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The Synthesis of a Superhydrophobic and Thermal Stable Silica Coating via Sol-Gel Process

Karmele Vidal, Estíbaliz Gómez, Amaia Martínez Goitandia, Adrián Angulo-Ibáñez and Estíbaliz Aranzabe *

IK4-Tekniker, Surface Chemistry and Nanotechnology Unit, Calle Iñaki Goenaga 5, 20600 Gipuzkoa, Spain; karmele.vidal@tekniker.es (K.V.); estibaliz.gomez@tekniker.es (E.G.); amaia.martinez@tekniker.es (A.M.G.); adrian.angulo@tekniker.es (A.A.-I.)

* Correspondence: estibaliz.aranzabe@tekniker.es; Tel.: +34-943206744

Received: 27 June 2019; Accepted: 26 September 2019; Published: 28 September 2019



Abstract: A super-hydrophobic surface at a high temperature (400 °C) using the sol-gel method with tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES) as precursors has been obtained. The effects of the coatings' ages, deposited times and thicknesses on the hydrophobicity of the silica coatings have been analysed. The morphology, chemical composition, thermal degradation and hydrophobicity of the resulting surfaces have been studied by scanning electron microscopy (SEM), Fourier transfer infrared spectrometer (FT-IR), Thermogravimetry (TGA) and water contact angle (WCA) measurement. The results show that an average water contact angle of 149° after been cured at 400 °C for a coating aged for 5 days, and four deposition cycles using a dipping rate of 1000 mm/min was achieved.

Keywords: superhydrophobic surface; sol-gel; silica coating; temperature stability

1. Introduction

The phenomenon of superhydrophobicity, also known as the “Lotus Effect” in a material, occurs when water droplets roll easily on its surface with a slip angle of less than 10° giving rise to a water contact angle (WCA) higher than 150°. This phenomenon occurs due to the reduction of the water contact area, which leads to a reduction of adhesion [1,2].

Several works have been reporting about the preparation of superhydrophobic surfaces and their potential applications (anti-corrosion, self-cleaning, anticontamination, non-stick wares, etc.) [3,4].

Artificial superhydrophobic surfaces can be achieved by: (i) creating a rough surface on a hydrophobic material or (ii) chemically modifying a rough surface with a hydrophobic coating [5]. For this, different methods have been used: lithographing, templating method, phase separation, plasma treatment, sputter coating, solution-immersion process, chemical vapor deposition, physical etching and sol-gel reaction, hydrothermal synthesis, and others [6,7].

Silica coatings prepared with TEOS are inherently hydrophilic due to the presence of surface active hydroxyl (–OH) end groups. However, the hydrophobic behaviour can be improved by replacing the –OH group with the hydrophobic organic functional group, O–Si–(CH₃)₃. For this purpose, the most employed precursors in the sol-gel synthetic route are methyltrimethoxysilane (MTMS), methyltriethoxysilane (MTES) and vinyltriethoxysilane (VTES) [8–19]. Guilong et al., fabricated a superhydrophobic SiO₂ film with TEOS and MTES as precursors by the sol-gel method, and then, the SiO₂ particles obtained were modified by dodecyltrimethoxysilane (DTMS) [20].

For these superhydrophobic coatings to be implemented to industry, they must be easily fabricated and durable during services. However, many superhydrophobic coating materials deteriorate at

relatively low temperatures, 300–350 °C, due to raw materials' low thermal stabilities, giving rise to a surface morphology or chemistry damage of the coatings surface [21–23].

The sol-gel synthetic route is appropriate to obtain superhydrophobic coatings with good properties and good thermal resistance [24–26]. Traditionally, most of these thin films have been prepared by sol-gel method because of it is a simple process and allows one to change the parameters to obtain the desired products [5].

On the other hand, generally, the studies of superhydrophobic surfaces are focused on rigid solid substrates, such as silicon wafers, glass slides and metal surfaces. These materials must be selected considering both the treatment processes and their final application [3,27].

In this work, a porous superhydrophobic and-stable-at-high-temperatures (~400 °C) silica film was synthesized via sol-gel method. To enhance the water repellence of the silica films, methyltriethoxysilane (MTES) was used as a hydrophobic reagent in the sol-gel process. The paper describes the influence of the aging period, dipping times and the thickness of coatings on the superhydrophobic, morphological, chemical and thermal stability properties of the silica films obtained using glass substrates. This investigation provides the optimal parameters to achieve, via sol-gel, superhydrophobic coatings suitable for high-temperature applications.

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), methyltriethoxysilane (MTES, 98%) and ammonium hydroxide solution (ACS reagent, 28% to 30% NH_3 basis) were purchased from Sigma Aldrich (Saint Louis, MO, USA). Absolute ethanol (EtOH , 99.5%) and distilled water (H_2O) from Scharlab (Scharlab, S.L., Barcelona, Spain) were used in this work.

2.2. Preparation of Superhydrophobic Coating

Silica particles were prepared through a process based on the Stöber method [28], using tetraethoxysilane (TEOS) as a starting material. TEOS was dissolved in ethanol. Separately, ammonia, water and ethanol were mixed. Then, two solutions were mixed, and heated at 60 °C under stirring for 90 min. Then, a solution of MTES and EtOH was added to the sol and the mixture was continuously stirred for 19 h at 60 °C with a condensation reflux device. The molar ratio of MTES:TEOS: H_2O : EtOH : NH_4OH was 0.16:0.24:4:14:1. The prepared white silica sol was kept for 2, 5 and 9 days under room temperature.

Glass substrates were vertically dipped using an immersion-extraction velocity of 200 mm/min into test beakers containing the sol solution for 0 and 5 min, repeating the procedure 1 and 4 times with a thermal treatment at 150 °C for 30 min after each process. Adding to this, the dipping velocity was also varied for the sol aged for 5 days; velocities of 500 and 1000 mm/min were used. Finally, the substrates obtained were annealed at 400 °C for 2 h. The thermal stability was confirmed by putting the SiO_2 coating samples in an oven at different temperatures (400, 450, 500 and 550 °C) for 2 h, and then, testing the water contact angles for each coating. In addition, the dipping rate was analysed in order to study the effect of the thickness on the hydrophobic properties.

2.3. Characterization Techniques

Fourier transform infrared spectroscopy (FTIR, FT/IR-4700LE, JASCO International Co., Ltd., Tokyo, Japan) was used in order to obtain information about the carbon–hydrogen, silica–oxygen and functional group bonds. FTIR was operated in the 4000–400 cm^{-1} range and the average of three scans for each sample was taken for the peak identification.

A goniometer (SURFTENS Universal, OEG GmbH, Frankfurt, Germany) was used to observe the hydrophobicity of the silica coatings by measuring the contact angle (θ) and sliding angle (α) of a water droplet of 5 μL placed on the surface of the coated glass substrates. The sliding angle was

measured by tilting the stage table of the goniometer. The average value of five measurements, made at different positions of the coating surface was adopted as the value of WCA.

Morphologies of the samples were observed using a scanning electron microscope Ultra Gemini-II de Carl Zeiss SMT (Thornwood, NY, USA). The thickness of the coatings was determined with a profilometer (Dektak 8, Karlsruhe, Germany).

Thermal degradation of coating material was carried out with thermal gravimetric analysis (TGA) in a TGA/DSC1 equipment from Mettler Toledo (GIEßen, Hesse, Germany) from room temperature up to 1000 °C at 10 °C/min.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy

The effect of the addition of MTES and the evolution of the condensation of the sol were studied by FTIR. The Figure 1 shows the FTIR spectra of sol before and after the addition of MTES (incorporation of MTES to the reaction for 2, 5 and 9 days). A broad intense band is detected between 3000 and 3800 cm^{-1} , with a peak at 3323 cm^{-1} , due to O–H vibrations and a weak deformation vibrations at 1649 cm^{-1} . The 3323 cm^{-1} and Si–OH (953 cm^{-1}) bands decrease gradually during condensation reaction. In addition, two sharp bands at 2971 cm^{-1} and 1272 cm^{-1} corresponding to the absorption vibration of C–H in methyl and Si–CH₃ groups, respectively, indicate the substitution of hydroxyl groups for methyl groups when MTES is added to the reaction. C–H bonds were detected at 2928 cm^{-1} in a symmetric stretching mode and at 2971 cm^{-1} in an asymmetric stretching mode. The presence of the methyl groups is beneficial for the hydrophobic properties.

The Si–O–Si symmetric stretching vibration mode observed at 1048 cm^{-1} and the asymmetric mode at 1084 cm^{-1} indicate the hybrid nature of the material, which is in good agreement with other works [20,29]. When MTES is incorporated to the reaction, the bands increase due to the increase of Si–OH groups, and therefore, more Si–O–Si groups are formed during the condensation steps.

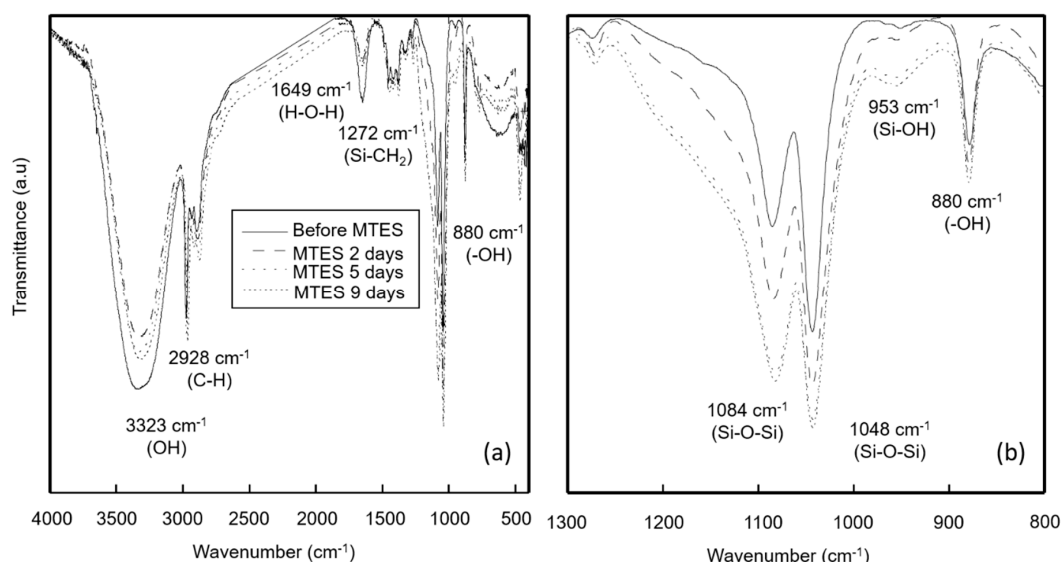


Figure 1. FTIR spectra of the sol before and after (2, 5 and 9 days) the addition of MTES.

A band of medium intensity at 953 cm^{-1} corresponds to Si–OH groups. However, this band is not univocally attributed to Si–OH modes. It can be overlapped with the Si–O of unreacted alkoxy groups from TEOS and MTES [30]. A weak Si–OH peak before MTES addition is observable, due to a complete hydrolysis and condensation of TEOS. After two days of MTES incorporation, the peak is sharper as a result of the presence of hydroxyl groups formed during the hydrolysis step, decreasing with time because of the condensation reaction and the transformation of these groups into Si–O–Si species.

The FTIR spectrum of the optimized hydrophobic SiO₂ coatings prepared by TEOS and MTES as precursors and aged for 5 days and cured at 400 °C is shown in Figure 2.

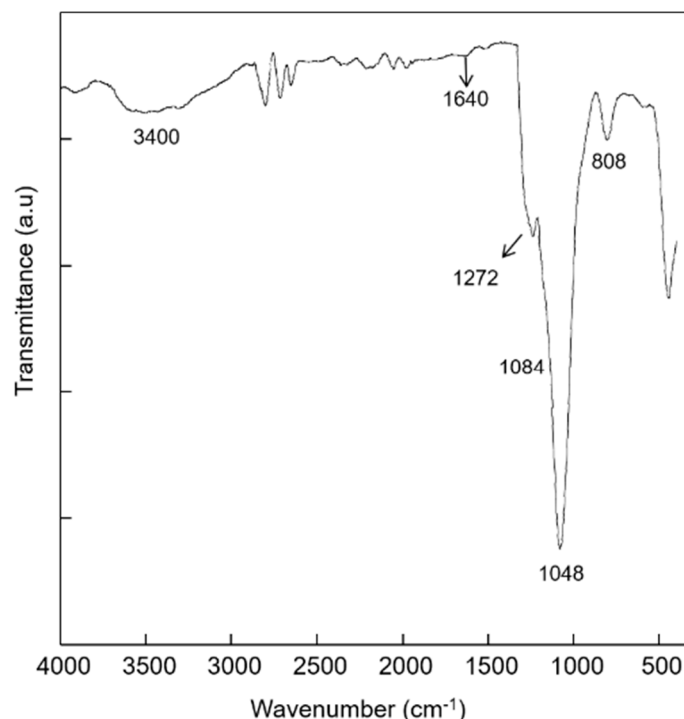


Figure 2. FTIR spectra of the SiO₂ particles for coating aged for 5 days.

As in the FTIR of the sol, the broad absorption bands at around 1649 and 3323 cm^{−1} indicate the presence of –OH groups. The stretching vibrations of the Si–O–Si bonds are represented by the 1048 cm^{−1} and 1084 cm^{−1} absorption bands. The presence of this peak confirms the formation of a network structure inside the coating. The peak at 1272 cm^{−1} indicates Si–CH₃ bonds due to the presence of MTES in the reaction. Finally, the absorption peaks observed at around 808 cm^{−1}, correspond to Si–C bonds. Si–C absorption peak indicates the presence of the CH₃SiO₃ groups on the surface of silica particles linked by condensation reaction of Si–OH, resulting in higher hydrophobicity [13].

3.2. Morphological Study

The representative images of the coatings deposited on glass substrates and treated at 150 °C and 400 °C are shown in Figure 3.

As expected, by comparing images for three cases, when the silica solution is deposited four times, a darker layer of particles is formed. It can be seen how the layer obtained for the case of the sol aged for 9 days, is more heterogeneous, showing zones with a higher concentration of silica particles because the degree of agglomeration of these particles increases with aging period [31–33].

Using ammonia, during the hydrolysis and condensation of TEOS, silica nanoparticles (with several Si–OH) progressively generate. According with other works [34,35], the hydrolysed MTES monomers cross-condense with Si–OH groups on the surface of silica particles, and then, link them into the porous network.

The Figures 4 and 5 show the SEM micrographs of the silica coatings with different dip-times and aging periods, respectively, all of them having been thermally treated at 400 °C. These reveal the size and shape of the prepared spherical silica particles, with the size of approximately 530 nm being uniform.

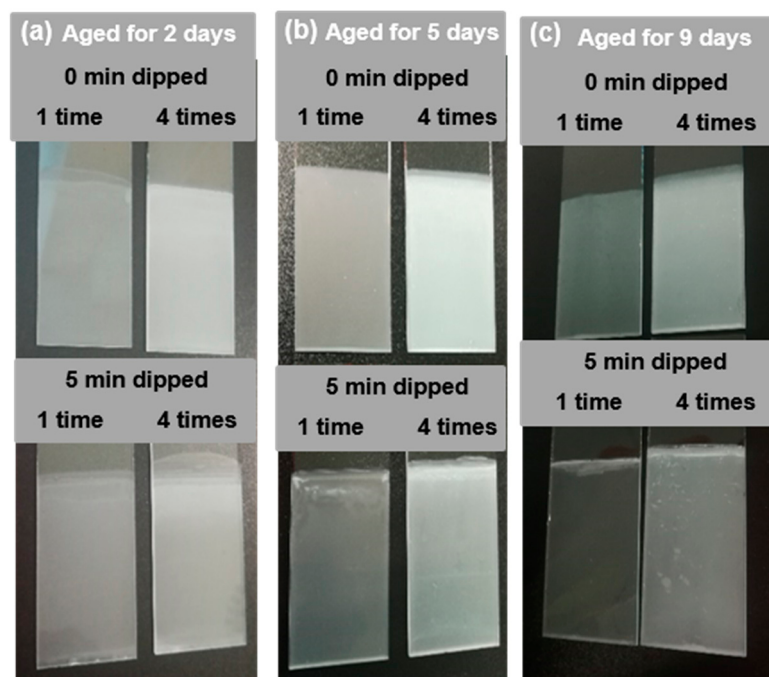


Figure 3. Representative images of the coatings aged for (a) 2, (b) 5 and (c) 9 days.

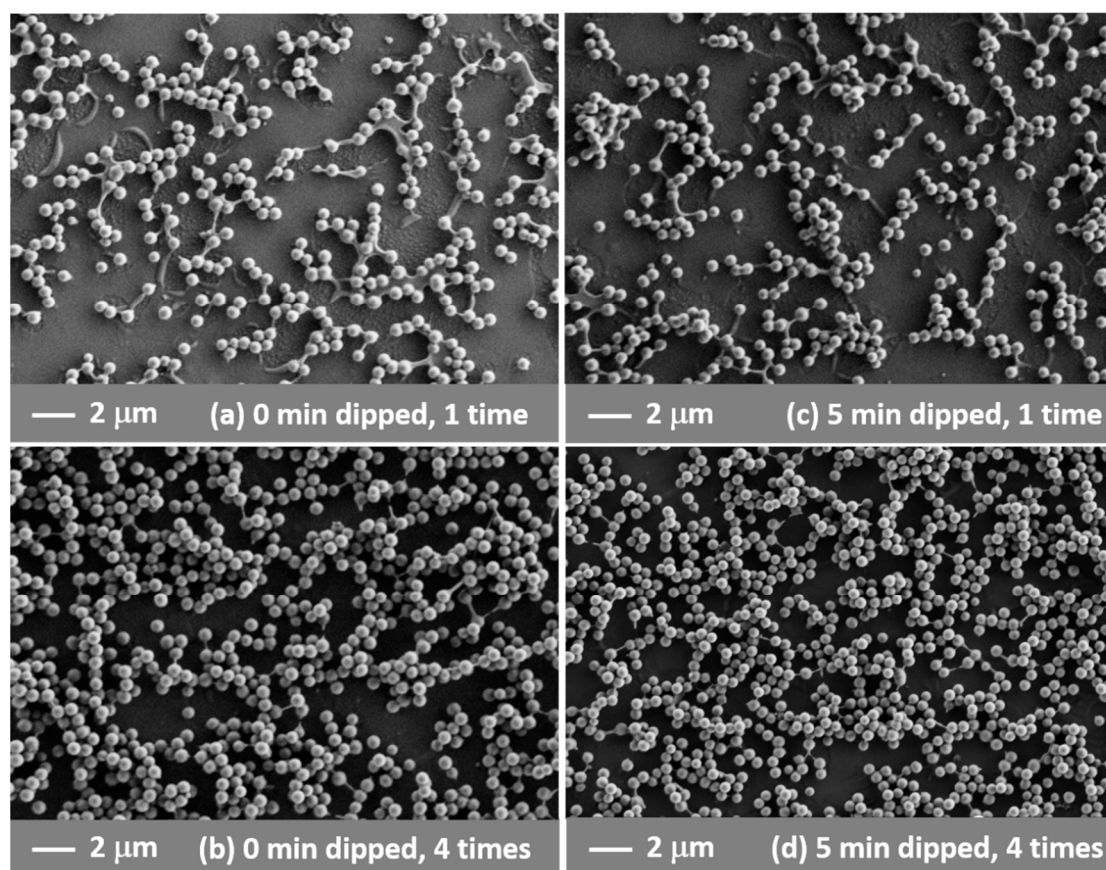


Figure 4. SEM images of hydrophobic silica coatings aged for 5 days, varying the dipping conditions: (a) dipped for 0 min once, (b) dipped for 0 min four times, (c) dipped for 5 min once and (d) dipped for 5 min four times.

As can be seen, the surface morphologies keep nearly the same after being immersed for 0 and 5 min. As the immersion times increase, however, the particle concentration increases, enhancing the surface roughness of the silica coating. In addition, after the aging, the SiO_2 particles begin to assemble, forming a nano-micro-binary structure (Figure 5) due to the condensation reaction of OH^- group between SiO_2 particles [20].

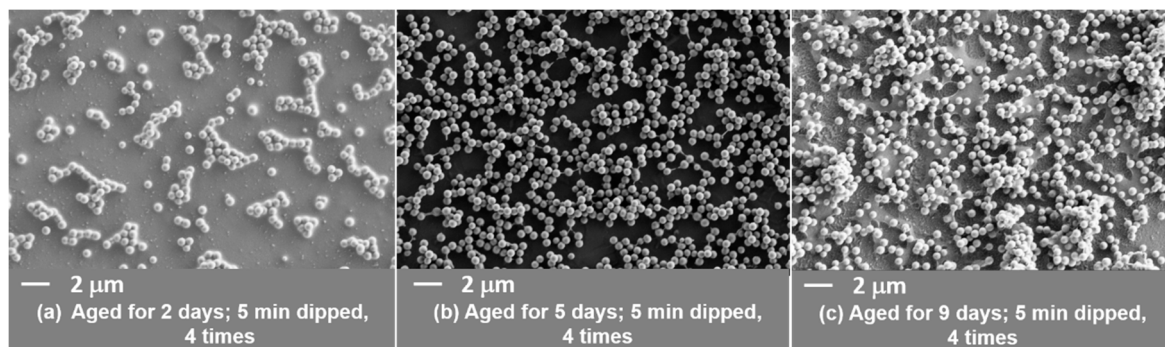


Figure 5. SEM images of hydrophobic silica coatings dipped for 5 min four times and aged for (a) 2 days, (b) 5 days and (c) 9 days.

However, the layer obtained by aging the sol for 9 days shows a surface more heterogeneous (Figure 3), being a handicap for its industrial application. Then, in order to improve the hydrophobic properties of the homogeneous obtained coatings, the coating aged for 5 days and with four immersions for 5 min was selected to study the effect of parameters such as dipping rate (and then, the thickness) on the hydrophobic properties.

Therefore, for this case, the glass substrates were dipped using faster dipping rates (500 and 1000 mm/min) for 5 min (four times). As is well known, the coating thickness increases with the coating cycle number and with the substrate velocity. Values of 520, 605–1150 and 774–1105 nm were obtained for the measured thickness of the coating using dipping rates of 200, 500 and 1000 mm/min, respectively. Therefore, in agreement with literature, the average coating thickness increases with increasing dipping rate [36–38].

The SEM images obtained for these coatings are shown in Figure 6. Using dipping rates higher than 200, in this case 500 and 1000 mm/min, as it is observed for more aging days, there is a condensation reaction of OH^- group between SiO_2 particles giving rise to a nano-micro-binary structure. Nevertheless, the coating shows a homogeneous distribution of particles (Figure 7).

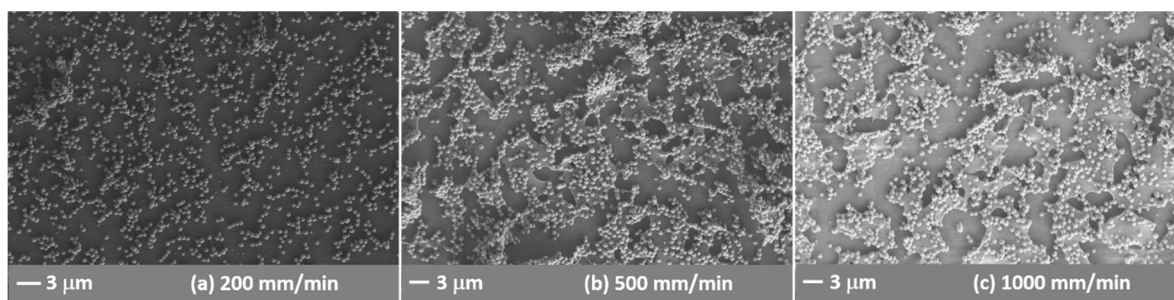


Figure 6. SEM images of hydrophobic silica coatings dipped for 5 min four times, and aged for 5 days with a dipping rate of (a) 200 mm/min, (b) 500 mm/min and (c) 1000 mm/min.



Figure 7. Representative appearance image of the coating aged for 5 days, obtained using a dipping velocity of 1000 mm/min.

The remaining SEM images, corresponding to the samples calcined at 150 and 400, 450, 500 and 550 °C are shown in Figure 8.

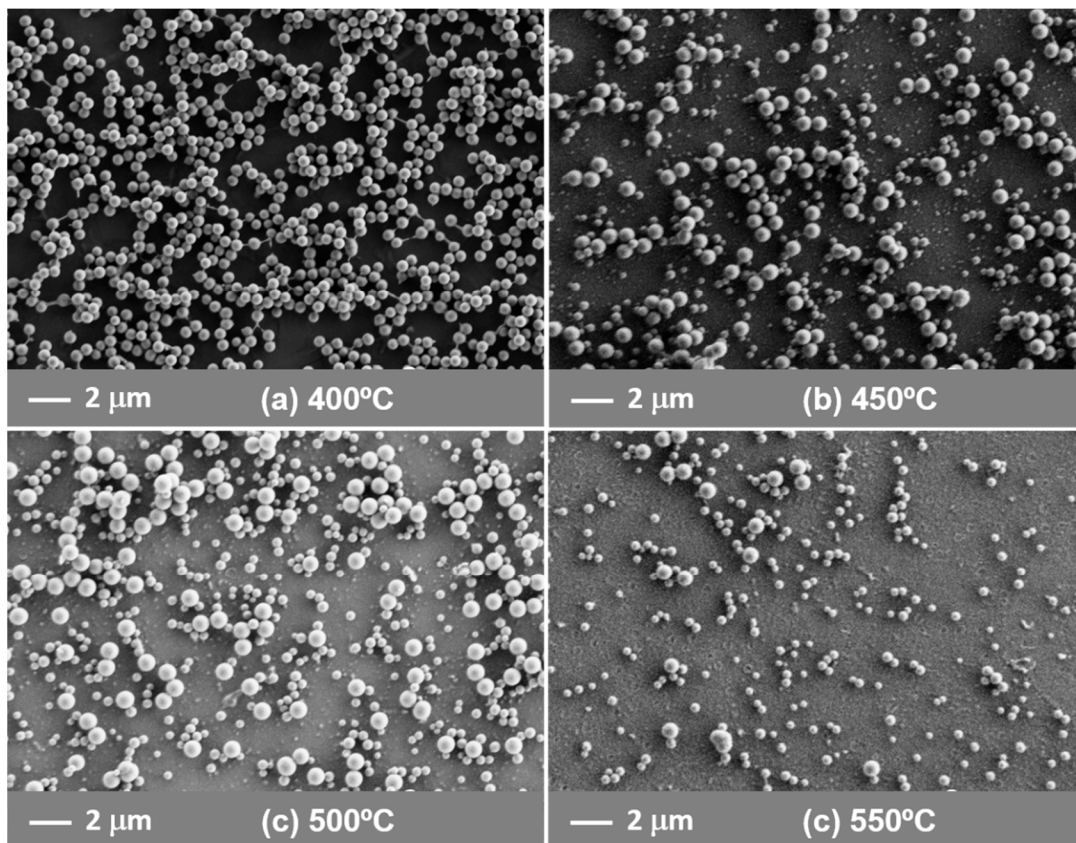


Figure 8. SEM images of silica coatings aged for 5 days and dipped for 5 min four times calcined at (a) 400, (b) 450, (c) 500 and (d) 550 °C.

The SEM images show that for calcination temperatures higher than 400 °C, the samples do not have a uniform size, with particle diameters being approximately, 220–710, 300–675 and 365–820 nm, for the samples calcined at 450, 500 and 550 °C, respectively. Then, as the temperature value of the thermal treatment increases, the size distribution is more heterogeneous. In addition, as can be observed, the particle concentration decreases slightly with the calcination temperature, which is caused by the adsorption between hydroxyl groups on the surface of SiO₂ particles [39].

3.3. Static and Sliding Water Contact Angle

The wetting behaviour of superhydrophobic surfaces depends on their chemical composition and surface microstructure.

The hydrophobic behaviour of silica coatings deposited on glass slides as a function of the duration of the dipping and the number of coatings was analysed by water contact angle (WCA). In all the cases the dipping speed was of 200 mm/min. As is well known, when a water droplet contacts a porous silica coating and spreads flat instantaneously on the surface, this coating shows a great superhydrophilic nature. The images of the static water contact angles measured for each experimental condition, are shown in Figure 9.

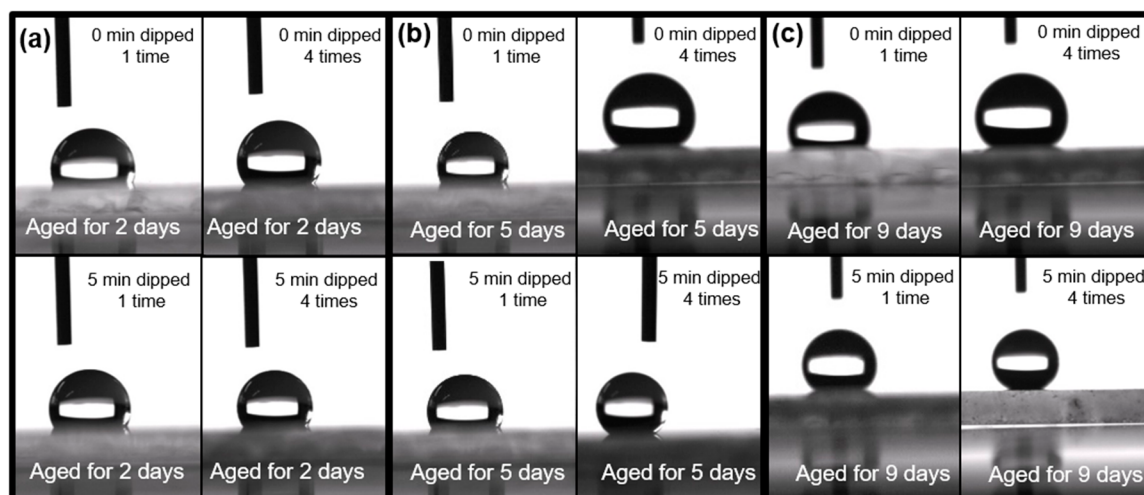


Figure 9. Water drop images on the coatings aged for (a) 2, (b) 5 and (c) 9 days.

The Table 1 lists the values of the static water contact angles and sliding angles (SA) obtained for all samples as a function of the duration of the dipping and the number of coatings.

Table 1. Values of water contact angle (WCA) and sliding angle (SA) obtained for samples as a function of the duration of the dipping and the number of coatings.

	Aged for 2 Days				Aged for 5 Days				Aged for 9 Days			
	0 min		5 min		0 min		5 min		0 min		5 min	
	WCA (°)	SA (°)	WCA (°)	SA (°)	WCA (°)	SA (°)	WCA (°)	SA (°)	WCA (°)	SA (°)	WCA (°)	SA (°)
1 time	108 ± 1	20 ± 1	115 ± 1	40 ± 1	116 ± 1	65 ± 2	117 ± 2	58 ± 2	118 ± 1	33 ± 1	120 ± 1	28 ± 1
4 times	123 ± 1	53 ± 1	121 ± 1	51 ± 2	124 ± 1	41 ± 2	132 ± 1	35 ± 1	137 ± 1	31 ± 1	149 ± 1	<5

As can be observed, the coatings obtained by dipping one time exhibit smaller values of contact angle than the obtained dipping four times for the three cases, showing that the number of times that the substrate is immersed has an important influence on the hydrophobic surface properties of the material under study. This behaviour can be explained due to the increase of the particle concentration with the immersion times (Figure 5) that enhances the surface roughness. Adding to this, an increase of the contact angle values was obtained by increasing the time during the substrate is dipped, especially for the samples aged for 5 and 9 days with four immersions, even though SEM did not show a significant difference of the particle concentration on the substrate surface (Figure 4). These results are in good agreement with the results obtained by H. Yang et al. [33].

In this study, the superhydrophobicity was reached when the number of assemblies increased up to four cycles, showing a water contact angle of $149^\circ \pm 1^\circ$ for the sol aged for 9 days and a sliding angle of nearly $<5^\circ$. This could be attributed to the increase of surface roughness [40]. The deposition

of the aggregated silica microspheres on the glass substrates provides a rough surface, and the grooves between particles and surface roughness increases with the number of deposition cycles. These rough structures of the films allow them to trap enough air in the grooves between particles, giving rise to a repellence of water.

On the other hand, when the coating thickness increases, the surface roughness and the hydrophobicity increase, but the transparency and mechanical stability decrease. In addition, as has been above mentioned, the layer obtained by aging the sol for 9 days showed a surface more heterogeneous.

Figure 10 shows the water contact angles measured for the sample aged for 5 days with four rounds of dipping using a dipping rate of 1000 mm/min (cured at 400 °C).

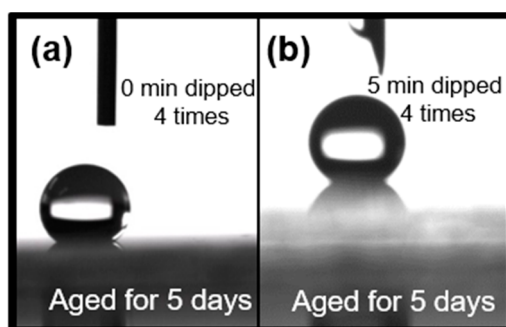


Figure 10. Water drops' images on the coatings using a dipping rate of 1000 mm/min.

The Table 2 lists the values of the water contact angles obtained for the coatings aged for 5 days and dipped for 5 min four times for the samples using different dipping rates. As is shown, using higher dipping rates, higher values of the water contact angles were obtained.

Table 2. Values of the WCA and SA obtained for the coatings aged for 5 days and dipped for 5 min times; samples used different dipping rates.

	200 mm/min		500 mm/min		1000 mm/min	
	WCA (°)	SA(°)	WCA (°)	SA(°)	WCA (°)	SA(°)
1 time	117 ± 1	58 ± 2	139 ± 1	10 ± 1	143 ± 2	<5
4 times	131 ± 1	35 ± 1	145 ± 1	<5	149 ± 1	<5

The above results suggested that the aging period, the deposition cycles, the time during the sample is dipped and the velocity used in the dip-coating process have great effects on the properties of the silica coatings that are critical for their desired application. The best results were obtained for the coating aged for 9 days and dipped for 5 min 4 times using a dipping rate of 200 mm/min (Table 1 and Figure 4c) and for the aged for 5 days and dipped for 5 min 4 times using a dipping rate of 1000 mm/min (Table 2 and Figure 5c). However, this last coating presents a superficial morphology more homogeneous.

3.4. Thermal Stability

The effect of the calcination temperature was confirmed by putting the SiO₂ superhydrophobic coating sample in an oven at 400, 450, 500 and 550 °C for 2 h, and then, it was tested by measuring the WCAs. The coatings were obtained by using a dipping speed of 1000 mm/min for those aged for 5 days and dipped four times.

The test results are shown in Figure 11, showing that above 400 °C the hydrophobicity decreases as coating curing temperature increases. In fact, when a calcination temperature of 550 °C is applied, the WCA decreased to nearly 0°, indicating that the wetting behaviour of the surface changed from

superhydrophobicity to superhydrophilicity. This phenomenon, shown at relatively low temperatures ($<600\text{ }^{\circ}\text{C}$) in other works about siloxane surfaces, was analysed in detail by Karapanagiotis et al., by studying the effects of thermal treatment temperature and time [41].

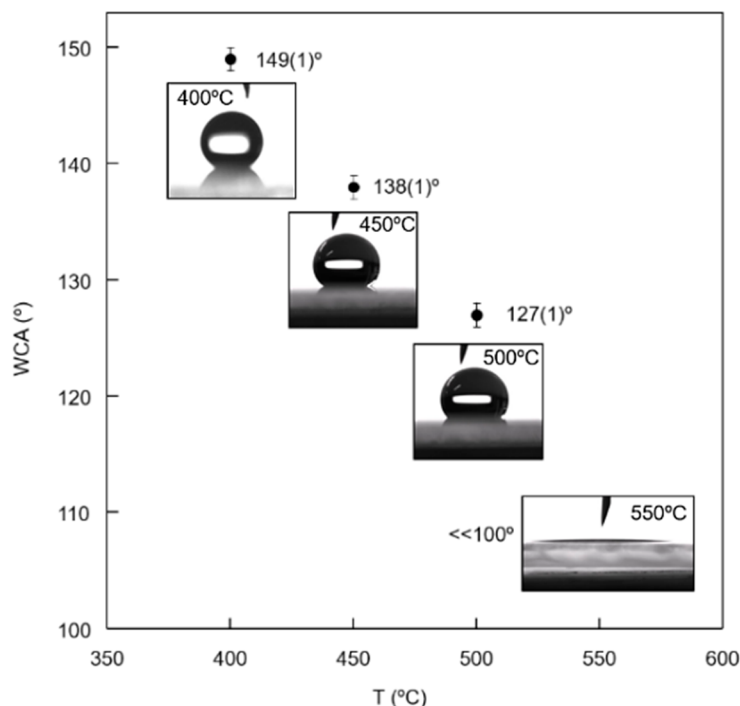


Figure 11. Water contact angle of the coating aged for 5 days and dipped four times at different curing temperatures.

That phenomenon takes place because the $-\text{CH}_3$ groups on the surface of SiO_2 particles are replaced by $-\text{OH}$ groups due to the decomposition of $-\text{CH}_3$ groups after calcining at a high temperature [34,41–43].

3.5. Thermal Degradation of the Superhydrophobic Coating

The thermogravimetric analysis (TGA) curves for the coatings aged for 5 days and cured at different temperatures are shown in Figure 12. The TGA curves had a main weight loss below $200\text{ }^{\circ}\text{C}$ due to the physically adsorbed water molecules of the environmental humidity. After that, in the coating materials cured at $400\text{ }^{\circ}\text{C}$ and $450\text{ }^{\circ}\text{C}$, the weight decreased gradually up to $750\text{ }^{\circ}\text{C}$, by means of the degradation of organic groups. For the coatings cured at $500\text{ }^{\circ}\text{C}$ the weight loss curve is flat up to $600\text{ }^{\circ}\text{C}$, due to the fact that methyl groups were degraded during the thermal treatment of the coating. The total weight loss for the coatings cured at $400\text{ }^{\circ}\text{C}$ and $450\text{ }^{\circ}\text{C}$ is at about 8%, and for the coatings cured at $500\text{ }^{\circ}\text{C}$ and $550\text{ }^{\circ}\text{C}$, is less than 5%, which indicates that they are thermally stable and inorganic.

For the sample cured at $400\text{ }^{\circ}\text{C}$, the weight-loss phenomena with respect to the increase in the temperature up to $500\text{ }^{\circ}\text{C}$ corresponds to the degradation of $-\text{CH}_3$, and the SiO_2 coating finally develops a superhydrophilic nature. This behaviour has been previously observed, showing a WCA near to 0° . As can be observed, as the curing temperature increases, the silica products show less loss of mass because they have already lost mass during the curing heating.

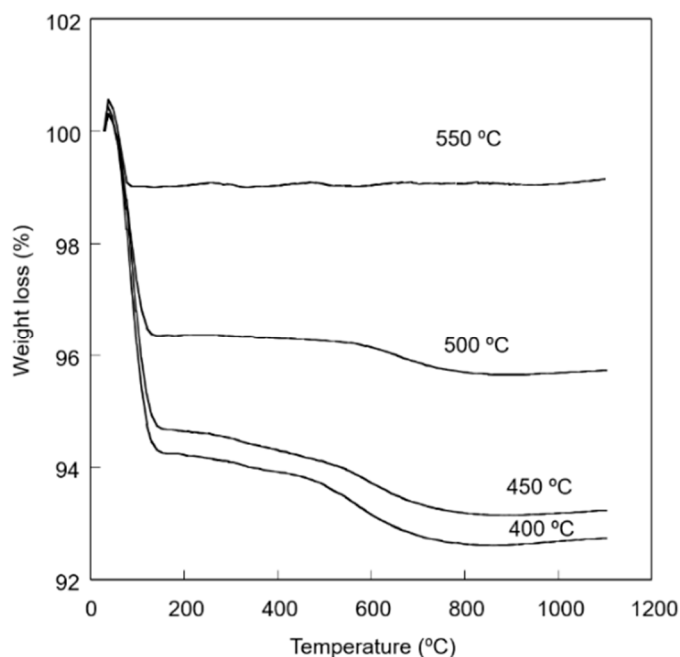


Figure 12. Thermogravimetric analysis (TGA) curves of the SiO₂ particles for a coating aged for 5 days and cured at 400, 450, 500 and 550 °C.

4. Conclusions

The superhydrophobic SiO₂ surface was successfully prepared with TEOS and MTES as precursors by a sol-gel method. The effect of the number of sol-gel coatings, the aging period and the dipping rate on the hydrophobic properties and thermal stability were analysed. Homogeneous silica coatings with static water contact angles as high as 149° were obtained for the sample aged for 5 days, dipped four times with a dipping rate of 1000 mm/min and cured at 400 °C. These thermally stable superhydrophobic coatings are potentially suitable for various industrial applications.

Author Contributions: Conceptualization, K.V., E.G., A.M.G., A.A.-I. and E.A.; methodology, K.V., E.G., A.M.G., A.A.-I. and E.A.; writing—review and editing, K.V., E.G., A.M.G., A.A.-I. and E.A.; supervision, E.G., A.M.G. and E.A.

Funding: This research received no external funding.

Acknowledgments: This work under “Multifunctional surfaces at the frontier of knowledge” project is supported by the Basque Government Industry Department under the ELKARTEK Programme.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Shahabadi, S.M.S.; Brant, J.A. Bio-inspired superhydrophobic and superoleophilic nanofibrous membranes for non-aqueous solvent and oil separation from water. *Sep. Purif. Technol.* **2019**, *210*, 587–599. [[CrossRef](#)]
- Kim, W.; Kim, D.; Park, S.; Lee, D.; Hyun, H.; Kim, J. Engineering lotus leaf-inspired micro- and nanostructures for the manipulation of functional engineering. *J. Ind. Eng. Chem.* **2018**, *61*, 39–52. [[CrossRef](#)]
- Xue, C.-H.; Jia, S.-T.; Zhang, J.; Ma, J.-Z. Large-area fabrication of superhydrophobic surfaces for practical applications: An overview. *Sci. Technol. Adv. Mater.* **2010**, *11*, 033002–033017. [[CrossRef](#)] [[PubMed](#)]
- Ganbavli, V.V.; Bangi, U.K.H.; Latthe, S.S.; Mahadik, S.A.; Rao, A.V. Self-cleaning silica coatings on glass by single step sol-gel route. *Surf. Coat. Technol.* **2011**, *205*, 53338–55344. [[CrossRef](#)]
- Mozumder, M.S.; Mourad, A.-H.I.; Pervez, H.; Surkatti, R. Recent developments in multifunctional coatings for solar panel applications: A review. *Sol. Energy Mater. Sol. Cells* **2019**, *189*, 75–102. [[CrossRef](#)]
- Yang, M.; Liu, W.; Jiang, C.; He, S.; Xie, Y.; Wang, Z. Fabrication of superhydrophobic cotton fabric with fluorinated TiO₂ sol by a green and one-step sol-gel process. *Carbohydr. Polym.* **2018**, *197*, 75–82. [[CrossRef](#)]
- Ma, M.; Hill, R.M. Superhydrophobic surfaces. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193–202. [[CrossRef](#)]

8. Fihri, A.; Bovero, E.; Al-Shahrani, A.; Al-Ghamdi, A.; Alabedi, G. Recent progress in superhydrophobic coatings used for steel protection: A review. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *520*, 378–390. [[CrossRef](#)]
9. Seraji, M.M.; Sameri, G.; Davarparah, J.; Bahramian, A.R. The effect of high temperature sol-gel polymerization parameters on the microstructure and properties of hydrophobic phenol-formaldehyde/silica hybrid aerogels. *J. Colloid Interface Sci.* **2017**, *493*, 103–110. [[CrossRef](#)]
10. Cui, S.; Liu, Y.; Fan, M.-H.; Coopere, A.T.; Liu, X.-Y.; Han, G.-F.; Shen, X.-D. Temperature dependent microstructure of MTES modified hydrophobic silica aerogels. *Mater. Lett.* **2011**, *65*, 606–609. [[CrossRef](#)]
11. Izarra, I.; Cubillo, J.; Serrano, A.; Rodríguez, J.F.; Carmona, M. A hydrophobic release agent containing SiO₂-CH₃ submicron-sized particles for water proofing mortar structures. *Constr. Build. Mater.* **2019**, *199*, 30–39. [[CrossRef](#)]
12. Sun, Z.; Liu, B.; Huang, S.; Wu, J.; Zhang, Q. Facile fabrication of superhydrophobic coating based on polysiloxane emulsion. *Progr. Org. Coat.* **2017**, *102*, 131–137. [[CrossRef](#)]
13. Latthea, S.S.; Imai, H.; Ganesan, V.; Rao, A.V. Porous superhydrophobic silica films by sol-gel process. *Microporous Mesoporous Mater.* **2010**, *130*, 115–121. [[CrossRef](#)]
14. Sheen, Y.-C.; Chang, W.-H.; Chen, W.-C.; Chang, Y.-H.; Huang, Y.-C.; Chang, F.-C. Non-fluorinated superamphiphobic surfaces through sol-gel processing of methyltriethoxysilane and tetraethoxysilane. *Mater. Chem. Phys.* **2009**, *114*, 63–68. [[CrossRef](#)]
15. Latthe, S.S.; Imai, H.; Ganesan, V.; Rao, A.V. Superhydrophobic silica films by sol-gel co-precursor method. *Appl. Surf. Sci.* **2009**, *256*, 217–222. [[CrossRef](#)]
16. Mahadik, S.A.; Kavale, M.S.; Mukherjee, S.K.; Rao, A.V. Transparent Superhydrophobic silica coatings on glass by sol-gel method. *Appl. Surf. Sci.* **2010**, *257*, 333–339. [[CrossRef](#)]
17. Shao, Z.; Luo, F.; Cheng, X.; Zhang, Y. Superhydrophobic sodium silicate based silica aerogel prepared by ambient pressure drying. *Mater. Chem. Phys.* **2010**, *257*, 333–339. [[CrossRef](#)]
18. Zhao, A.; Li, Y.; Li, B.; Hu, T.; Yang, Y.; Li, L.; Zhang, J. Environmentally benign and durable superhydrophobic coatings based on SiO₂ nanoparticles and silanes. *J. Colloid Interface Sci.* **2019**, *542*, 8–14. [[CrossRef](#)]
19. Zheng, X.; Fu, S. Reconstructing micro/nano hierarchical structures particle with nanocellulose for superhydrophobic coatings. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *560*, 171–179. [[CrossRef](#)]
20. Guilong, X.; Pihui, P.; Ermei, H.; Xiufang, W.; Dafeng, Z.; Zhuoru, Y. Preparation and characterization of superhydrophobic/superoleophilic silica film. *J. Chim. Ceram. Soc.* **2011**, *39*, 854–858. [[CrossRef](#)]
21. Jiang, Z.; Fang, S.; Wang, C.; Wang, H.; Ji, C. Durable polyorganosiloxane superhydrophobic films with a hierarchical structure by sol-gel and heat treatment method. *Appl. Surf. Sci.* **2016**, *390*, 993–10001. [[CrossRef](#)]
22. Zhang, Y.; Dong, B.; Wang, S.; Zhauo, L.; Wan, L.; Wang, E. Mechanically robust, thermally stable, highly transparent superhydrophobic coating with low-temperature sol-gel process. *RSC adv.* **2017**, *7*, 47357–47365. [[CrossRef](#)]
23. Rao, A.V.; Latthe, S.S.; Mahadik, S.A.; Kappenstein, C. Mechanically stable and corrosion resistant superhydrophobic sol-gel coatings on copper substrate. *Appl. Surf. Sci.* **2011**, *257*, 5442–5776. [[CrossRef](#)]
24. Xu, J.; Liu, Y.; Du, W.; Lei, W.; Si, X.; Zhou, T.; Lin, J.; Peng, L. Superhydrophobic silica antireflective coatings with high transmittance via one-step sol-gel process. *Thin Solid Films* **2017**, *631*, 193–199. [[CrossRef](#)]
25. Nguyen-Tria, P.; Tran, H.N.; Plamondon, C.O.; Tuduri, L.; Vo, D.-V.N.; Nanda, S.; Mishra, A.; Chao, H.-P.; Bajpai, A.K. Recent progress in the preparation, properties and applications of superhydrophobic nano-based coatings and surfaces: A review. *Prog. Org. Coat.* **2019**, *132*, 235–256. [[CrossRef](#)]
26. Pantoja, M.; Velasco, F.; Abenojar, J.; Martinez, M.A. Development of superhydrophobic coatings on AISI 304 austenitic stainless steel with different surface pretreatments. *Thin Solid Films* **2019**, *671*, 22–30. [[CrossRef](#)]
27. Jeevahan, J.; Chandrasekaran, M.; Joseph, G.B.; Durairaj, R.B.; Mageshwaran, G. Superhydrophobic surfaces: A review on fundamentals, applications, and challenges. *J. Coat. Technol. Res.* **2018**, *15*, 231–250. [[CrossRef](#)]
28. Stöber, W.; Fink, A.; Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* **1968**, *26*, 62–69. [[CrossRef](#)]
29. Criado, M.; Sobrados, I.; Sanz, J. Polymerization of hybrid organic-inorganic materials from several silicon compounds followed by TGA/DTA, FTIR and NMR techniques. *Progr. Org. Coat.* **2014**, *77*, 880–891. [[CrossRef](#)]
30. Montejo, M.; Partal Ureña, F.; Márquez, F.; Ignatyev, I.S.; López González, J.J. Vibrational spectrum of methoxytrimethylsilane. *J. Mol. Struct.* **2005**, *744–747*, 331–338. [[CrossRef](#)]

31. Innocenzi, P. Infrared spectroscopy of sol-gel derived silica-based films: A spectra-microstructure overview. *J. Non-Cryst. Solids* **2003**, *316*, 309–319. [[CrossRef](#)]
32. Azlina, H.N.; Hasnidawani, J.N.; Norita, H.; Surip, S.N. Synthesis of SiO₂ Nanostructures Using Sol-Gel Method. *Acta Phys. Pol. A* **2016**, *129*, 842–844. [[CrossRef](#)]
33. Yang, H.; Pi, P.; Cai, Z.-Q.; Wen, X.; Wang, X.; Cheng, J.; Yang, Z.-R. Facile preparation of super-hydrophobic and super-oleophilic silica film on stainless steel mesh via sol-gel process. *Appl. Surf. Sci.* **2010**, *256*, 4095–4102. [[CrossRef](#)]
34. Zhong, M.; Zhang, Y.; Li, X.; Wu, X. Facile fabrication of durable superhydrophobic silica/epoxy resin coatings with compatible transparency and stability. *Surf. Coat. Technol.* **2018**, *347*, 191–198. [[CrossRef](#)]
35. Wen, X.-F.; Wang, K.; Pi, P.-H.; Yang, J.-X.; Cai, Z.-Q.; Zhang, L.-J.; Qian, Y.; Yang, Z.-R.; Zheng, D.-F.; Cheng, J. Organic-inorganic hybrid superhydrophobic surfaces using methyltriethoxysilane and tetraethoxysilane sol-gel derived materials in emulsion. *Appl. Surf. Sci.* **2011**, *258*, 991–998. [[CrossRef](#)]
36. Strawbridge, I.; James, P.F. The factors affecting the thickness of sol-gel derived silica coatings prepared by dipping. *J. Non-Cryst. Solids* **1986**, *86*, 381–393. [[CrossRef](#)]
37. Guglielmi, M.; Zenezini, S. The thickness of sol-gel silica coatings obtained by dipping. *J. Non-Cryst. Solids* **1990**, *121*, 303–309. [[CrossRef](#)]
38. Brinifer, C.J.; Frye, G.C.; Hurd, A.J.; Ashley, C.S. Fundamentals of sol-gel dip coating. *Thin Solid Films* **1991**, *201*, 97–108. [[CrossRef](#)]
39. Li, K.; Zeng, X.; Li, H.; Lai, X.; Xie, H. Effects of calcination temperature on the microstructure and wetting behavior of superhydrophobic polydimethylsiloxane/silica coating. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *445*, 111–118. [[CrossRef](#)]
40. Shang, Q.; Zhou, Y. Fabrication of transparent superhydrophobic porous silica coating for self-cleaning and anti-fogging. *Ceram. Int.* **2016**, *42*, 8706–8871. [[CrossRef](#)]
41. Karapanagiotis, I.; Manoudis, P.; Zurba, A.; Lampakis, D. From hydrophobic to superhydrophobic and superhydrophilic siloxanes by thermal treatment. *Langmuir* **2014**, *30*, 13235–13243. [[CrossRef](#)] [[PubMed](#)]
42. Yang, H.; Zhang, X.; Cai, Z.-Q.; Pi, P.; Zheng, D.; Wen, X.; Cheng, J.; Yang, Z.-R. Functional silica film on stainless steel mesh with tunable wettability. *Surf. Coat. Technol.* **2011**, *205*, 5387–5393. [[CrossRef](#)]
43. Kuo, C.Y.; Gau, C. Control of Superhydrophilicity and Superhydrophobicity of a Superwetting Silicon Nanowire Surface. *J. Electrochem. Soc.* **2010**, *157*, k201–k205. [[CrossRef](#)]



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