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Superhydrophobic PVC/SiO_2 Coating for Self-Cleaning Application

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A lotus leaf like self-cleaning superhydrophobic coating has high demand in industrial applications. Such coatings are prepared by alternative dip and spray deposition techniques. A layer of polyvinyl chloride is applied on glass substrate by dip coating and then spray coated a suspension of hydrophobic silica nanoparticles at substrate temperature of 50 °C. This coating procedure is repeated for three times to achieve rough surface morphology which exhibits a water contact angle of 169 ± 2° and sliding angle of 6°. The superhydrophobic state of the coating is still preserved when water volume of 1.2 L is used to impact the water drops on coating surface. The stability of the wetting state of the coating is analyzed against the water jet, adhesive tape and sandpaper abrasion tests. The prepared superhydrophobic coating strongly repelled the muddy water suggesting its importance in self-cleaning applications.

1. Introduction

Lotus leaf is a perfect model of self-cleaning superhydrophobic surface with specific combination of surface chemistry (surface energy) and surface topography (surface roughness).[1,2] A low surface energy hierarchical surface structure of lotus leaf surface revealed unusual wettability (water contact angle (WCA) greater than 150° and sliding angle less than 10°) which inspired to create artificial superhydrophobic surface by increasing surface roughness along with decreasing surface energy. Such superhydrophobic surfaces have numerous applications including self-cleaning, anti-corrosion, drag-reduction, oil-water separation, and etc.[3–8] So far, SiO_2, TiO_2, ZnO, Al_2O_3, candle soot and various polymers have been used to fabricate self-cleaning superhydrophobic coatings.[9–14] Among them, polymer/SiO_2 nanocomposite is a promising in preparation of self-cleaning superhydrophobic coatings.[15,16]

The self-cleaning property of superhydrophobic coatings has attracted significant interest in industrial applications. Recently, Latthe et al. have applied suspension of hydrophobic SiO_2 nanoparticles (NPs) on different types of substrates including body of motorcycle, building wall, mini boat, solar cell panel, window glass, cotton shirt, fabric shoes, cellulose paper, metal, wood, sponges, plastic, and marble which revealed high water repellency and excellent self-cleaning property.[17] Many reports are available on the preparation of superhydrophobic polyvinyl chloride (PVC) thin films using ethanol.[18–20] Seyfi et al. have drop casted a mixture of PVC, Ag_3PO_4, and ethanol on thermoplastic

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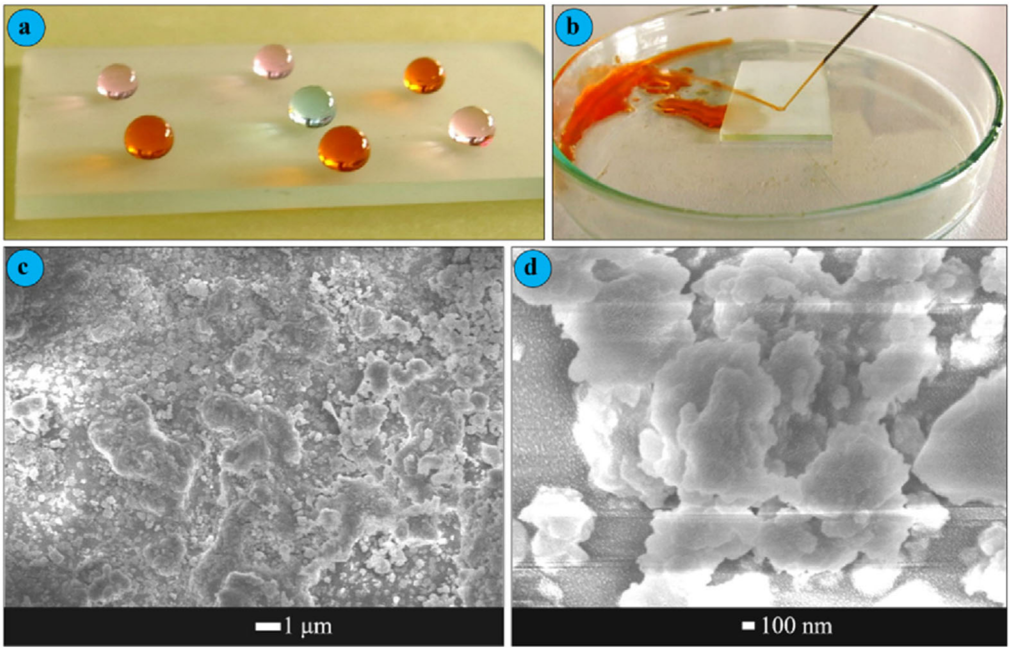

Figure 1. a) Optical photograph of color water drop on superhydrophobic coating, b) the image of water jet impacting on coating, c and d) different magnification SEM images of superhydrophobic coating.

polyurethane (TPU) substrate and achieved antibacterial superhydrophobic surface.[21] The as prepared superhydrophobic TPU surface showed WCA ≈ 156° and SA ≈ 2° with self-cleaning performance. Also, Guo et al.[15] have reported that water drops rolled off immediately on the coating prepared by casting of polymer (PVC, PMMA, and PE) and SiO_2 NPs composite on various substrates like copper, aluminum, stainless steel, silicon, glass and filter paper. Rivero et al.[22] have prepared superhydrophobic surface by depositing ZnO NPs incorporated polystyrene (PS) and PVC polymeric solution on aluminum alloy substrate using the electrospinning technique. Yuan et al.[23] have obtained lotus-leaf-like superhydrophobic PVC film by casting PVC solution on negative template of PDMS. Other than this, Zhang et al.[24] have obtained superhydrophobic coating by pouring PVC/SiO_2 mixture on negative template of PDMS and reported that superhydrophobicity depends on weight percentage of SiO_2 particles in PVC. Chen et al.[25] have prepared water-repellent SiO_2/polymer (PS and PVC) composite coating without any surface chemical modification by spin coating. The amount of hydrophobic SiO_2 NPs in PVC or PS affects the surface roughness and hence the wettability of the coating.

Herein, we have prepared superhydrophobic surface on glass by dip coating followed by spray coating method. The hydrophobic SiO_2 NPs were prepared by sol–gel technique. A thin layer of PVC was applied on glass substrate by dip coating and dried at room temperature. After that, a suspension of SiO_2 NPs in hexane was sprayed on PVC coated glass substrate at substrate temperature of 50 °C. The superhydrophobic coating was obtained by applying multiple alternative layers of PVC and SiO_2 NPs on glass substrate.

2. Result and Discussion

2.1. Surface Microstructure and Wettability

The multiple layers of PVC/SiO_2 were applied on glass substrate to obtain desired surface roughness which is the main requirement of extreme water repellency. **Figure 1**c represents the surface microstructure of three bilayer of PVC/SiO_2 coating, where the aggregated SiO_2 NPs were distributed on the PVC layer. The PVC layer can help SiO_2 NPs to adhere firmly on the coating surface. The aggregation of SiO_2 NPs is not uniform and the grain sizes from 5 μm to 100 nm were observed (Figure 1d). These different size scale grains provide hierarchical surface morphology. Nearly similar surface morphology was reported for the PVC/SiO_2 nanocomposite coating prepared by spin coat technique.[25] This hierarchical surface morphology tends to trap small air pockets in the rough voids and hence a water drop can sit on the air-solid composite structure with minimum contact to the solid fraction of the surface. A water drop can only touch a small solid fraction of the coating, as the trapped air pushes away the water drops and not allowing the water drops to wet the inner portion of a rough surface. As shown in the Figure 1a, the water drops hardly stay on the three bilayer of PVC/SiO_2 superhydrophobic coating. Every water drop takes spherical shape at different positions on the coating surface confirming the uniform deposition of PVC/SiO_2 on the substrate. The superhydrophobic coating was appeared opaque due to the presence of micrometer scaled grains which allows scattering of the visible light. Also the water jet was impacted on the superhydrophobic coating which rebounds off the surface quickly after impacting (Figure 1b). The trapped air in the rough surface resists the water jet to invade the

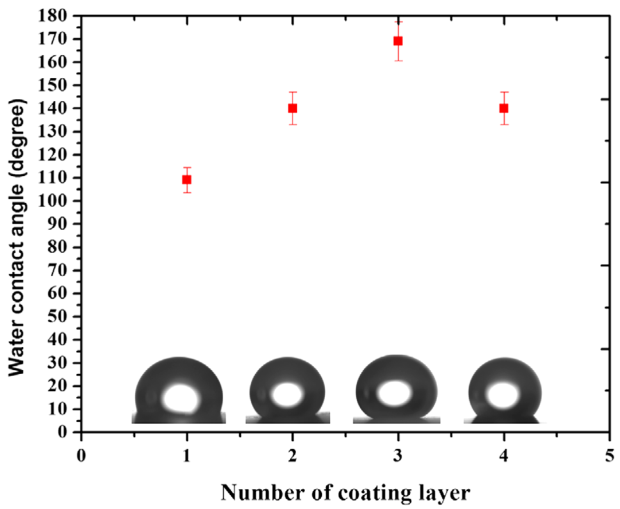

Figure 2. The variation of water contact angle with layer of polyvinyl chloride and SiO_2 particles.

rough structure. Also water jet rebounding confirms the robustness of the coating.

A systematic study was performed on the dependence of numbers of bilayers on the wettability of the coating (**Figure 2**). A first bilayer coating exhibited a WCA of 110±5° confirming hydrophobic nature of the coating. The surface roughness of the coating is quite low to trap the air pockets and hence the wettability falls in the Wenzel's state[26] where the solid fraction of the coating was partially wetted by the water drops. Though the WCA increased to 140 ± 6° with considerable decrease in solid-liquid contact area in case of two bilayer coating, the wettability was still in the Wenzel's wetting state. The WCA of 169 ± 7° and SA of 6° was observed for three bilayer coating confirming superhydrophobicity in Cassie-Baxter's wetting state.[27] A water drop floats on the layer of air having minimum contact with solid fraction of the coating surface and hence readily roll off the surface. For next bilayer coatings, the WCA tends to decrease as a result of increase in thickness which creates visible cracks in the coatings during evaporation of solvent.

2.2. Durability Tests

The mechanical durability of superhydrophobic coating can be evaluated by water jet and water drop impact, sand paper abrasion and adhesive tape peeling test.[28] Here, the water jet was developed by 15 mL syringe. The water jet was immediately spread on uncoated glass slide due to smooth surface structure with hydrophilic nature. On the other hand, the water jet bounced off the superhydrophobic coating as shown in Figure 1b. The air trapped hierarchical structure strongly avoids pinning of water jet on the surface.[5,29] The wettability of the coating was checked after water jet impact study and the coating showed no change in its superhydrophobic property confirming its robustness. Water drop impact test was carried out by adjusting the distance between superhydrophobic coating and tip of tap about 10 cm as shown in schematic (**Figure 3**a). Nearly 2 L of water was dropped on the superhydrophobic coating inclined at 30° with drop falling rate of 90 drops min^{-1}. The effect of water drop impact on the wetting properties of the superhydrophobic coating was estimated. The superhydrophobic state of the coating was intact for the impact of 1.2 L of the water as a result of stable air pockets in the rough microstructure of the coating which avoids water drop penetration inside the coating structure. However, the trapped air starts to evacuate from the rough structure and also the rough structure might have partly ruined due to continuous impact of water drops and as a result, WCA decreased to less than 140° for impacting 2.0 L of water (Figure 3b).

The adhesive tape peeling test was carried by using Cellotape No.405 having adhesiveness of 3.93 N/10 mm. A tape was applied firmly on the superhydrophobic coating with the help of 200 g weighted disk rolling back and forth on it (**Figure 4**a).[28] After slowly peeling off the tape, some amount of the coating material was observed stacked on the adhesive tape; however, the coating showed the WCA of 165° (Figure 4b). The superhydrophobicity of the coating was found intact for two cycles of adhesive tape test, and then the WCA decreased to 80° for five cycles of adhesive tape test confirming the exhaustive loss of PVC/SiO_2 from the coating (Figure 4c).

In large scale applications, superhydrophobic coatings can be damaged by scratch, rubbing and finger contact. To sustain the hierarchical micro/nanostructure and low surface energy of superhydrophobic coating under mechanical abrasion is one of the important issue. Here, the mechanical abrasion test was performed using sandpaper grit no. 400. The schematic of sandpaper abrasion process is illustrated in **Figure 5**a. A weight (100 g) was placed on superhydrophobic coating and dragged for 10 cm length on sandpaper at the average speed of 0.5 cm sec^{-1}. The effect of abrasion distance on the wettability of the superhydrophobic coating was studied (Figure 5b). The wettability of the coating was found in the superhydrophobic state for dragging the coating for nearly 30 cm on the sandpaper which confirms no significant loss in the surface roughness of the coating. However, the WCA decreased to 93° for dragging the coating for 60 cm on sandpaper confirming substantial damage to the coating.

2.3. Self-Cleaning Property

High water repellent property of the surface with low water sliding angle helps to keep the surface clean like a lotus leaf. In open air, many solid surfaces are contaminated by various types of dust particles. On superhydrophobic surface, spherical shaped water drop roll away easily by collecting dust particles, performing self-clean ability. The self-cleaning ability of the prepared superhydrophobic coating was tested by muddy water. The muddy water was prepared by dispersing fine particles of soil in water. This muddy water was poured on the superhydrophobic coating. In the process of pouring muddy water, it eventually get repelled off the superhydrophobic coating (**Figure 6**a–c). After pouring 50 mL of muddy water, surface becomes clean similar to lotus leaf (Figure 6c). This indicates prepared superhydrophobic coating was highly water repellent with excellent self-cleaning property.

3. Conclusions

We have used a conventional dip and spray coating techniques to prepare superhydrophobic coating by applying consecutive layers

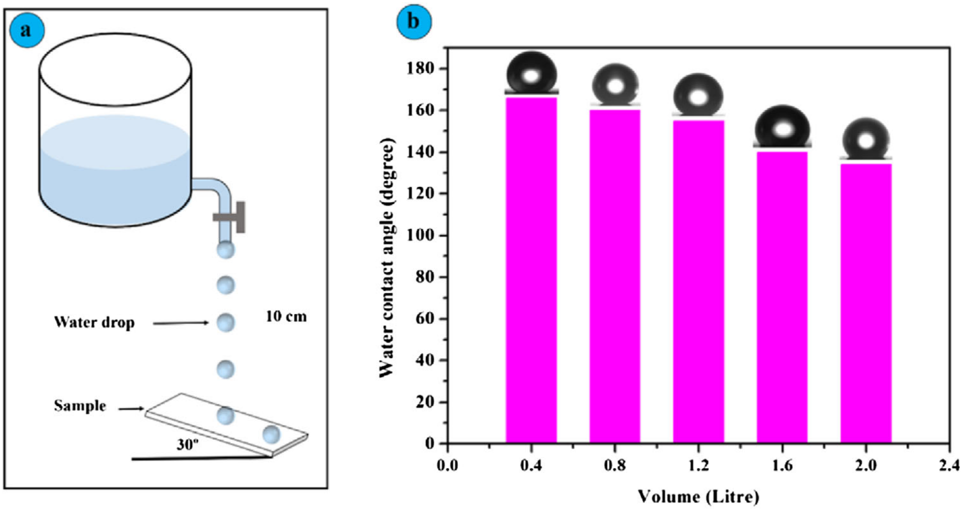

Figure 3. a) A schematic of water drop impact test, b) the effect of water drop impact on wettability of the superhydrophobic coating.

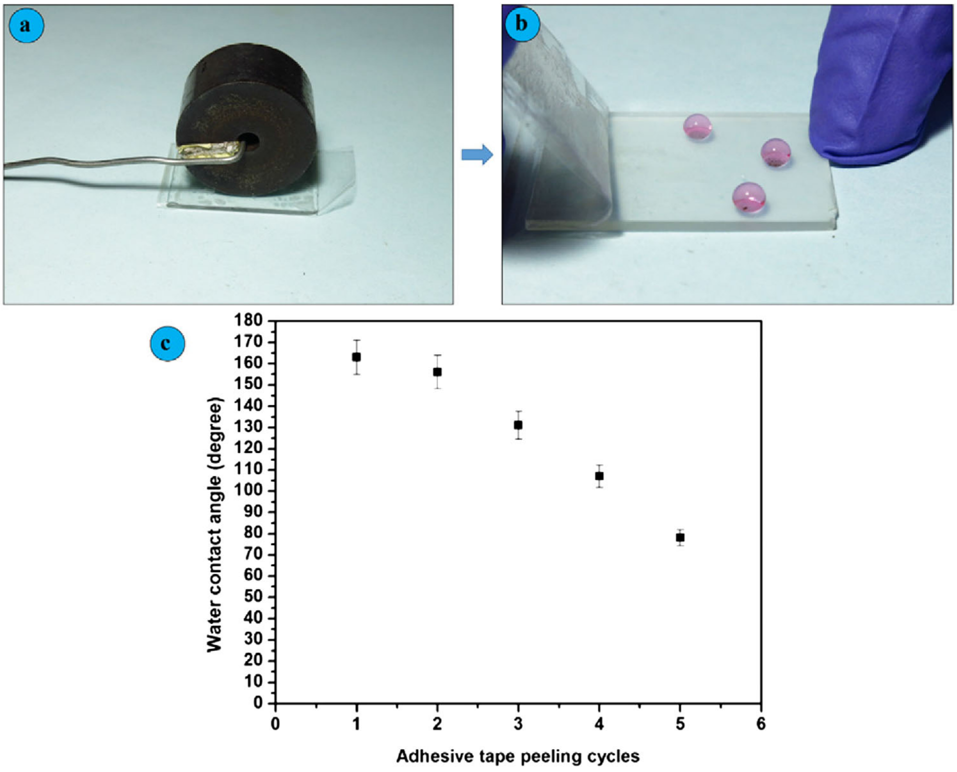

Figure 4. a) Rolling of 200 g weighted disc on adhesive tape placed on coating, b) adhesive tape peeling off and c) effect of adhesive tape peeling cycles on the wettability of the superhydrophobic coating.

of PVC and hydrophobic SiO_2 NPs on glass substrate. The hierarchical rough microstructure with different scaled grains of SiO_2 NPs was observed. The self-cleaning superhydrophobic coating with WCA of 169 ± 2° and sliding angle of 6° was achieved by applying three bilayers of alternate PVC followed by hydrophobic SiO_2 NPs. The water jet bouncing off the surface indicates the air pockets trapped in dual scale rough structure. After dripping the water of volume 1.2 L, the water drop impacted coating showed invariable wettability. The superhydrophobic coatings were moderately stable against adhesive tape and sandpaper abrasion tests. Future practical applications of these coating can be found in windshields of vehicles, solar cell panels and windows of buildings, if their transparency and mechanical stability could be further enhanced.

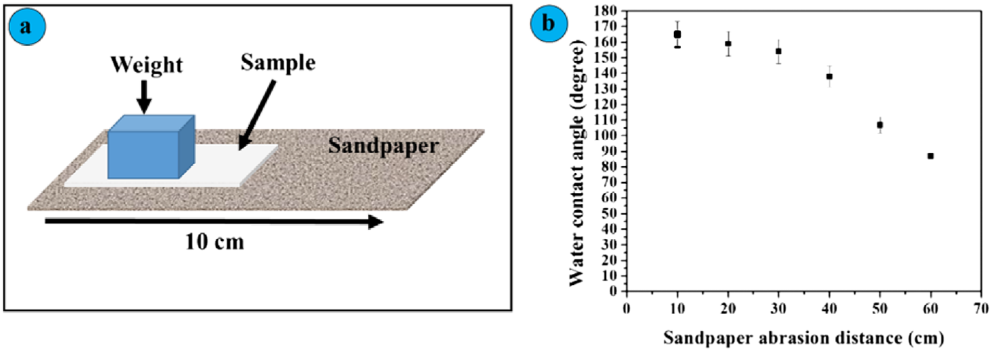

Figure 5. a) Schematic of sandpaper abrasion test and b) the variation of water contact angle with sandpaper abrasion distance.

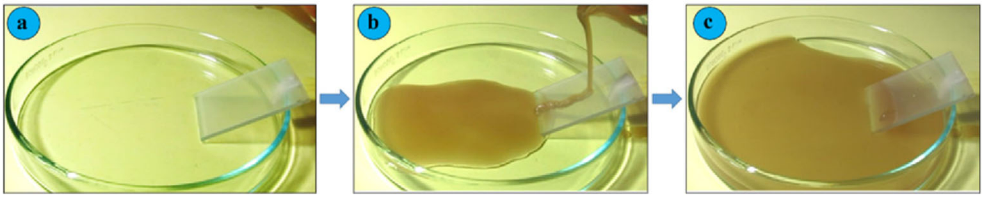

Figure 6. a-c) Self-cleaning behavior of superhydrophobic coating.

4. Experimental Section

Materials: Methyltrimethoxysilane (MTMS) and PVC were purchased from Sigma-Aldrich, USA. Ethanol, methanol, ammonia solution, tetrahydrofuron (THF) and hexane were bought from Spectrochem PVT. LTD., India. Micro-Glass slides (75 × 25 × 1.35 mm) were obtained from Blue star, Polar Industrial Corporation, India.

Synthesis of Hydrophobic SiO_2 NPs: The hydrophobic SiO_2 NPs were synthesized using sol–gel method reported in literature.[30] The mixture of 2 mL MTMS, 20 mL methanol and 4 mL distilled water was stirred for 20 min. After that ammonia solution was added dropwise and kept for stirring for 30 min. The prepared gel was aged for overnight and dried at 80°C for 5 h. The dried gel was grinded well using mortar and pestle to obtain fine powder of silica particles.

Preparation of Superhydrophobic Coating: At first, the glass substrates were ultrasonically cleaned with distilled water and ethanol for 30 min and dried at room temperature. The cleaned glass substrate was dipped in the PVC solution for 30 s. The solution was prepared by dissolving 100 mg PVC powder in 10 mL THF using magnetic stirrer (200 rpm for 30 min). A thin layer of PVC deposited glass substrate was dried at room temperature. A suspension of SiO_2 NPs (100 mg) was prepared by dispersing in 10 mL hexane and sprayed on PVC deposited glass substrate at substrate temperature of 50 °C. Finally PVC/SiO_2 deposited glass substrate was annealed at 100 °C for 1 h. In this way, one bilayer of PVC/SiO_2 was applied on glass substrate. This procedure was repeated to deposit two, three and four bilayers of PVC/SiO_2 on glass substrate.

Characterizations: The wettability of prepared coatings was evaluated by measuring WCA and sliding angle (SA) using contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India). The surface morphology of coating was characterized by field emission scanning electron microscopy (FESEM, JEOL, JSM-7610F, Japan). The water jet impact test was carried out by using 15 mL syringe. For water drop impact test, the coated glass substrate was kept at 30° inclination and water drops were dropped from the height of 10 cm. The mechanical stability of the coating was checked by adhesive tape peeling and sandpaper abrasion test. The self-cleaning behavior was observed by pouring muddy water on the coating.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

PVC, roughness, superhydrophobic and self-cleaning, wetting

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