Macromolecular Symposia

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# Superhydrophobic Coating Using $TiO_2$ NPs/PMHS Composite for Self-Cleaning Application

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**In the present research work, spray deposition technique is adopted for the fabrication of superhydrophobic coating on glass slide using $TiO_2$ nanoparticles and polymethylhydrosyloxane (PMHS) composite. The prepared superhydrophobic coating revealed hierarchical surface morphology due to different micro and nanoscaled grains of $TiO_2$ NPs/PMHS composite. The water drops hardly stay on the superhydrophobic coating and roll off the surface at sliding angle of 6° due to high water contact angle of 163 ± 2°. As a result, the prepared superhydrophobic coating revealed excellent self-cleaning performance. To evaluate the mechanical durability the prepared superhydrophobic coating, the coating surface is exposed to water jet, water drop impact, adhesive tape peeling, and sandpaper abrasion tests. This coating approach can be applied to the substrates of any size and shape.**

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**DOI: 10.1002/masy.202000033**

## 1. Introduction

Super-antiwetting surfaces having remarkable surface microstructures on which water achieves contact angle greater than 150° and roll off at 10° are found in the nature including plants as well as animals. A lotus leaf exhibits high water repellency and hence exceptional self-cleaning ability due to the presence of epicuticular wax crystals on micro papillae. A water strider is able to walk and move easily on the surface of water because of the presence of wax composed hairs of 50 μm length and about 3 μm diameter on their legs.[1,2] In both these studies, it has been recognized that the combination of low surface energy material and micro-nanoscaled hierarchical surface structure plays a crucial role in the superhydrophobicity of surface.[3–5] Many research groups have succeeded in the preparation of artificial superhydrophobic surfaces by using a variety of nanoparticles, including $SiO_2$, $TiO_2$, ZnO, and others with a combination of low surface energy polymers.[6–9] Many reports are available where the silica and $TiO_2$-based aerogel technique was utilized for the preparation of superhydrophobic coatings.[10–14]

Latthe et al.[15] have prepared superhydrophobic coating on various substrates, including body of motorcycle, building wall, mini boat, solar cell panel, window glass, cotton shirt, fabric shoes, paper (currency notes), metal, wood, sponge, plastic, and marble self-cleaning application. Recently, Dalawai et al.[16] have reviewed on the fabrication techniques used for self-cleaning superhydrophobic coating in various fields such as textiles, cotton-fabrics garments, buildings construction, lavatories, domestic-automobiles windows, architectural heritage, and photovoltaic and solar cells. Contreras et al.[17] have fabricated micro and nanoscale hierarchical surface of polypropylene (PP) stick by using trimethoxypropyl silane functionalized $TiO_2$ nanoparticles. The PP stick showed self-cleaning phenomenon in both methods, such as dispersion of functionalized $TiO_2$–xylene and functionalized $TiO_2$–xylene–PP pellets with WCA of 164 ± 7° and 160 ± 3°, respectively. Xu et al.[18] have fabricated superhydrophobic surface of perfluorooctanoic acid modified $TiO_2$/polystyrene nanocomposites using spray coating method. The study confirmed the dependence of wettability on the drying temperature and the ratio of $TiO_2$ nanoparticles to polystyrene. Huang et al.[19]

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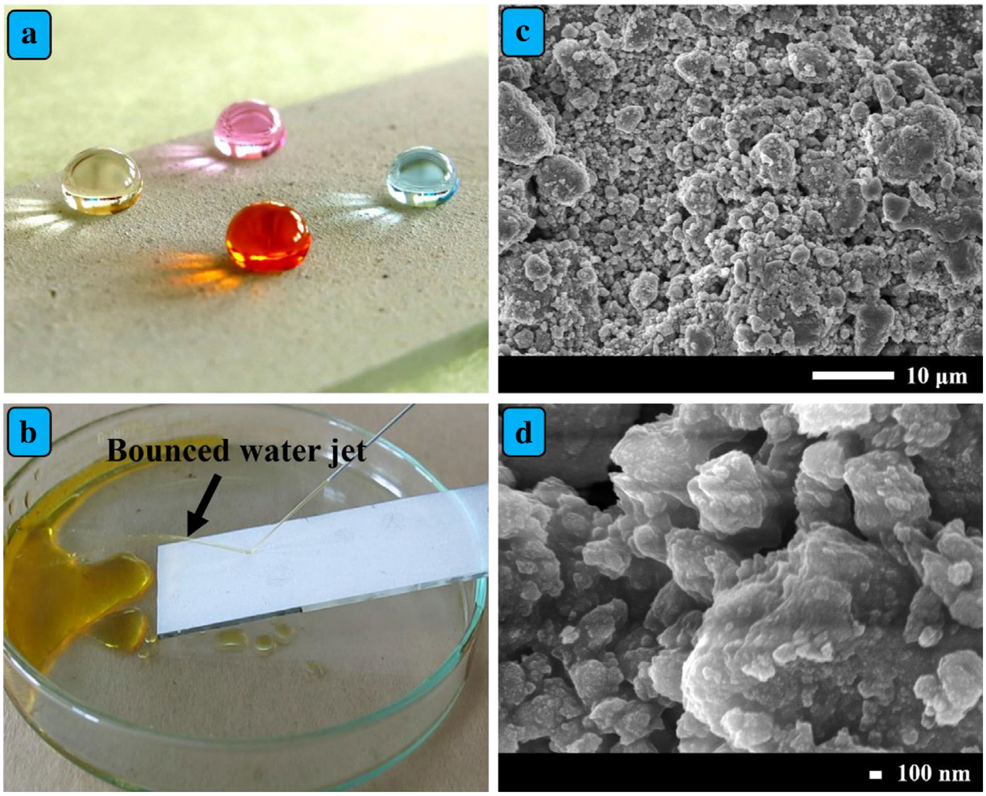


**Figure 1.** a) Color water drops on P–2 sample, b) Bouncing water jet on P–2 sample, c and d) SEM images of P–2 sample at different magnifications.

have reported green and facile method for fabricating superhydrophobic coatings using $TiO_2$ nanoparticles and fluorinated acrylate copolymers composite. Ding et al.[20] have achieved superhydrophobicity by casting fluorinated polysiloxane/$TiO_2$ nanocomposite on aluminum foil, glass slide, wood panel, paper, and PP. This superhydrophobic coating not only showed excellent durability at various environments such as various pH values, wide temperature range, and UV irradiation, but also is recoverable even when stained by oily contaminants. The FAS-$TiO_2$/PVDF composite surface exhibits micro/nanostructures due to the cross-linked structure of the PVDF entangled with the FAS-$TiO_2$ through attractive electrostatic forces. The FAS-$TiO_2$/PVDF composite deposited on Cu substrate showed water contact angle of 160° and a sliding angle of 5°.[21]

In this research paper, a facile and inexpensive spray technique is used for the preparation of superhydrophobic coating using as-synthesized hydrophilic $TiO_2$ NPs and polymethylhydrosiloxane. The $TiO_2$ NPs get embedded in the network structure of polymethylhydrosiloxane by increasing the overall surface roughness of the coating. After spray coating, the various size grains, mostly micrograins of $TiO_2$ NPs/PMHS composite, were formed on the surface resulting in opaque appearance of the coating due to scattering of visible light. However, the prepared superhydrophobic coating showed excellent self-cleaning ability.

## 2. Result and Discussion

### 2.1. Microstructure and Wettability of Superhydrophobic Coating

Usually, wettability of the solid surface can be analyzed by measuring water contact angle, which mostly depends on the surface roughness of low surface energy material.[9,23] An optical photograph of P–2 sample is shown in **Figure 1a**, where the water drops (volume, 20 µL) exhibiting perfectly sphere shape having contact angle of nearly 163°. A water jet hit on the coating surface was readily bounced off without spreading (Figure 1b). The water jet is scanned on whole P–2 sample and then targeted at a definite location. This confirmed that the prepared SHP surface was stable against water jet hitting. Such a high water repellency of the P–2 sample was due to its high surface roughness and low surface energy. The surface morphology of the P–2 sample consists of different micro and nanoscaled grains of $TiO_2$ NPs/PMHS composite (Figure 1c,d). The $TiO_2$ NPs get aggregated in the network structure of PMHS and resulted in the formation of micro and nanoscaled grains. These grains are uniformly deposited on the glass substrate. Qing et al.[24] have also observed a similar surface morphology for the superhydrophobic coatings prepared from $TiO_2$ and PMHS. Mostly, the surface of the coatings consists of microscaled grains, which effectively hampers the optical transparency of the coating due to scattering of visible light from the rough surface. Mainly, the $TiO_2$ NPs helps to increase the surface roughness of the coating. A simple


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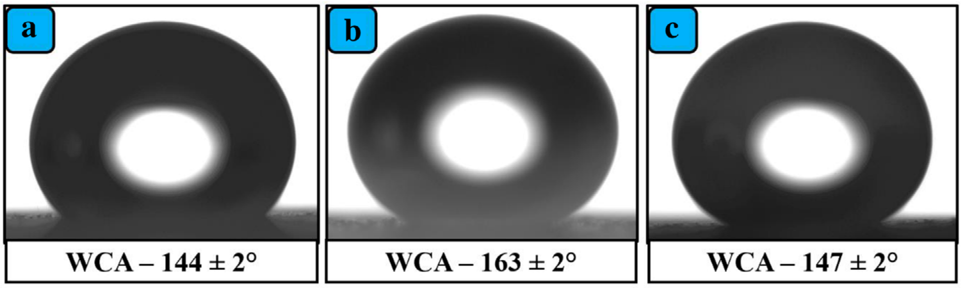


**Figure 2.** The WCA of a) P-1, b) P-2, and c) P- 3 samples.

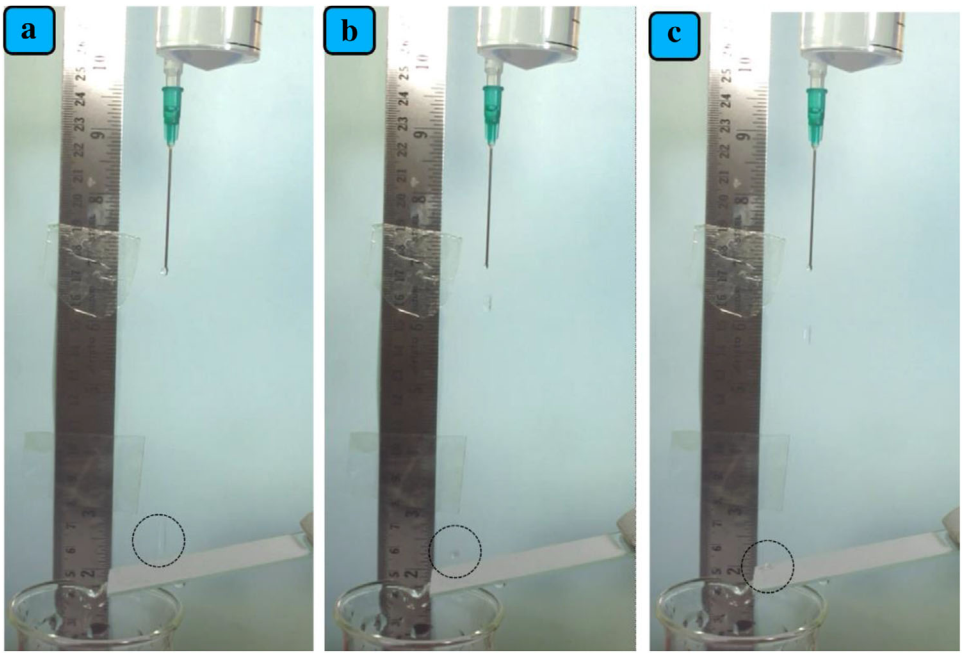


**Figure 3.** The water droplet dropping process on P–2 sample.

PMHS coating may not attain superhydrophobicity. The formation of micro and nanoscaled grains of $TiO_2$ NPs/PMHS composite promotes air trapping inside the structure, which eventually decreases the solid–liquid contact area. Hence the water drops floats on the composite of solid–air interface. It confirms the Cassie–Baxter state of wettability.

It was confirmed that, the contact angle of the coating increased gradually with increasing amount of PMHS in the coating solution (**Figure 2a–c**). For 0.01 mL of PMHS, the coatings showed a water contact angle of 144°, which might be due to the exposure of hydrophilic $TiO_2$ NPs to the surface of the coating. The surface is revealing the wettability in Wenzel's state. For an optimum addition of 0.03 mL PMHS, the coatings exhibited Cassie–Baxter's wetting state with a contact angle of 163°. However, a further increase in PMHS to 0.05 mL may smoothen the surface roughness and hence the contact angle decreases to 147°.

### 2.2. Stability of Superhydrophobic Coating

For practical application, the stability of SHP surface is one of the most important issue. The water drop impact, sand paper abrasion, and adhesive tape peeling test were mostly used to characterize the stability of SHP surfaces.[25] The water droplets dropping process is shown in **Figure 3**. The P–2 sample was fixed with tilting angle nearly 30° and water droplets dropped by syringe from height of nearly 10 cm at rate 60 drops min$^{-1}$. In Figure 3b, the water drops bounce off in an upward direction after impact, indicating that the Cassie–Baxter type surface was formed by spray coating of $TiO_2$/PHMS nanocomposite. The superhydrophobicity of P–2 sample was lost after 13 min of continuous impact of water drops. By the time, due to impact of water drops, the composite material was removed off the coating surface and hence the roughness of the coating gets damaged resulting in loss of the superhydrophobicity.

The fragile and week micro-nanostructure gets destroyed under sandpaper and adhesive tape peeling test. The wettability is strongly dependent on surface structure of coating. The P-2 sample was placed on sandpaper of grit no. 400 and 50 g weight kept on it. Then, the sample was dragged with speed ~ 5 mm s$^{-1}$ for 10 cm and is considered as one cycle of sandpaper test. After every cycle, WCA was measured. The real-time arrangement of sandpaper abrasion test is shown in **Figure 4a**. The wettability

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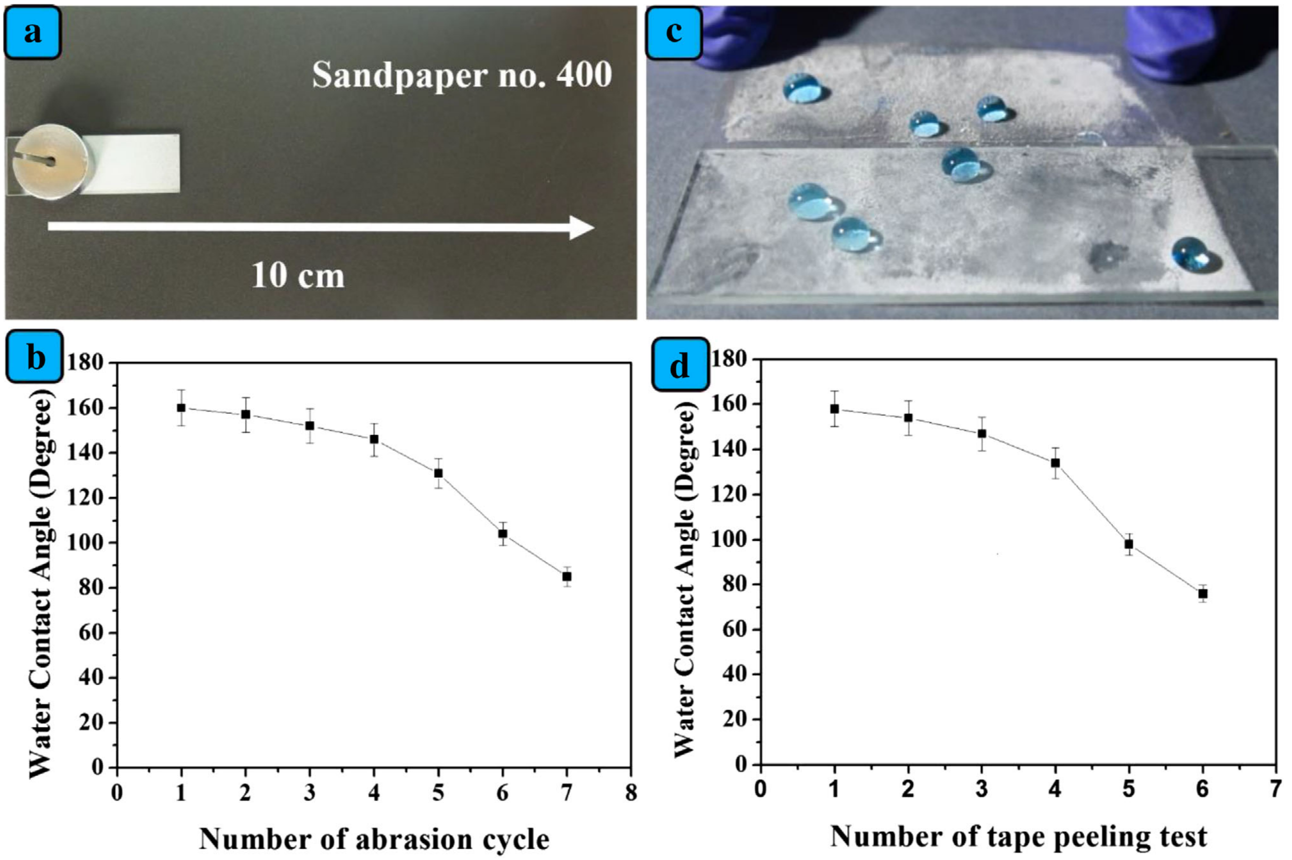


**Figure 4.** a) The arrangement of sandpaper abrasion test, b) The change in water contact angle with number of abrasion cycles, c) The optical image after first adhesive tape peeling test, and d) The variation of water contact angle with number of adhesive tape peeling test

of P-2 sample was drastically changed after sandpaper abrasion test. The change in wettability with sandpaper abrasion cycle is shown in graph Figure 4b. After three cycles of sandpaper abrasion test, the WCA of P-2 sample was decreased to 150°, and for seven cycles, the WCA decreased to 90°.

The Cello tape no.405 having adhesiveness 3.93 N/10 mm was placed on P-2 sample and gently pressed by fingertip to make good contact between surface and tape. The tape was peeled off slowly to test the adhesion of $TiO_2$/PMHS composite with glass surface. The superhydrophobic composite material sticks on tape as shown in Figure 4c. The water drop showed the water contact angle about 158° on both P-2 sample and peeled tape on which the coating material got adhered firmly. The effect of adhesive tape peeling cycles on the wettability of the coating is shown in Figure 4d. Like sandpaper abrasion test, the coatings showed decrease in WCA of 150° after three cycles of peeling test and WCA further decreased to 78° after six cycles. This confirms loosing of coating material off the coating surface against adhesive tape test.

### 2.3. Self-cleaning Behavior of SHP Surface

In the daily life, various types of dust particles inevitably contaminate the solid surface, and hence, the application of self-cleaning superhydrophobic coating is highly desirable. The self-cleaning performance of P–2 sample was demonstrated by spreading artificial soil dust as shown in **Figure 5a**. A sample was kept at a tilting angle about 30°, and the water droplets are dropped on it to clean the surface (Figure 5b). The rolling water droplet picks up the dust from SHP surface and eventually cleans the surface (Figure 5c). The reason for this is multiscale roughness with low surface material, which endowed the higher adhesion between dust and water than water and SHP surface, so that dust particles were easily carried away.[26]

## 3. Conclusion

We have demonstrated a facile method for fabrication of superhydrophobic surface using $TiO_2$ NPs/PMHS nanocomposite. The water contact angle of $163 \pm 2°$ and rolling angle of 6° was achieved by spraying $TiO_2$/polymethylhydrosiloxane nanocomposite on glass substrate. The bouncing water jet indicates stable air trapping inside the multiscale rough structure of the coating. The superhydrophobic coating exhibited excellent self-cleaning property. The mechanical durability tests confirmed the poor mechanical stability of the coating and hence the superhydrophobicity. We are further working in our laboratory to improve the transparency and mechanical durability of $TiO_2$ NPs/PMHS nanocomposite-based coating by optimization of size of $TiO_2$ NPS, its dispersion in PMHS, amount of PMHS, spray conditions, and annealing temperature.


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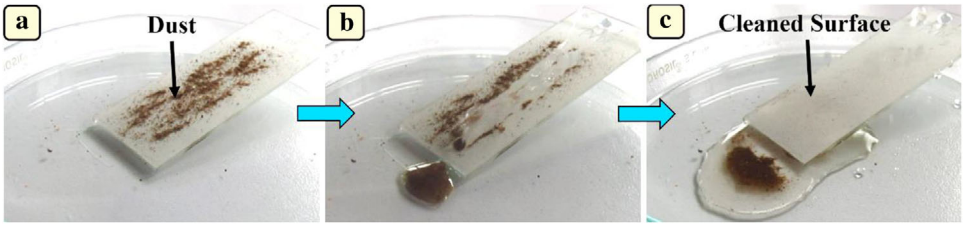


**Figure 5.** A self-cleaning behavior of P- 2 sample.

## 4. Experimental Section

*Materials*: Polymethylhydrosiloxane was bought from Sigma-Aldrich, USA. Titanium tetra isopropoxide (TTIP), ethanol, ammonium solution, and chloroform were purchased from Spectrochem PVT. LTD., India. Microglass substrates (75 × 25 × 1.35 mm) were obtained from Blue star, Polar Industrial Corporation, India.

*Preparation of $TiO_2$ NPs and Fabrication of Superhydrophobic Coatings*: The $TiO_2$ naoparticles were prepared by hydrothermal method using TTIP as a precursor.[22] At first, a mixture was prepared by adding 20 mL ethanol in 30 mL distilled water under constant stirring. Then, a mixture of 20 mL TTIP and 20 mL ethanol was added dropwise in above solution and stirring was continued for 3 h at 400 rpm. This solution was transferred to stainless steel autoclave and kept at 80°C for 24 h in oven. The residue was collected by paper filtration, dried at 40°C, and finally calcinated at 400°C for 2 h. The as-prepared $TiO_2$ NPs are hydrophilic in nature and used for preparation of superhydrophobic coating without hydrophobic modification. Next, a 0.01 mL PMHS was added in 5 mL of chloroform and stirred using magnetic stirrer. After 10 min of stirring, 100 mg $TiO_2$ NPs was added and stirred further for 1 h at 100 rpm. This solution was transferred to spray gun and sprayed on the clean glass substrate. The deposited glass substrate was dried at 100°C in oven for 1 h. The different samples were prepared by varying amount of PMHS, such as 0.01, 0.03, and 0.05 mL, and labeled by P-1, P-2, and P-3 samples, respectively.

*Characterizations*: The water contact angle and sliding angle were measured by using contact angle meter (HO-IAD-CAM-01; Holmarc Opto-Mechatronics Pvt. Ltd. India). Field emission scanning electron microscopy (SEM, JEOL, JSM-7610F, Japan) was used to observe surface morphology of the coating. A water jet was hit on the coating surface from 15 mL syringe. For water drop impact test, the coated glass substrate was kept at 30° inclination angle and water drops 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 ability was tested by spreading artificial dust particle and pouring water drops on it.

## Acknowledgements

This work is financially supported by DST–INSPIRE Faculty Scheme, Department of Science and Technology (DST), Govt. of India. [DST/INSPIRE/04/2015/000281]. SSL acknowledges financial assistance from the Henan University, Kaifeng, P. R. China. The authors greatly appreciate the support of the National Natural Science Foundation of China (21950410531).

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

Lotus effect and durability, nanocomposite, self-cleaning, superhydrophobic

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