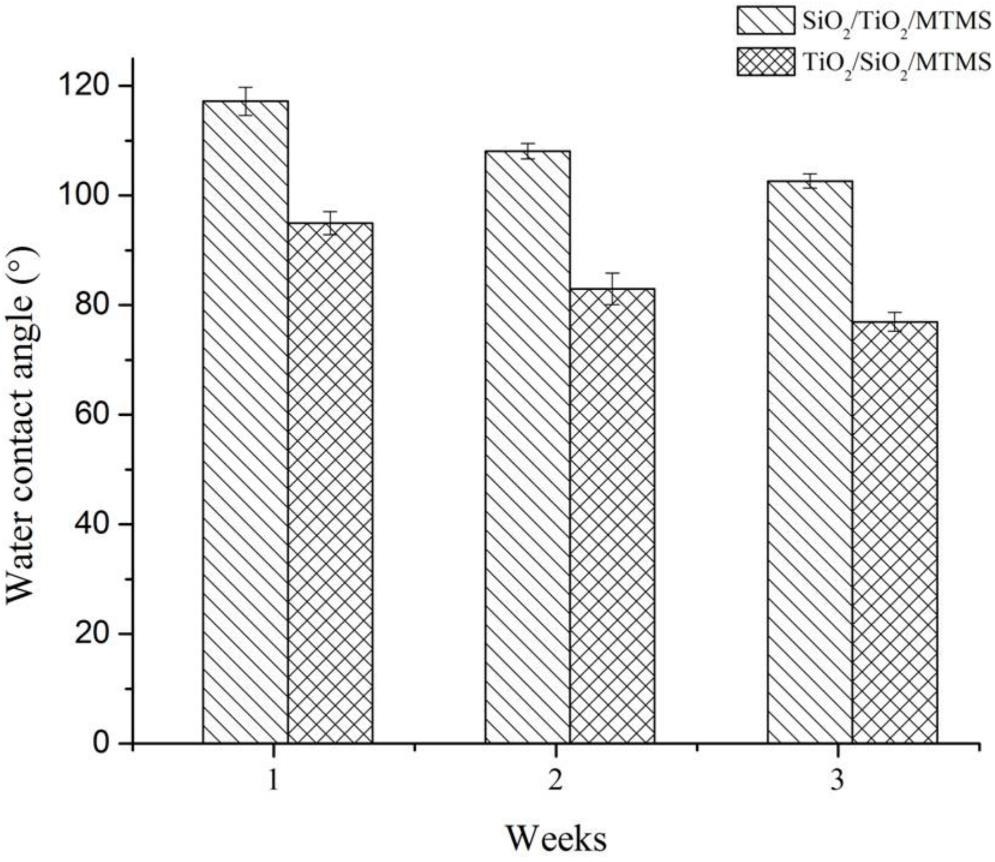
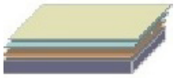


Figure 5: The water contact angle of STM and TMS coated glass under outdoor exposure.

Table 2: The coating illustration of SiO_2/TiO_2/MTMS (STM) and TiO_2/SiO_2/MTMS (TMS).

Sample	First (bottom) layer	Second (middle) layer	Third (top) layer	Static water contact angle (°)	Illustration of coatings
STM	SiO_2	TiO_2	MTMS	115.56±1.01°	
TSM	TiO_2	SiO_2	MTMS	95.62±1.96°	

▰ SiO_2 ▰ TiO_2 ▰ MTMS

Table 3: The roughness parameter of SiO_2/SiO_2/MTMS (SSM), TiO_2/TiO_2/MTMS (TTM), and SiO_2/TiO_2/MTMS (STM) coated glasses by AFM measurements.

Sample	Height of surface (nm)	rms (nm)
SSM	60-140	67.7
TTM	2-18	7.13
STM	10-120	115

bonding. Si–O– [Si] chemical bonds were present between STM and glass, while Si–O–[Ti] chemical bonds were present between TSM and glass. The bond energies of Si–O–[Si] and Si–O–[Ti] were 421 and 366.7 kJ/mol, respectively [20]. Hence, the chemical bond of Si–O–[Si] is stronger than that of Si–O–[Ti]. Previous work has shown that these materials are known to exhibit stability due to high bond energies.

Figure 5 showed the change in the water contact angles of STM and TSM after outdoor exposure for 2 weeks. TSM exhibited lower stability than STM. From the first week, the water contact angle of TSM decreased, related to the lower bond strength of TSM on glass than STM. For outdoor applications, hydrophobic coatings need to survive under moist conditions. The presence of hydroxyl groups on the coatings can adsorb moisture from the atmosphere, thereby decreasing the water contact angle [21].

4 Conclusions

The rougher surface of methyltrimethoxysilane-coated glasses was developed using bimodal particles, i.e., SiO_2 and TiO_2. Effects of SiO_2 and TiO_2 were examined by contact angle measurements and surface topography.

The deposition of SiO_2 and TiO_2 on the MTMS-coated glass (SiO_2/TiO_2/MTMS) led to the high surface roughness; hence, it increases the hydrophobicity of coatings. When the layer sequence was changed to TiO_2/SiO_2/MTMS, the water contact angle and stability of the coated glass decreased. In addition, SiO_2/TiO_2/MTMS maintained its hydrophobicity even after treatment under outdoor exposure. For future research, it is imperative to examine the effect of SiO_2/TiO_2 on the adhesion of coatings and mechanical properties as these are key factors for industrial applications.

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Conflicts of interest : There are no conflicts to declare.

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