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Spray Deposition of PDMS/Candle Soot NPs Composite for Self-Cleaning Superhydrophobic Coating

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The preparation of superhydrophobic coating using cheap candle soot nanoparticles (CS NPs) collected from candle flame is a very novel research topic. A less than 30 nm sized candle soot particles are collected by passing through stainless steel mesh of pore size~30 nm. An optimum suspension of CS NPs and polydimethylsiloxane (PDMS) in chloroform is sprayed on clean glass substrate and dried at 100°C for 1 hour. The coating surface with water contact angle~173° and rolling angle~ 4° is achieved by spraying suspension of 100 mg CS NPs and 0.3 mL PDMS in chloroform. The stability of superhydrophobic coating is studied by finger-wiping, water jet hitting, water dripping, adhesive tape, and sandpaper abrasion test. Result showed that the coatings prepared with an optimum 100 mg CS NPs in suspension are stable under water jet hitting and water dripping test. The superhydrophobicity is destroyed for four cycles of adhesive tape peeling and seven cycles of sandpaper abrasion tests. The coated substrate showed good self-cleaning performance. The high water repellent and self-cleaning property of the prepared coating can be adopted for industrial applications.

1. Introduction

Candle soot nanoparticles (CS NPs) have gained significant attention of researchers for its potential applications in various fields such as self-cleaning superhydrophobic coating,[1–3] anti-icing/anti-frosting,[4,5] oil-water separation,[6,7] drag-reduction,[8,9] lithium ion batteries,[10] infrared sensor,[11] and supercapacitor.[12] The water droplets display spherical shape on the surface prepared from inner flame soot particles, which leads to superhydrophobic property, whereas the water droplets spread out on the surface prepared from tip flame soot particles confirming hydrophilic property.[13,14] The combination of low surface energy material/nanoparticles with hierarchical rough surface exhibits water contact angle above 150° and rolling angle less than 10° and such surfaces are known as superhydrophobic surfaces. Nowadays, various techniques are used to develop superhydrophobic coating, including dip coating,[15] spray coating,[16] chemical vapor deposition (CVD),[3] and so on.[17–20] In nature, lotus leaves exhibit micro and nanoscale roughness along with epicuticular wax component (low surface energy material) on its surface. The existence of binary hierarchical structure on lotus leaf surface entrap air packets, which reduces water contact area on its surface. The water droplets roll off easily on such surfaces with collecting dust particles, and such phenomenon is known

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as self-cleaning effect or lotus effect.[21,22] The structure of lotus leaf gives key element to researcher for artificial development of the self-cleaning superhydrophobic surfaces.

To date, many reports are available on the preparation of CS NPs based superhydrophobic surfaces. Sahoo et al.[16] have spray coated the PDMS/camphor soot composite on epoxy resin coated glass and stainless steel substrate, which revealed self-healing and self-cleaning superhydrophobic property with water contact angle 174°. Also, the floatable superhydrophobic cotton gauge was prepared by depositing PDMS/carbon black composite.[23] The mechanical stability of superhydrophobic carbon soot coating was improved by decreasing the oxygen level during incomplete combustion of carbon particles that appeared in rapeseed oil.[24] A CVD of methyltrichlorosilane on candle soot template was responsible for superhydrophobic self-cleaning property and resisted water drop impact. This surface was also stable in corrosive liquid (pH-2–12) and at high temperature (up to 300°C).[3] Asthana et al.[25] have prepared superhydrophobic coating by casting three kinds of CS NPs namely, carbon black (CB), carbon nanotubes (CNTs), and grapheme nanoplatelets (GNPs) dispersion in fluropolymer. After comparison, it was confirmed that 50 wt % CB or CNT coating is highly resisting droplet impalement by water drops impacting at 3.7 m s^{-1}. Sahoo et al.[26] have prepared the EPF (expanded polystyrene foam)/candle soot and EPF/camphor soot composite coating on glass substrate by spin and spray coating method. They have concluded that, in comparison, the spray-coated EPF/camphor soot coating showed good superhydrophobic property with higher water contact angle of 165° and roll off angle of 2°. The candle soot deposition on electroless-modified aluminum surface depicted lotus leaf like texture with water contact angle 174°.[27] Similarly, the soot layer deposition on silicone-coated substrate revealed superhydrophobicity as well as good thermal and water flow impact stability.[28] Zhang et al.[29] have deposited silica film on soot-coated glass substrate by CVD with TEOS and ammonia. After calcination, the film was modified by flurosilane, which exhibited superhydrophobicity, good transparency, and self-cleaning performance. Seo et al.[30] used paraffin wax as a binder to fix fragile candle soot particles on substrate and fabricated stable superhydrophobic surface. The various surfaces, such as metal, ceramic, wood, plastic, and even paper, were coated by paraffin wax-fixed candle soot (PFCS). Sahoo and Balasubramanian[31] reported that PVDF/DMF/camphor soot and PVDF/DMF/candle soot composite coating revealed nano broccoli and nano cauliflower like hierarchical structure with water contact angle of 172° and 169°, respectively. In this process, quenching time effectively changes surface morphology and has an effect on superhydrophobicity.

Here, we prepared self-cleaning superhydrophobic coating using PDMS/CS NPs composite. The 30 nm sized CS NPs were obtained by passing soot particles through stainless steel mesh of pore size 30 nm. The different amount of CS NPs was dispersed into the mixture of PDMS and chloroform and coated on clean glass substrate using spray coating method. The hierarchical rough structure of coating reduces water contact area on it. The high water contact angle and low sliding angle of coating revealed excellent self-cleaning property. Hence, low-cost and simple preparation method of superhydrophobic coating is very applicable for practical applications.

2. Result and Discussion

2.1. Surface Morphology and Wettability of the Prepared Coating

A coating surface with superhydrophobic wetting properties was achieved by varying amount of CS NPs in coating solution. The surface morphology of PC-1, PC-2, and PC-3 samples was analyzed by SEM micrographs (**Figure 1d-f**). A highly porous and rough morphology was observed for all the samples. The CS NPs with nearly 30 nm in size got aggregated in PDMS network and forms nanoscale roughness. Also, many nanovoids were observed on the surface, which can ultimately trap the air pockets.[32] The nanoscale roughness and trapping of air pockets in the voids can be responsible for reduction in contact area of water on the surface. As shown in Figure 1g-i, the water drops takes the shape of ball on PC-1, PC-2, and PC-3 samples with WCAs of 167±2°, 173±2°, 171±2°, respectively, and rolls off at angle less than 5°. It is observed that, the WCA on coating surface increases from 167° to 173° with increasing amount of CS NPs, however decreased slightly (171°) for further increase in CS NPs in composite. This might be due to increased amount of CS NPs above optimum amount can fill up the roughness and ruining the chances of possible air trapping. Figure 1a-c depicts the shape of water drops on PC-1, PC-2, and PC-3 samples, respectively. The water drops kept at different positions on the samples show same spherical shape confirming uniform deposition of the PDMS/ CS NPs composite by spray coating.

2.2. Mechanical Durability Test

In outdoor use, the stability of the superhydrophobic coating is the most important factor. Mostly, rough surface of the coatings get damaged in rainy season due to water drops hitting the surface with high speed. The mechanical durability of the superhydrophobic coatings is generally tested by water jet impact, water dripping, finger-wiping, sandpaper abrasion, and adhesive tape peeling test.[33] The water jet impact test was carried by hitting water jet on PC-2 sample as shown in **Figure 2a**. The water was filled in 20 mL syringe and the force applied on syringe to produce water jet. The jet was bounced off in an opposite direction without spreading when it comes in contact of superhydrophobic coating. It was confirmed that only air pockets entrapped superhydrophobic coatings can repel water jet and bounces off.[34] The water jet was targeted at random spot on coating until the syringe was emptied. The water contact angle was measured at targeted spot of coating and confirmed the same wettability value as before testing. The stream of water droplets was formed by using water container connected with 5 mm diameter capillary tube as shown in Figure 2b. The PC-2 sample kept at 30° inclination angle and water stream dripped continuously on coating from the height of 5 cm. After dripping 1.0 L volume water, the wetting property of the sample was checked by measuring water contact angle. The value of contact angle reduced by 8°, and confirms that the PDMS/CS NPs composite surface with trapped air resists penetration of water drop.

A cello tape no.405 having adhesiveness value of 3.93 N/10 mm was applied on PC-2 sample. To make good contact between tape and coating, a 200 g weight was placed on it and dragged.[33] As shown in **Figure 3a**, after peeling off the tape, the

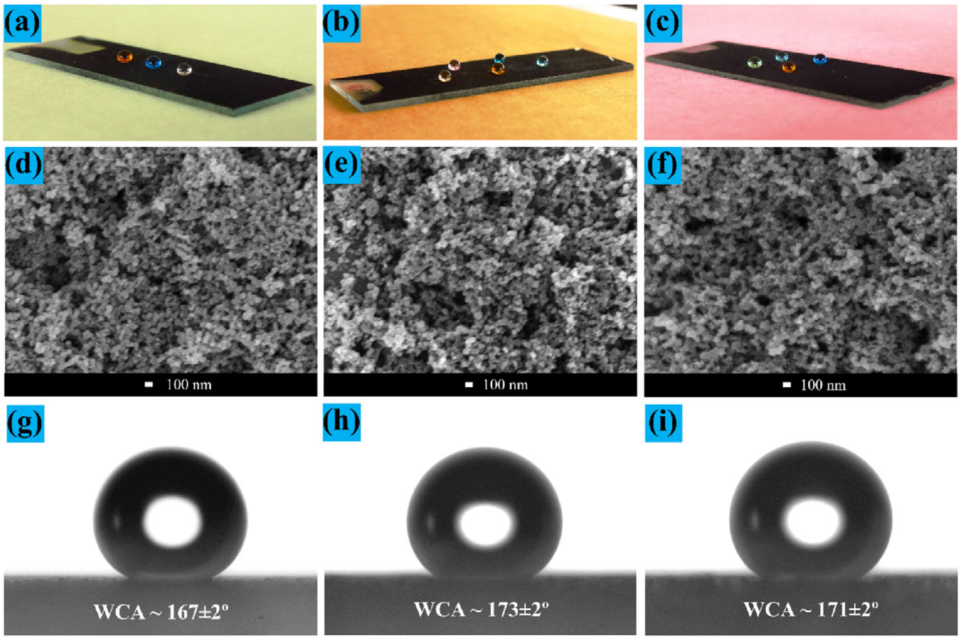

Figure 1. a–c) Optical images of color dyed water droplets, d–f) SEM micrographs, g–i) contact angle of water drops on PC-1, PC-2, and PC-3 samples, respectively.

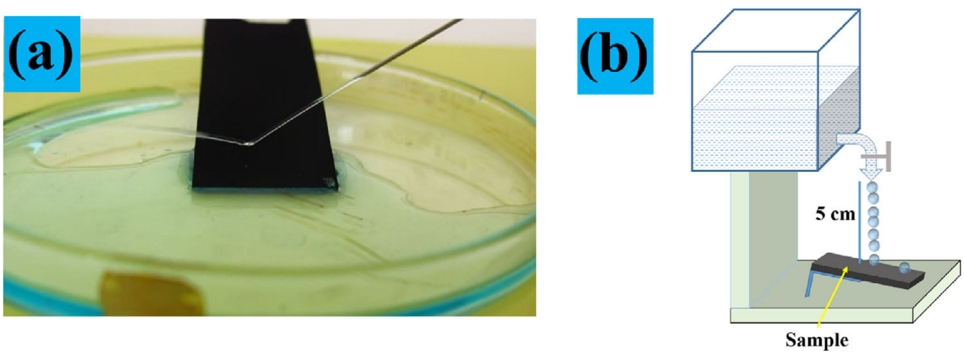

Figure 2. a) The optical image of water jet hitting, and b) schematic of water dripping on superhydrophobic PC-2 sample.

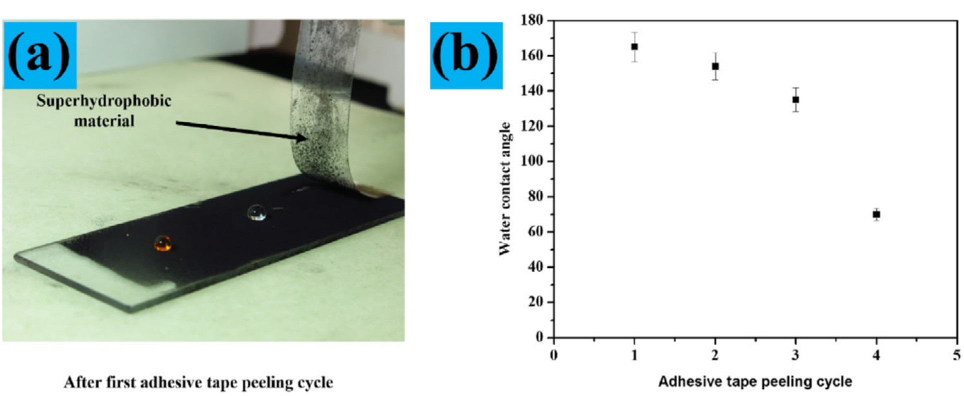

Figure 3. a) Adhesive tape peeling test, and b) relation between WCA and peeling cycles on PC-2 sample.

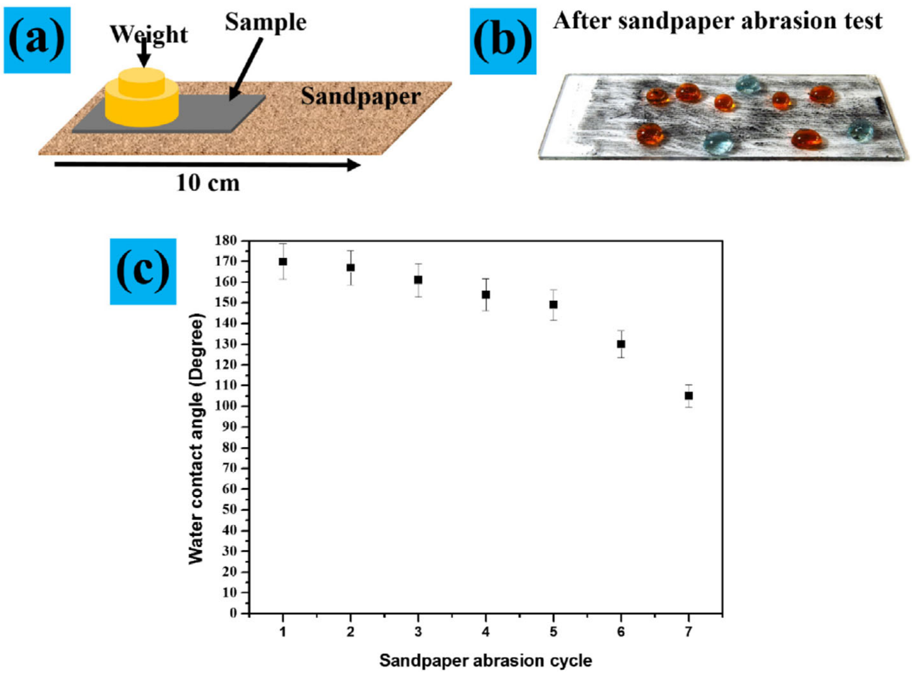

Figure 4. a) Schematic of sand paper abrasion test, b) PC-2 sample after abrasion test, and c) effect of abrasion cycle on WCA of PC-2 sample.

wettability was checked. The adhesive tape peeling experiment was carried out for multiple cycles, and at every cycle, contact angle was measured. For every cycle, fresh adhesive tape was used. After fourth cycle, coating showed hydrophilic nature with WCA of 74°. This was because, at every cycle of peeling test, the upper part of the coating material was removed (Figure 3a, on peeled tape). Hence, the thickness of the coating was gradually decreased, and henceforth, the roughness was deteriorated leading to a decrease in contact angle.

The mechanical abrasion can destroy the micro/nanoscale rough structure and hence the superhydrophobicity of surface can be lost. Usually, the sandpaper is used to check an abrasion resistance property of the superhydrophobic coating. In the schematic shown in **Figure 4a**, the sample with load (100 g) was dragged linearly for 10 cm on sandpaper grit no. 400. This is considered as one cycle of abrasion. The superhydrophobicity of the PC-2 sample was lost after seven abrasion cycles. After 07 sandpaper abrasion cycle, the wettability of the coated glass substrate turned into hydrophobic state as shown in Figure 4b. Also, the color of the coating was changed as a result of removal of PDMS/ CS NPs composite due to sandpaper abrasion. As depicted in Figure 4c, the WCA of the coating decreases gradually with sandpaper abrasion cycle. In each abrasion cycle, upper part of the coating was removed and hence the WCA of the surface got decreased due to loss of roughness.

2.3. Self-cleaning Property

Generally, the water and detergents are used to clean the surfaces. In cleaning process, the surface gets scratches, which eventually help to trap huge amount of dust particles. In repeated cleaning process, it reduces life span of the substrate. To avoid this problem, the surface modification is essential in current days. The self-cleaning ability of the prepared surface was tested by spreading artificial dust particles on the surface. **Figure 5** demonstrates the self-cleaning property of superhydrophobic PC-2 sample. The artificial dust particles were spread on superhydrophobic coating as shown in Figure 5a. It was clearly observed that, when water drop rolled on dust-contaminated superhydrophobic coating, the water drops picked up dust particles quickly and left the surface clean (Figure 5b). Hence, the prepared superhydrophobic coatings exhibited self-cleaning ability.

3. Conclusion

We have reported a simple and cheap way to prepare PDMS/CS NPs composite based superhydrophobic coating using spray coating method. The coating prepared with 100 mg of CS NPs in PDMS showed water contact angle of 173° and also exhibited excellent self-cleaning performance. The air trapped in the porous and rough surface structure of the coating boosts self-cleaning performance. The PDMS/CS NPs composite based superhydrophobic coating was studied under stability tests, including water jet hitting, water dripping, adhesive tape peeling, and sand paper abrasion tests. The coating lost their superhydrophobic property in four adhesive tape peeling and seven sandpaper abrasion cycles. The mechanical durability of the CS NPs based superhydrophobic coatings can still be improved by checking its compatibility with different polymers. This method can be extended to large surface area and wide range of substrate.

4. Experimental Section

Material: Candles (height 15 cm X diameter 2 cm) were bought from Delta Industries, India, and microglass slides (75 × 25 × 1.35 mm) were purchased from Blue star, Polar Industrial Corporation, India.

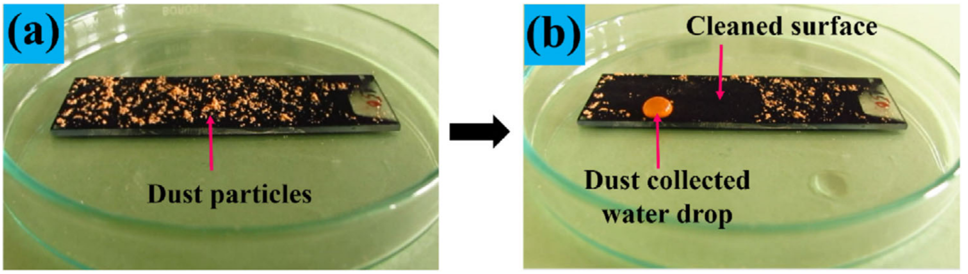

Figure 5. a) The dust particles spread on PC-2 sample and b) the water drops adsorbed the dust particles while rolling.

Polymethyldisiloxane was procured from Sigma-Aldrich, USA, and chloroform was purchased from Spectrochem PVT. LTD., India. A laboratory reagent was bought from Molyclean 02 Neutral, from Molychem, India.

Collection of Candle Soot Nanoparticles: A single candle was placed in silica crucible and candle soot was collected in a layered pattern on glass substrate by moving back and forth by holding in a middle part of a flame.[14,30] The soot particles were collected by scratching out from glass substrate and stored in glass bottle. A 500 mg candle soot was dispersed in 100 mL chloroform under sonication for 20 min. After that, a dispersion of candle soot was passed through stainless steel mesh (less than 30 nm pore size). The collected dispersion of CS NPs was dried at 40°C on hot plate to evaporate chloroform completely. Finally, dried CS NPs were stored in glass bottle.

Preparation of Superhydrophobic Coatings: The superhydrophobic coating was prepared on glass substrate through a spray coating process. Initially, glass slides were washed using tap water and the laboratory reagent. Finally, glass slides were ultra-sonicated for 20 min in ethanol/water and then by distilled water for 5 min.[16] The coating solution was prepared in following two steps. At first, 0.3 mL PDMS was added in 5 mL chloroform and stirred at rate of 100 RPM using magnetic stirrer. Then, after 10 min, 50 mg CS NPs were dispersed in above solution and stirring was continued for next 1 h. Eventually, the coating solution was transferred to cup of spray gun and sprayed on glass substrate at normal speed with nozzle to substrate distance of nearly 10 cm. The amount of CS NPs was varied from 50 to 150 mg in the coating solution. The spray-coated glass substrates were dried at 100°C for 1 h in oven. The coatings prepared with 50, 100, and 150 mg of CS NPs were labeled as PC-1, PC-2, and PC-3 samples, respectively.

Characterizations: The surface morphology of the prepared coating was investigated by scanning electron microscopy (SEM, JEOL, JSM-7610F, Japan). The water contact angle and sliding angle were measured on at least three places on samples by using contact angle meter (HO-IAD-CAM-01; Holmarc Opto-Mechatronics Pvt. Ltd., India). The average values of WCA and SA of samples were noted. The self-cleaning performance of the coatings was checked by spreading the fine particles of chalk as dust contaminant on the coating. The stability of coatings was examined by finger-wiping, beating water jet by syringe, and dropping water drops from the height of 5 cm on the coating. Adhesive tape test and sandpaper abrasion test were used to test mechanical stability of the coatings.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

candle soot, PDMS, superhydrophobic, wetting and self-cleaning

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