Research Article

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Design of SiO\textsubscript{2}/TiO\textsubscript{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\textsubscript{2}/TiO\textsubscript{2} that increases the surface roughness and hydrophobicity of methyltrimethoxysilane (MTMS) coated glass. The deposition of SiO\textsubscript{2}, TiO\textsubscript{2}, and MTMS were conducted using a layer by layer dip coating technique. The SiO\textsubscript{2}/TiO\textsubscript{2} coating was derived from complete hydrolysis of tetraethylorthosilicate and titanium tetraisopropoxide. In order to evaluate and compare the performance of SiO\textsubscript{2}/TiO\textsubscript{2}/MTMS coated glass, the SiO\textsubscript{2}/SiO\textsubscript{2}/MTMS and TiO\textsubscript{2}/TiO\textsubscript{2}/MTMS were also fabricated. SiO\textsubscript{2}/TiO\textsubscript{2}/MTMS samples displayed the highest water contact angle. The topography of surfaces showed that SiO\textsubscript{2}/TiO\textsubscript{2}/MTMS exposed higher surface roughness with micro-nanoscale structures. The sequence of SiO\textsubscript{2} and TiO\textsubscript{2} in the coatings influenced the water contact angle and the stability of the coatings. SiO\textsubscript{2}/TiO\textsubscript{2}/MTMS produced higher contact angle and stability than TiO\textsubscript{2}/SiO\textsubscript{2}/MTMS.

Keywords: SiO\textsubscript{2}/TiO\textsubscript{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.

\begin{equation}
\cos \theta \text{w} = r \cos \theta
\end{equation}

\begin{equation}
\cos \theta \text{CB} = f_1 \cos \theta - f_2
\end{equation}

where \( \cos \theta \text{w} \) and \( \cos \theta \text{CB} \) 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. \( f_1 \) and \( f_2 \) are the fractions of the surface occupied by solid/liquid
and air/liquid respectively. \( \cos \theta \) is the contact angle of the flat surface.

Various metal oxides, such as \( \text{SiO}_2 \), \( \text{TiO}_2 \), \( \text{Al}_2\text{O}_3 \), and \( \text{ZnO} \), were reportedly used to produce a rough surface [5-9]. \( \text{SiO}_2 \) and \( \text{TiO}_2 \) 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 \( \text{SiO}_2 \) and \( \text{TiO}_2 \), on wettability. The combination of crystalline/amorphous \( \text{SiO}_2 \) and crystalline \( \text{TiO}_2 \) was reported to enhance the photocatalytic performance of coatings [12-14]. Moreover, crystalline \( \text{TiO}_2 \) is not suitable to prepare hydrophobic surfaces. Under light conditions, crystalline \( \text{TiO}_2 \) absorbs UV irradiation from sunlight and performs photocatalysis. During photocatalysis, the photocatalyst \( \text{TiO}_2 \) produces hydrophilic hydroxyl groups which decrease the surface hydrophobicity [15].

Ramirez-Garcia et al. reported the use of amorphous \( \text{SiO}_2 \) and amorphous \( \text{TiO}_2 \) on surface coatings [16]. The \( \text{SiO}_2/\text{TiO}_2 \) layer enhances the durability and adhesion of coatings. Nevertheless, limited studies reported the effects of \( \text{SiO}_2/\text{TiO}_2 \) on the hydrophobicity of coatings. In this study, the effects of amorphous \( \text{SiO}_2 \) and amorphous \( \text{TiO}_2 \) on the hydrophobicity of coated glasses were comprehensively investigated. For this purpose, \( \text{SiO}_2 \) and \( \text{TiO}_2 \) were prepared by a sol–gel method using tetraethylorthosilicate and titanium isopropoxide as the precursors and ethanol as the solvent. \( \text{MTMS} \) was used as a hydrophobic agent to lower the surface energy. \( \text{SiO}_2 \), \( \text{TiO}_2 \), and \( \text{MTMS} \) were deposited on glass by the layer-by-layer dip-coating technique. For comparison, \( \text{SiO}_2/\text{SiO}_2/\text{MTMS} \) and \( \text{TiO}_2/\text{TiO}_2/\text{MTMS} \) layers were also fabricated. In addition, the effect of the sequences \( \text{SiO}_2/\text{TiO}_2/\text{MTMS} \) and \( \text{TiO}_2/\text{SiO}_2/\text{MTMS} \) was investigated. By this design, data regarding the effect of the \( \text{SiO}_2 \) and \( \text{TiO}_2 \) 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 \( \text{SiO}_2 \), \( \text{TiO}_2 \), and MTMS Sols

In this experiment, \( \text{SiO}_2 \), \( \text{TiO}_2 \), and MTMS sols were prepared in different containers. \( \text{SiO}_2 \) 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 \( \text{TiO}_2 \) 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 \( \text{SiO}_2 \) 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 \( \text{TiO}_2 \) sol was deposited on \( \text{SiO}_2 \)-coated glasses. Finally, the as-obtained \( \text{SiO}_2/\text{TiO}_2 \)-coated glass was immersed into the MTMS sol to fabricate \( \text{SiO}_2/\text{TiO}_2/\text{MTMS} \)-coated glasses. At each deposition step of \( \text{TiO}_2 \) and MTMS, a procedure similar to that described above for the preparation of \( \text{SiO}_2 \)-coated glasses was employed. To investigate the effects of \( \text{SiO}_2 \) and \( \text{TiO}_2 \), \( \text{SiO}_2/\text{SiO}_2/\text{MTMS} \) and \( \text{TiO}_2/\text{TiO}_2/\text{MTMS} \) were also prepared. Table 1 summarizes the three coating designs.

To examine the effect of the layer sequence, two films (\( \text{SiO}_2/\text{SiO}_2/\text{MTMS} \) and \( \text{TiO}_2/\text{SiO}_2/\text{MTMS} \)) were fabricated. The films were different with respect to the positions of \( \text{SiO}_2 \) and \( \text{TiO}_2 \) as the bottom or middle layer. \( \text{SiO}_2/\text{TiO}_2/\text{MTMS} \)-coated glass was prepared by the procedure discussed in the previous paragraph. The amounts of \( \text{SiO}_2 \), \( \text{TiO}_2 \), and MTMS were 75, 30, and 2 mmol, respectively. Moreover, \( \text{TiO}_2/\text{SiO}_2/\text{MTMS} \)-coated glass was prepared by the immersion of the cleaned glasses into the \( \text{TiO}_2 \) 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, \( \text{TiO}_2 \)-coated glasses were immersed into the \( \text{SiO}_2 \) sol. The top layer of MTMS was introduced by the deposition
Table 1: The composition and schematic design of SiO₂ and TiO₂ layer on MTMS coated glass.

| Sample | First (bottom) layer | Second (middle) layer | Third (top) layer | Illustration of coatings |
|--------|----------------------|-----------------------|------------------|-------------------------|
| SSM    | 15 mmol of SiO₂      | 15 mmol of TiO₂       | 2 mmol of MTMS   | ![Diagram SSM]          |
| TTM    | 15 mmol of TiO₂      | 15 mmol of SiO₂       | 2 mmol of MTMS   | ![Diagram TTM]          |
| STM    | 15 mmol of SiO₂      | 15 mmol of TiO₂       | 2 mmol of MTMS   | ![Diagram STM]          |

of MTMS on the TiO₂/SiO₂-coated glass making the TiO₂/SiO₂/MTMS. Table 2 summarizes the coating illustration of SiO₂/TiO₂/MTMS and TiO₂/SiO₂/MTMS.

2.4 Characterizations

TiO₂ 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 SiO₂ and TiO₂

Prior to analysis the sol was heated at 70°C, ground into a powder, and then ready to use in XRD analysis. Heating the sol at 70°C did not change the crystallinity of the SiO₂ and TiO₂. Figure 1 shows the diffractogram of the prepared TiO₂ and SiO₂. The diffractogram of SiO₂ displayed a broad peak at 15-35° which is related to amorphous SiO₂ [17]. The XRD pattern of TiO₂ also revealed the amorphous phase. Under light or dark conditions, amorphous TiO₂ kept the same water contact angle. This is because amorphous TiO₂ does not exhibit the photocatalytic process which produces the hydrophilic OH groups. Previous research also reported that amorphous SiO₂-TiO₂ increased the adhesion of coatings compared to crystalline SiO₂-TiO₂ [12].

3.2 The Role of SiO₂ and TiO₂ Layer on the Coated Glass

The role of SiO₂ and TiO₂ on the coating was investigated by comparing the water contact angles of three samples: (i) SiO₂ in the first and second layers (SSM), (ii) TiO₂ in the first and second layers (TTM), and (iii) SiO₂ in the first layer, followed by TiO₂ in the second layer (STM). All these samples were coated with MTMS as the third (top layer). To examine the effects of SiO₂ and TiO₂ on coatings, it is crucial that their amounts are the same. In this study, the amount of SiO₂ and TiO₂ 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., SiO₂ and TiO₂, 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, 71.3, 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
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Figure 1: The diffractogram of prepared $\text{TiO}_2$ and $\text{SiO}_2$.

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

### Table 2: The coating illustration of SiO$_2$/TiO$_2$/MTMS (STM) and TiO$_2$/SiO$_2$/MTMS (TSM).

| 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°                  | ![STM coating illustration](image1) |
| TSM    | TiO$_2$              | SiO$_2$               | MTMS              | 95.62±1.96°                   | ![TSM coating illustration](image2) |

### 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      |

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.

### References

[1]. Liu H., Gao S., Cai J., He C., Mao J., Zhu T., et al., Recent progress in fabrication and applications of superhydrophobic coating on cellulose-based substrates, Materials, 2016, 9, 124-160.

[2]. Song J., Rojas O.J., Approaching super-hydrophobicity from cellulosic materials: A review, Nord. Pulp & Pap. Res. J., 2013, 28(2), 216-238.

[3]. Kumar S., Wu X., Fu Q., Ho J.W.C., Kanhere P.D.K., Li L., et al., Development of durable self cleaning coating using organic-inorganic hybrid sol-gel method, Appl. Surf. Sci., 2015, 344, 205-212.

[4]. Ragesh P., Ganesh V.A., Nair S.V., Nair A.S., A review on ‘self cleaning and multifunctional materials’, J. Mater. Chem. A., 2014, 2, 14773-14797.

[5]. Gobara M., Effect of TiO$_2$/SiO$_2$ reinforced nanoparticles on the mechanical properties of green hybrid coating, Int. Lett.Chem. Phy.Astron., 2015, 47, 56-66.
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[6]. Li J., Zhang Y., Ma K., Pan D., Li C., Yang G., et al., Microstructure and transparent super-hydrophobic performance of vacuum cold-sprayed Al$_2$O$_3$ and SiO$_2$ aerogel composite coating, J. Therm. Spray Tech., 2018, 27(3), 471-482.

[7]. Nimitttrakoolchai O., Supothina S., Deposition of transparent, hydrophobic polydimethylsiloxane-nanocrystalline TiO$_2$ hybrid films on glass substrate, Songklanakarin J. Sci. Technol., 2010, 3(2), 157-162.

[8]. Chakradhar R.P., Dinesh K.V., Water-repellent coatings prepared by modification of ZnO nanoparticles, Spectrochim. Acta A Mol Biomol. Spectrosc., 2012, 94, 352-356.

[9]. Widati A.A., Nuryono N., Kartini I., Martino N.D., Silica-methyltrimethoxysilane based hydrophobic coatings on glass substrate, J Chem. Technol. Metall., 2017, 52, 1123-1128.

[10]. Kumar S., Wu X., Fu Q., Ho I.C., Kanhere P.D.K., Li L., et al., Development of durable self-cleaning coating using organic-inorganic hybrid sol-gel method, Appl. Surf. Sci., 2015, 344, 205-212.

[11]. Karunakaran R.G., Lu C., Zhang Z., Yang S., Highly transparent superhydrophobic surfaces from the coassembly of nanoparticles (≤100 nm), Langmuir, 2011, 27, 4594-4602.

[12]. Latthe S.S., Liu S., Terashima C., Nakata K., Fujishima A., Transparent, adherent, and photocatalytic SiO$_2$-TiO$_2$ coatings on polycarbonate for self-cleaning applications, 2014, 4, 497-507.

[13]. Kapridaki C., Maravelaki-Kalaitzaki P., TiO$_2$-SiO$_2$-PDMS nanocomposite hydrophobic coating with self-cleaning properties for marble protection, Prog. Org. Coat., 2013, 76(2-3), 400-410.

[14]. Wu K.R., Wang J.J., Liu W.C., Chen Z.S., Wu J.K., Deposition of graded TiO$_2$ films featured both hydrophobic and photoinduced hydrophilic properties, Appl. Surf. Sci., 2006, 252, 5829-5838.

[15]. Huang J., Lin Y., Lu L., Li L., The photocatalytic properties of amorphous TiO$_2$ composite films deposited by magnetron sputtering, Res. Chem. Intermed., 2012, 38, 487-498.

[16]. Ramírez-Garcia, R E., González-Rodríguez J.A., Arroyo-Ortega M., Pérez-García S.A., Licea-Jiménez L., Engineered TiO$_2$ and SiO$_2$-TiO$_2$ films on silica coated glass for increased thin film durability under abrasive conditions, Int. J. Appl. Ceram. Technol., 2016, 1-11.

[17]. Singh D., Kumar R., Kumar A. Rai K.N., Synthesis and characterization of rice husk silica, silica-carbon composite and H$_3$PO$_4$ activated silica, Ceramica, 2008, 54, 203-2127.

[18]. Wenzel R.N., Resistance of solid surfaces to wetting by water, Ind. Eng. Chem., 1936, 28, 988-994.

[19]. Kim K.D, Kim H.T. Comparison of the effect of reaction parameters on particle size in the formation of SiO$_2$, TiO$_2$, and ZrO$_2$ nanoparticles. Mater. Lett., 2003, 3211-3216.

[20]. Plotnikov E.N., Stolyarova V.L., Bond energies in glass forming oxide systems : calculated and experimental data, Phys. Chem. Glasses, 2005, 46(2), 187-189.

[21]. Widati A.A., Nuryono N., Kartini I., Water repellent glass coated with SiO$_2$-TiO$_2$-methyltrimethoxysilane through sol-gel coating, AIMS Mater. Sci, 2019, 6(1), 10-24.