

# Sol-gel Processed Superhydrophobic Silica Coatings for Self-cleaning Applications

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## Abstract

*Both surface morphology and surface energy of solid surface conclude its wettability, either in Wenzel's hydrophobic or Cassie-Baxter's superhydrophobic wetting state. The sol-gel processed superhydrophobic silica coatings are prepared in a single-step for self-cleaning applications. Organosilane compounds holding hydrophobic end group are used in sol-gel synthesis and rough microstructure on the coating surface was achieved to gain super hydrophobicity. The static and dynamic water contact angle of 158° and 9° were achieved on the coating surface. The consequence of deposition time on the wettability of the sol-gel coatings was precisely studied. The stable wetting property of the coatings contrary to the repetitive impact of high speed water jet was examined. The self-cleaning ability of the superhydrophobic coating was also confirmed.*

**Keywords:** Superhydrophobic, contact angle, self-cleaning, lotus effect, sol-gel

## I. INTRODUCTION

Depending on the wettability of the solid surface, a shape of water drop varies from concave (complete or partial wetting) to convex (complete non-wetting) shape [1]. Rough hierarchical solid surfaces with low surface energy would show superhydrophobic wetting properties [2]. Water drops quickly begin to run off the superhydrophobic surface at very miniature disturbance due to its round shape having contact angle greater than 150°. Such low water adhesion originating from high contact angle and low sliding angle is quite often observed on many biological plant and insects surfaces [3, 4]. This low adhesion of water drop on the surface favors self-cleaning properties to the biological surfaces, where dirt particles adhered on the surface can be easily removed by merely rolling water drops. The self-cleaning behaviour observed in nature can be mimicked, which can find potential industrial application for self-cleaning purpose [5-10].

Sol-gel processing of organosilanes is attracting much attention in preparation of superhydrophobic coatings. The hydrolysis and co-condensation of one or more organosilanes compounds in sol-gel system can alone achieve super hydrophobicity in a single step without post

surface chemical modification [11]. The sol-gel parameters can be easily adjusted to tune the surface morphology from porous to rough hierarchical microstructure which is prerequisite to achieve super hydrophobicity [12]. Such sol-gel systems are advantageous to apply the homogeneous, stable and large-area coating on the solid surface of any type, shape and size with ease [13]. Lavish scientific reports on superhydrophobic sol-gel coatings on glass [14], papers [15], metals [16], wood [17], textile [18], meshes [19], and polymeric substrates [20] are available. The simple and conventional dip, spin, and spray coating methods are perfectly compatible with the sol-gel alcosol and hydrosol systems.

Zhang and researchers [21] have prepared template-free, organically modified antireflective superhydrophobic silica thin films through one-pot sol-gel processing of tetraethylorthosilicate (TEOS) and subsequent surface modification of prepared silica nanoparticles with hexamethyldisilazane (HMDS). The same research group [22] has reported the preparation of antireflective superhydrophobic silica thin films by simply incorporating dimethyldiethoxysilane (DDS) as co-precursor in the above mentioned sol-gel system to improve environment-resistance property of the superhydrophobic thin film. Liu et al [23] have prepared washing-durable superhydrophobic cotton fabrics through immersing the fabric in silica hydrosol prepared from sol-gel processing of water glass (sodium silicate) and then the silica coated fabric was padded with hydrolyzed hexadecyltrimethoxysilane (HDTMS) to lower its surface energy. Daoud and researchers [24] have developed transparent and robust superhydrophobic silica coating on knit and woven cotton substrates by simply dip coating sol-gel processed composite alcosol of TEOS, HDTMS and 3-glycidyloxypropyltrimethoxysilane (GPTMS).

Huang and Lin [25] have synthesized silicic acid using TEOS in sol-gel process and added in the suspension of silica nanoparticles to prepare coating solution. The silica

coatings prepared on glass by dip coating were modified from FAS containing ethanol solution to achieve superhydrophobicity. Wang et al [17] have applied silica nanoparticles on wood surface from base catalyzed sol-gel processing of TEOS and the superhydrophobic wood surface was resulted by chemical vapor deposition of fluoroalkylsilane (FAS). Instead of post surface chemical modification by FAS, Lin research group [13] have prepared particulate silica alcosol in single-step by hydrolysis and condensation of TEOS and FAS together in ammonia containing ethanol solution. This fluoro-containing silica nanoparticle coating solution was applied on range of flexible and flat solid substrates to achieve stable superhydrophobicity. Owing to stable superhydrophobic wetting properties of surfaces developed by one-pot sol-gel synthesis of mixture of more than two organosilanes are of great interest. Here, we report the fabrication of superhydrophobic silica coating from coating sol contained of sol-gel processed alkylsilane and fluoroalkylsilane which showed stable superhydrophobicity with excellent self-cleaning properties.

## II. EXPERIMENTAL SECTION

### 2.1 Materials

The materials used in the experiments are methyltrimethoxysilane (MTMS) (Sigma-Aldrich Chemie, Germany), (Heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (17FTMS) (Gelest, Inc. Morrisville, PA), ethanol and ammonia (28%) (Nanjing Chemical Reagent Co., Ltd, China). The glass substrates were obtained from Sinopharm Chemical Reagent Co. Ltd, China. Deionized water was used during the experiments.

### 2.2 Preparation of Superhydrophobic Coatings

Following the process described in previous report [26], the glass substrates were thoroughly cleaned. In typical sol-gel process, 17FTMS (0.2 ml), deionized water (2.5 ml) and ammonia (1 ml) were mixed in ethanol (40 ml) and magnetically stirred slowly for 4 h. Finally, MTMS (5 ml) was added slowly in above solution under constant stirring. After 24 h of continuous stirring, the pre-cleaned glass substrates were immersed in the above solution for 1, 6, 12, 18, 24 and 48 h and taken out with withdrawal rate of 2 mm/s. The coatings prepared from 1, 6, 12, 18, 24 and 48 h of deposition time were named as D-1, D-6, D-12, D-18, D-24 and D-48, respectively. The coatings were dried at room temperature for 2 h and 80 °C for 2 h.

### 2.3 Characterization

The surface morphology and surface roughness of the coatings were obtained from field emission scanning electron microscope (FE-SEM) (Hitachi, S-4800) and laser microscopy (KEYENCE, VK-X200 series), respectively. The photographs of coatings were taken by Canon digital camera (G 15 series). The static and dynamic water contact angle values were obtained by using contact angle meter (Ramehart Instrument Co., USA). A water drop (~ 5 µl) was gently dropped on the coating surface and the contact angle value was recorded after the drop acquired its equilibrium state. After placing water drop (~ 5 µl), the coated substrate was slowly tilted (0.5°/sec) to obtain sliding angle values. All the wettability measurements were carried out on 5 different locations on the sample and average was taken as a final value.

## III. RESULTS AND DISCUSSION

### 3.1 Surface morphology and roughness of the coatings

While developing the superhydrophobic coatings, deposition time has showed significant effect on the surface morphology and roughness [27]. The substrate area gets homogeneously covered and the surface roughness increased with deposition times. In most of the cases, higher deposition time or multiple depositions helps to achieve surface superhydrophobicity at the cost of optical transparency [28, 29]. **Fig. 1** shows the surface morphology of the coatings prepared from different deposition times. The effect of deposition time on the surface morphology of the coatings was clearly observed. At lower deposition time, D-1 coatings showed smooth morphology, however the coverage of the sol-gel material is not uniform over the glass substrate. D-6 coatings exhibited complete coverage of the coating material on the substrate with smooth interconnected network-like microstructure. The coating material protrudes on the substrate as the deposition time increases and as a result D-12 coatings showed interconnected and over-hanged porous surface morphology. Whereas, this porous morphology was obscured at higher deposition times and the D-18, D-24 and D-48 coatings depicted well-covered rough surface morphology. The diminutive cracks observed on the coatings surface are as a result of solvent evaporation during drying process.

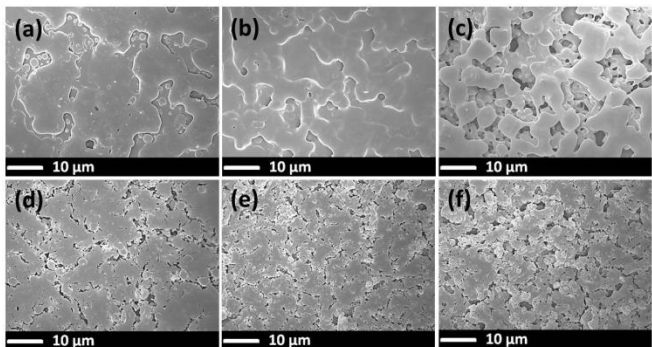


Fig. 1: FE-SEM images of the coatings prepared from different deposition times, (a) D-1, (b) D-6, (c) D-12, (d) D-18, (e) D-24 and (f) D-48 coatings.

LASER microscope was used to analyze the surface roughness of the coating. **Fig. 2** depicts the topological images of the coatings prepared from increasing deposition times. The 70×70 μm<sup>2</sup> area of the coatings was scanned to obtain the values of surface roughness. The average roughness of the coatings was gradually increased with increasing deposition times. As the substrates were kept in the coating solution for longer times, the more amount of coating material protrudes on the surface of the substrate resulting high surface roughness. The D-1, D-6, D-12, D-18, D-24 and D-48 coatings showed the surface roughness of 0.40, 0.45, 0.81, 0.72, 0.97, and 1.26 μm, respectively. The D-12 coatings showed little high surface roughness of 0.81 μm due to the porous morphology and the ample gaps between the interconnected structures.

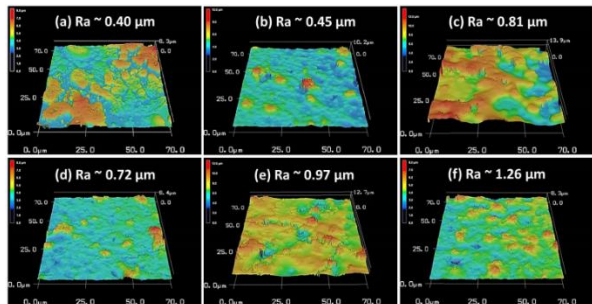


Fig. 2: Laser microscopy images of the coatings prepared from different deposition times, (a) D-1, (b) D-6, (c) D-12, (d) D-18, (e) D-24 and (f) D-48 coatings.

3.2 Wetting characteristics of the coatings

With increasing deposition times, the surface morphology and roughness of the coatings were increased, however, the hydrophobicity was also improved. **Fig. 3** shows the effect of deposition time on the wettability of the coatings. The coating prepared from lower deposition times showed less hydrophobicity. The D-1 and D-6 coatings showed hydrophobic behavior with water contact angle of 93 and 99°, respectively. These coating surfaces revealed smooth

morphology, however the hydrophobic behavior observed due to the low surface energy properties of the coating material. The water drops placed on the surface of D-1 and D-6 coatings acquired Wenzel’s wetting state and rolled off the surface at the higher sliding angles of 86 and 79°, respectively. No air pocket trapping can be observed in the smooth microstructures and as a result water drops makes contact with the most of the solid fraction showing higher adhesion towards the surface. The Wenzel’s wetting state was preserved so far on the D-12, D-18, and D-24 coatings with the water contact angles of 114, 127, and 139°, respectively. This improved hydrophobicity is solely due to the gradual increase in surface roughness and change in the surface morphology. The sliding angles for water drops observed on the D-12, D-18, and D-24 coatings were 63, 41 and 26°, respectively.

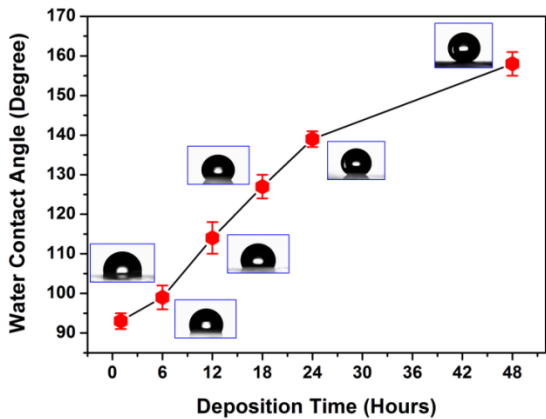


Fig. 3: Water contact angles on the coatings prepared from different deposition times

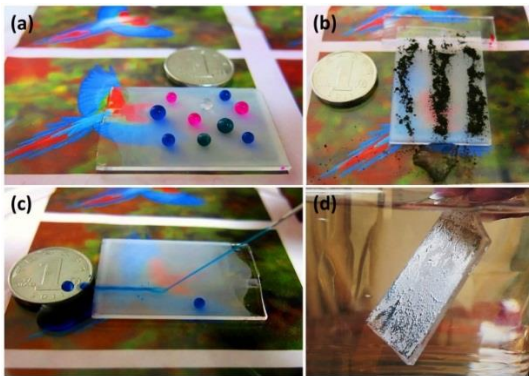
The coatings prepared from 1 to 24 h of deposition times showed Wenzel’s wetting state with strong water drop adhesion on the coatings surface. This Wenzel’s wetting state was transformed to Cassie-Baxter’s wetting state for the coatings prepared from 48 h of deposition time. A water drop placed on the D-48 coatings acquired round shape with contact angle of 158° and promptly rolled off the coating surface at sliding angle of 9°. The sufficient amount of air pockets trapped in the interstices of the rough structure prohibits water drop to invade. As a result, water drop sits on the composite solid-air structure with almost no adhesion.

3.3 Properties of the superhydrophobic coatings

Wetting properties of the prepared coatings were analysed. **Fig. 4a** shows the optical photograph of spherical water drops relaxed on the D-48 coating. To get optical clarity, the water drops were colored green, pink and blue using food colors. All the water drops placed at different positions



on the coating surface have acquired perfect round shape, confirming the uniform sol-gel deposition. The prepared D-48 coatings are almost opaque due to visible light scattering (Mie scattering) from rough structures [30]. In nature, lotus leaf shows superb self-cleaning performance and as a result they look clean and fresh forever. The accumulated dust particles of any size, shape and density can be efficiently self-cleaned by the flowing water droplet on an ideal superhydrophobic surface [31]. The excellent self-cleaning ability of the superhydrophobic surfaces has been extensively studied [32-34]. In this study, the carbon black powder was used as substitute for the dust particles and copiously spread on the superhydrophobic D-48 coating as shown in **Fig. 4b**. This coated substrate was mounted with nearly 10° of tilt angle. The water drops (~5µl) were gently dripped on the contaminated area using syringe needle. The water drops quickly rolled off the surface by effectively collecting the carbon black powder as depicted in **Fig. 4b**. At the beginning, first water drop dropped on the contaminated surface adequately carry away as much dust particle as it can and subsequent water drops completely cleans the surface. Using almost 10-12 rolling water drops, the contaminated superhydrophobic D-48 coating surface was effectively self-cleaned.



**Fig. 4:** (a) an optical photograph of water drops, (b) self-cleaning performance, (c) Water jet impact study and (d) plastron layer on superhydrophobic D-48 coating.

The stable wetting state of superhydrophobic surface was generally characterized by water drop impact or water jet impact. The high speed water jet can either impale or rebound off the superhydrophobic surface. In this study, the water jet was generated by applying normal pressure to the syringe needle. The superhydrophobic D-48 coating was placed horizontally and the water jet was impacted on it (**Fig. 4c**). The moment water jet strikes on the superhydrophobic coating surface; it was reflected off. The stable air cushion present in the rough structure avoids water jet to invade and immediately repel it off. This confirms the stable wetting properties of superhydrophobic

D-48 coating. The air pockets trapped in the rough structures of superhydrophobic surface can be confirmed by immersing the surface in water. A shiny layer (plastron layer) appears on the superhydrophobic surface after immersion in water [35]. Seeger and researchers have observed stable plastron layer for period of weeks on the superhydrophobic silicone nanofilaments coatings [36]. However, other researchers confirmed the decay of plastron layer from underwater superhydrophobic surface due to the application of hydraulic pressure and/or with immersion time [37]. **Fig. 4d** shows the formation of plastron layer between the water and superhydrophobic D-48 coating surface due to total light reflection from the trapped air. This plastron layer is the result of air pockets trapped in the microstructure of superhydrophobic surface. The plastron layer was intact even after immersion in water for 2h. This stable plastron layer present on underwater superhydrophobic surface can be helpful in technological drag reduction applications.

#### IV. CONCLUSIONS

The superhydrophobic silica coatings were successfully prepared by controlling the surface roughness and morphology. The deposition times showed significant role on the superhydrophobicity of the coatings. The prepared superhydrophobic coatings showed static and dynamic water contact angle of 158° and 9°. The low water roll-off angle observed on the superhydrophobic coatings was utilized to perform self-cleaning ability. The superhydrophobic wetting property of the coating was invariable under the impact of water jet. The stable plastron layer observed on the coatings can find potential applications in marine industry.

#### V. ACKNOWLEDGEMENTS

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