



ARTICLE

Fabrication of robust self-cleaning superhydrophobic coating by deposition of polymer layer on candle soot surface

Rajaram S. Sutar¹ | Sanjay S. Latthe¹ | Saravanan Nagappan² | Chang-Sik Ha² | Kishor Kumar Sadasivuni³ | Shanhu Liu⁴ | Ruimin Xing⁴ | Appasaheb K. Bhosale¹

¹Self-cleaning Research Laboratory, Department of Physics, Raje Ramrao College (Affiliated to Shivaji University, Kolhapur), Maharashtra, India

²Department of Polymer Science and Engineering, Pusan National University, Busan, Republic of Korea

³Center for Advanced Materials, Qatar University, Doha, Qatar

⁴Henan Key Laboratory of Polyoxometalate Chemistry, Henan Joint International Research Laboratory of Environmental Pollution Control Materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, China

Correspondence

Sanjay S. Latthe and Appasaheb K. Bhosale, Self-cleaning Research Laboratory, Department of Physics, Raje Ramrao College (Affiliated to Shivaji University, Kolhapur), Jath 416404, India. Email: latthes@gmail.com (S. S. L.) and akbhosale1@gmail.com (A. K. B.)

Ruimin Xing and Shanhu Liu, Henan Key Laboratory of Polyoxometalate Chemistry, Henan Joint International Research Laboratory of Environmental Pollution Control Materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China. Email: rmxing@henu.edu.cn (R. X.) and liushanhu@vip.henu.edu.cn (S. L.)

Funding information

National Natural Science Foundation of China, Grant/Award Number: 21950410531; Henan University; DST – INSPIRE Faculty Scheme, Department of Science and Technology (DST), Govt. of India, Grant/Award Number: DST/INSPIRE/04/2015/000281

Abstract

A facile and inexpensive way have been developed to fabricate robust self-cleaning superhydrophobic coating by depositing polymer layer on candle soot (CS) surface using dip coating method. The stability and robustness of the CS deposited superhydrophobic surface is much weaker due to weak interaction and nonchemical bonding with the substrate. We introduced a thin layer of polystyrene, polyethylene, polypropylene (PP), and polyvinylidene fluoride on CS surface in order to improve its mechanical properties. The fabricated surfaces with the use of respective polymers exhibited water contact angles of nearly 170, 174, 175, and 171° with sliding angles of 2, 1, 1, and 3°, respectively. Although, all the polymers used in this work exhibited excellent superhydrophobic and self-cleaning surface property, we found that the PP deposited CS surface exhibit better stability against water jet hitting and water drop impact tests. The PP deposited CS surface almost maintained their surface properties even after 50 cycles of sandpaper abrasion and 20 cycles of adhesive tape peeling tests. The mechanical durability tests confirmed that PP is a better polymer to improve the long-term durability of CS surface. Therefore, this simple, time saving, and inexpensive method for fabricating superhydrophobic coating can be used for potential industrial application.

KEYWORDS

Candle Soot, Lotus leaf, Polypropylene, Self-Cleaning, Superhydrophobic

1 | INTRODUCTION

Candle soot (CS) particles possess a unique wettability property and expressed as a promising material to fabricate

superhydrophobic coating. The hydrophobic CS particles can be collected easily and ecofriendly from the middle zone of candle flame without any further chemical modification. The CS based self-cleaning superhydrophobic

coating is emerging as a novel research topic. The superhydrophobic surface can show a water contact angle (WCA) higher than 150° and sliding angle (SA) less than 10° . The brief theory of wettability of solid surfaces was introduced independently by Wenzel,¹ and Cassie–Baxter² in the middle of the 20th century. Few decades later, German Botanist Barthlott³ have disclosed that the lotus leaf surface consisting of microscale papillae (rough surface) and nanostructured wax crystalloids (low surface energy material) which enables high repellency towards water. These literatures suggest that creating rough hierarchical surfaces with low surface energy materials is a primary requirement to achieve WCA of the surface higher than 150° . Since, the last two decades, the researchers are attracted towards the fabrication of superhydrophobic surfaces because of their potential applications in self-cleaning,^{4,5} oil–water separation,^{6,7} anticorrosive,⁸ antiscratching,⁹ anti-icing,^{10,11} drag-reduction,¹² antibacterial,¹³ and other fields.^{14,15} To date, many techniques have been developed for the preparation of superhydrophobic coatings including sol–gel coating,¹⁶ spray coating,¹⁷ dip coating,¹⁸ spin coating,¹⁹ chemical vapor deposition,²⁰ layer-by-layer deposition,²¹ and other techniques.^{22,23} The high-end applications of superhydrophobic coating can be achieved by a facile, low cost, and time-saving techniques.

CS is defined technically as the solid product of the incomplete combustion of hydrocarbons in the controlled atmosphere.²⁴ Liang et al.²⁵ have confirmed that the inner (middle) flame soot particles are superhydrophobic as well as superoleophilic and have a diameter of 20–55 nm due to the incomplete combustion of wax vapor. The weak Van der-Waals force of interaction become the major drawback of the CS deposited surface due to their fragile network.²⁶ The particles can be detached easily from the coated surface by simple mechanical pressing or by the contact of continuous water droplets due to nonchemical bonding and hence reduces the wetting property from superhydrophobic to hydrophobic or even hydrophilic.^{27,28} Latthe et al.²⁹ have discussed recent progress in the preparation of smart superhydrophobic surfaces using CS particles for self-cleaning and oil–water separation applications. The hydrophobic CS particles act as a fillers in development of superhydrophobic coating.

Recently, much attentions have been paid to improve the stability of CS deposited superhydrophobic surface in order to hold the deposited soot particles in the coated surface. The use of various binders or adhesives or cross-linking agents can help to improve the drawback of CS deposited superhydrophobic surface and enhance the surface adhesion and binding of CS particles in the coating.^{30–33} The materials such as paraffin wax,²⁸

polydimethylsiloxane (PDMS),³⁰ epoxy resin,³³ and polyvinylidene fluoride (PVDF)³² were used effectively to withhold the CS particles and enhancing the stability of the fabricated surface. Yuan et al.³⁴ have deposited CS particles on low-density polyethylene (LDPE) plate which is covered with a glue layer by holding on the top of candle flame with a height of 2 cm. The CS deposited LDPE plate showed WCA $\sim 160 \pm 2^\circ$ and SA $\sim 1^\circ$. Qahtan et al.³⁵ have prepared superhydrophobic surfaces by spraying dispersion of carbon nanoparticle on glass substrate. The prepared surface was thermally stable and exhibited robust surface property against water jet. Sahoo et al.³⁶ have deposited the composite solution of EPF (expanded polystyrene foam)/CS particle and EPF/camphor soot particles on glass slide using spin coater and spray gun separately. The spray coated EPF/CS and EPF/camphor soot composites showed WCA of 161 and 165° with rolling angle of 4 and 2° , respectively after curing at 373 K. In contrast, WCA of 152 and 155° were observed on spin coated EPF/CS and EPF/camphor soot composite, respectively. Xiao et al.³⁷ have fabricated superhydrophobic CS surface by modifying the CS deposited surface with methyltrichlorosilane (MTCS) and achieved WCA $\sim 161^\circ$ and a low SA $\sim 3^\circ$ in air. The fabricated surface also showed the WCA more than 150° in different oils and with low SA of 1° , which results to good self-cleaning property in air and oil. The superamphiphobic property of the surface is mainly due to the formation of coral-like microstructure by the deposition of MTCS on the CS layer.

The CS deposited superhydrophobic surface is playing a vital role in various applications.^{38–40} Wu et al.⁴⁰ have developed a photothermal icephobic surface by simple surface modification of soot coated glass substrate. The surface modification was performed by chemical vapor deposition of tetraethoxysilane (TEOS) on the soot coated glass surface followed by immersion in 2% PDMS-hexane solution. The fabricated substrate showed excellent photothermal icephobic property by rapid increase of temperature to 53°C with illumination intensity of one sun, which prevent the ice formation on the coated substrate. Similarly, a durable, self-healing, and self-cleaning superhydrophobic surface on glass and stainless steel substrates were fabricated by combining the spraying technique and solution immersion process of PDMS/camphor soot composite coating.³⁹ A biocompatible and stable superhydrophobic surface was also prepared by using a simple one-step method in which the soot particles get embedded in the PDMS matrix. The WCA of the prepared surface depends on the concentration of PDMS in n-hexane, sooting time, and coating speed.³⁸ The fabricated substrate showed excellent superhydrophobicity and superior blood repellent surface property. The silver-doped

superhydrophobic carbon soot coating surface was also prepared by spray coating technique. This coating displayed good surface adhesion under finger-wiping and high-impact water jetting, wear resistance towards sandpaper abrasion and antimicrobial performance.⁴¹

In order to address the aforementioned challenges in the literature about CS based coatings, it requires a facile approach to fabricate mechanically stable superhydrophobic CS surface. In the present work, a facile method for fabrication of robust self-cleaning superhydrophobic CS surface has been reported. The superhydrophobic CS layer was deposited on a clean glass slide by holding in the middle of a candle flame and subsequently immersed in the polymer solution. The dipping and withdrawal speed of the substrate in the polymer solutions were controlled by dip-coating machine. Herein, the effect of a various polymer layers on the CS particles loaded surfaces was examined. Generally, polymers offered stable and mechanically robust film on substrate as well as enhances the bonding between coating and substrate. Thermoplastic polymers such as polystyrene (PS), polyethylene (PE), polypropylene (PP), and PVDF were selected for this study because of the hydrophobic property as well as ease of availability of the polymers for mass production. Our fabricated surfaces by using the respective polymers on the CS deposited surfaces showed excellent stability and maintained the robust self-cleaning surface property. The results suggests that the simple surface modification using the commercial polymers can play an effective role for developing stable superhydrophobicity as well as self-cleaning property.

2 | EXPERIMENTAL

2.1 | Materials

Polystyrene (PS; 192,000 g/mol), polypropylene (PP; 12,000 g/mol), polyethylene (PE; 4000 g/mol), and

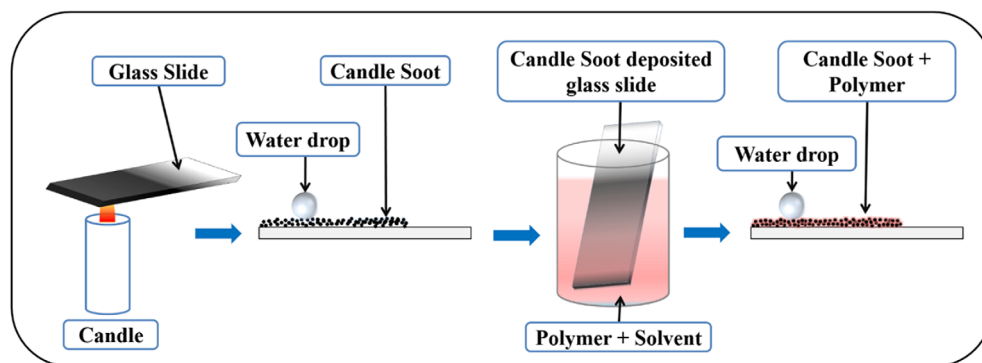
polyvinylidene fluoride (PVDF; 534, 000 g/mol) were purchased from the Sigma-Aldrich. The solvents toluene, acetone, and o-xylene were purchased from the Spectrochem Pvt. Ltd., India. Microglass slides ($75 \times 25 \times 1.35 \text{ mm}^3$) were obtained from the Blue star, Polar Industrial Corporation, India. Candles (height 15 cm \times diameter 2 cm) were bought from Delta Industries, India. A candle was used as source material for the generation of soot particles.

2.2 | Substrate cleaning and deposition of CS

The microglass slide was washed and cleaned with laboratory detergent (Molyclean O2 Neutral, from Molychem, India) and distilled water. The cleaned glass slide was dried at room temperature ($\sim 30^\circ\text{C}$) followed by uniform deposition of CS particles on the three-fourth area of the glass slide for about 30 s by moving back and forth in the middle part of candle flame in the open air.²⁸ The process of deposition of CS layer is shown in Scheme 1.

2.3 | Fabrication of superhydrophobic coating

The schematic process of deposition of polymer layer on the fragile network of CS surface is shown in Scheme 1. A polymer was used to fix the CS particles on the glass substrate. Various polymers were dissolved in their respective solvents (given in Table 1) such as PS solution prepared by using toluene and PVDF in acetone followed by 20 min ultrasonication. The solution of PE and PP were prepared by dissolving in the mixture of o-xylene and toluene in volume ratio of 1:1 at 40°C for 30 min. The CS deposited glass slides were dipped in various polymer solution under the optimized dipping time at constant dipping and withdrawal speed. The CS deposited glass slides were dipped for 4 min in PS and PVDF solution, 2 min in PE and



SCHEME 1 Preparation of superhydrophobic surface by candle soot/polymer [Color figure can be viewed at wileyonlinelibrary.com]

Polymer	Solvents	D/W speed of candle soot deposited glass slide (mm/s)	Dipping time (min)	Drying temperature (°C)
PS (0.2 g)	20 ml toluene	50	4	100
PE (1 g)	10 ml toluene + 10 ml o-xylene	50	2	100
PP (1.5 g)	10 ml toluene + 10 ml o-xylene	50	2	100
PVDF (0.2 g)	20 ml acetone	50	4	100

TABLE 1 Various polymers used to fabricate superhydrophobic coating

PP solution with dipping and withdrawal speed of 50 mm/s. All the samples were dried at 100°C for 1 h in an oven. Hereafter, PS, PE, PP, and PVDF layer deposited CS surfaces are named as P-1, P-2, P-3, and P-4 samples, respectively.

2.4 | Characterizations

The WCA and SA on the coatings were measured randomly at three different locations of samples by using contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India) and averaged the results to get a reliable value. The field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7610F, Japan) was used to investigate the surface microstructure of coating. The chemical compositions present in the coated material were investigated by energy dispersive spectroscopy (EDS). The samples were fixed on the carbon tape and gold was sputtered on the surface for obtaining better imaging. The self-cleaning performance of the coating was tested by spreading the chalk powder, orange color dye as dirt contaminant on the coating. A water drop impact resistance of the coating was investigated by dripping water droplets from the height of 20 cm and hitting water jet by syringe on the coating. The plastron stability and floating test were carried to confirm water repellent property of coating. Adhesive tape and sandpaper abrasion tests were used to test mechanical stability of the coatings using the commercial adhesive tape and sandpaper.

3 | RESULTS AND DISCUSSION

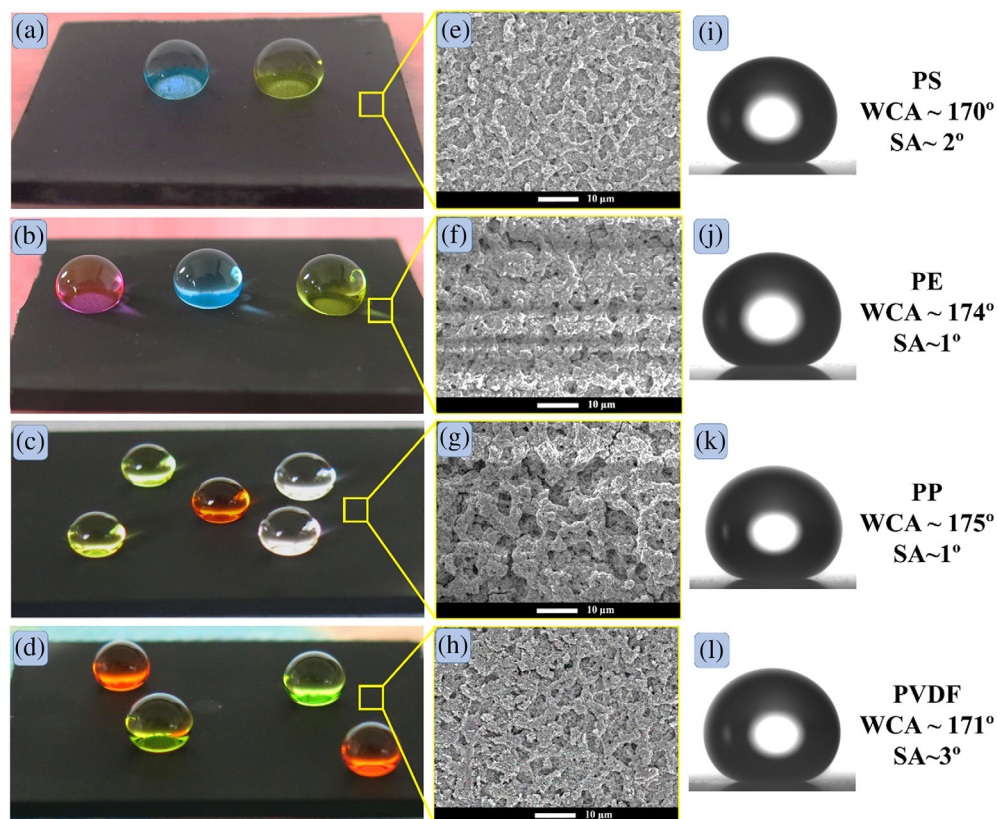
3.1 | Surface morphology and elemental composition of superhydrophobic coating

At first, soot was deposited on cleaned glass slide from candle flame. A polymer solution was prepared and then

applied to soot deposited glass through dip-coating method. The loosely bounded soot particles provided space for polymer solution to penetrate in and attach to the glass substrate as well as covering the surface of CS particles. The coated glass substrate dried at 100°C in order to remove the solvent and to create microscale pores in order to increase the surface roughness. The polymer nucleation is a heterogeneous nucleation and it starts on nonpolymeric particles.³² Here, CS particles act as a nonpolymeric particle, which are entangled in polymeric nucleation. The CS particles are interconnected with polymer chain forming ordered network like structure. The FE-SEM image of the CS covered with PS revealed the formation of plenty of microscale concave pits with sub-micrometer scale pores (Figure 1(e)). Similar microstructure was also observed when CS covered with PVDF as shown in Figure 1(h). The porous and coarse coating surface is found divided into microscale pits. Figure 1(f,g) reveals the combination of micro and nanoscale concave pits. The CS particles gathered to form porous structure. Thus, composite of air and solid surface was formed similar to Cassie–Baxter model.² The highly porous structure enables the entrapment of air pockets underneath the water droplets, which forms a layer of air cushion below these droplets. As a result, the fabricated surface revealed increased WCA and decreased SA, which leads water droplets to easily roll off the surface. The obtained results also suggest that the trapped air layer plays a vital role in the superhydrophobicity.^{42,43}

The higher magnification FE-SEM images of P-1 to P-4 samples are provided in Figure S1. The magnified FE-SEM images clearly showed the porous and branched hierarchical micro-nanostructure of the samples, which are nearly similar to the structure of nanoscale epicuticular wax crystals found on lotus leaf. The CS particles plays the role of additives to increase roughness and porosity of surface. The formation of micro-nano hierarchical surface morphology due to the aggregation of CS nanoparticles and coverage of polymers on it can lead to enhance the surface roughness. So that all the prepared

FIGURE 1 (a–d) Colored water droplets images, (e–h) field emission scanning electron microscopy images, and (i–l) optical images of water drop captured from candle soot meter of the P-1, P-2, P-3, and P-4 samples, respectively. PE, polyethylene; PP, polypropylene; PS, polystyrene; PVDF, polyvinylidene fluoride; WCA, water contact angle [Color figure can be viewed at wileyonlinelibrary.com]



coatings showed superhydrophobic property. The water droplets that were colored with different dyes exhibit spherical shape on P-1, P-2, P-3, and P-4 samples, respectively, as shown in Figure 1(a–d) respectively. Figure 1(i–l) displayed the optical photographs captured by CA meter along with WCA and SA values on P-1, P-2, P-3, and P-4 samples, respectively. All the fabricated samples showed excellent superhydrophobic property with WCAs higher than 170° with quite lower SAs less than 5° .

Further, the superhydrophobicity can be discussed by the Cassie–Baxter model.² The porous coating is considered to be a composite surface of air and solid fraction. The relationship between the CA of water droplet on smooth surface (θ) and that on a heterogeneous surface (θ_c) composed of air and solid was described by the Cassie–Baxter equation.

$$\cos \theta_c = f_1 \cos \theta - f_2, \quad (1)$$

where, θ_c is WCA on rough porous surface and θ ($\sim 38^\circ$) is WCA on smooth glass slide, f_1 and f_2 are the fraction of the solid surface and air in contact with water drop, respectively (i.e., $f_1 + f_2 = 1$).

This equation indicates that increasing the fraction of air (f_2) increases contact angle (θ_c) of rough surface. With the help of Equation (1), the f_2 values of P-1, P-2, P-3, and P-4 samples were calculated and given in Table 2.

TABLE 2 Calculation of air fraction in the prepared superhydrophobic coatings

Sample	Water contact angle (θ_c°)	f_2
P-1	170	0.980
P-2	174	0.993
P-3	175	0.995
P-4	171	0.984

The result suggest that the air occupies about 98.0%, 99.3%, 99.5%, and 98.4% of contact area between the water droplet and P-1, P-2, P-3, and P-4 samples, respectively.

EDS was used to detect the chemical composition of the coating. The inner flame soot particles consists of 91 atom% carbon (C) and 9 atom% oxygen (O).²⁵ In all the prepared coatings, C element appear at maximum percentage, which indicates that coating mainly consist of carbon atoms. The numerical values of atom percentage of carbon and oxygen in coating are given in Table 3. P-1 sample presented 69.04 atom% C and 30.96 atom% O. P-2 sample consist of 87.30 atom% C and 12.70 atom% O. P-3 sample contain of 93.30 atom% C and 6.70 atom% O. In P-4 sample, the atom% of C reach 99.62 and 0.38 atom% O only. The EDS graphical spectra of coatings are shown in Figure S2.

3.2 | Wetting stability of the prepared superhydrophobic coating

The water repellent property of the P3 sample was investigated by immersing it in the water (Figure 2(a)). A bright and silvery plastron layer observed clearly on the P3 sample was due to the excellent water repellent behavior as well as total reflectance of light at the air layer trapped in the coating. This trapped air layer prevents the coating from wetting by water (Figure 2(a)). The similar plastron layer was also observed for P-1, P-2, and P-4 samples when immersed in water (Figure S3(a-c)). These results suggest the formation of Cassie-Baxter type of superhydrophobicity in the coating.² In addition, the superhydrophobicity of the samples were further checked by a floating test. The test was carried out by leaving the superhydrophobic sample (2 cm length and 1 cm width) to float on water surface in Petri dish. The prepared superhydrophobic samples were able to float on water surface like a water strider. The floating ability of the P-3 sample was displayed in Figure 2(b), whereas, P-1, P-2, and P-4 samples were shown in Figure S4, respectively. The wetting stability of the prepared P-1, P-2, P-3, and P-4 samples were investigated by floating on water surface for several days. P-1 and P-4 samples were sink down after 2 days and P-2 sample after 5 days. On the other hand, P-3 sample showed excellent floating ability up to

10 days. The obtained result indicates the excellent superhydrophobic property as well as stability of P-3 sample than other polymer coated soot samples. While floating on the water surface, an air entrapped in the rough porous structure of the superhydrophobic coating remained trapped and will not allow water entity to wet the porous structure for long time.

3.3 | Water-jet and water-drop impact test

The water-jet and water-drop impact tests are important to analyze the mechanical durability of the superhydrophobic coating. Generally, micro-nano structured superhydrophobic coatings are fragile and the superhydrophobicity can be ruined by mild mechanical force. Many research groups stated that superhydrophobicity of the coating degrade by impacting water-jet or continuous water-drop.^{11,44} In present study, 10 ml syringe was filled by water and the water-jet was directed on the coating surface by applying normal force. At first, water-jet and water-drop impact tests were carried out on the merely CS deposited surface. We observed that CS particles were washed out completely with continuously hitting water jet and dripping water droplets and hence the superhydrophobicity was destroyed. It is due to the fact that the CS particles are weakly bounded with each other and also show very poor surface adhesion. Similarly, the water-jet was targeted on the same position of the prepared P-1 to P-4 samples for more than 1 min and then scanned over the coating surface Figure 3(a-d). The polymer-coated samples (P-1 to P-4) showed the continuous bouncing of the water-jet in the opposite direction due to excellent superhydrophobicity of the surface. This is due to the presence of low surface energy material and trapped air pockets in the porous structure, which do not

TABLE 3 Atom percentage obtained from energy dispersive spectroscopy of superhydrophobic coating

Sample	C (at %)	O (at. %)
P-1	69.04	30.96
P-2	87.30	12.70
P-3	93.30	6.70
P-4	99.62	0.38

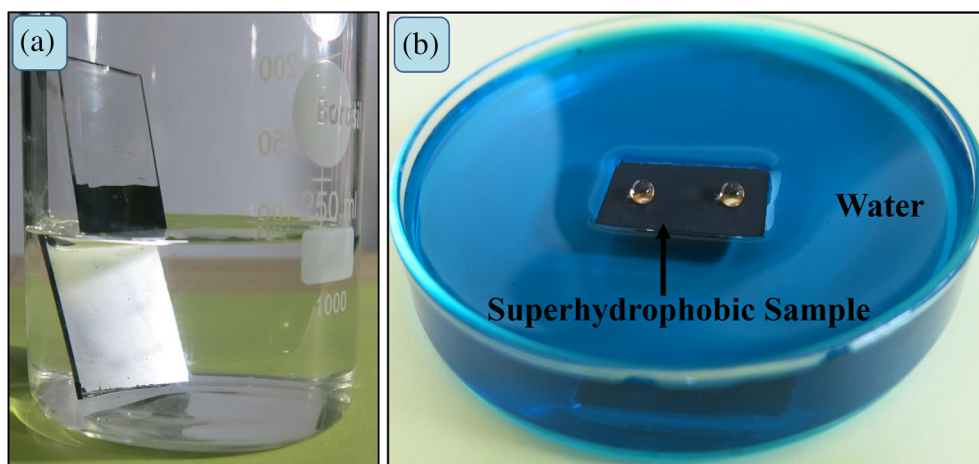


FIGURE 2 (a) Optical image of plastron layer on superhydrophobic P-3 sample, and (b) floating of superhydrophobic P-3 sample on water surface [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 The optical photographs of water-jet hitting on (a) P-1, (b) P-2, (c) P-3, and (d) P-4 samples [Color figure can be viewed at wileyonlinelibrary.com]

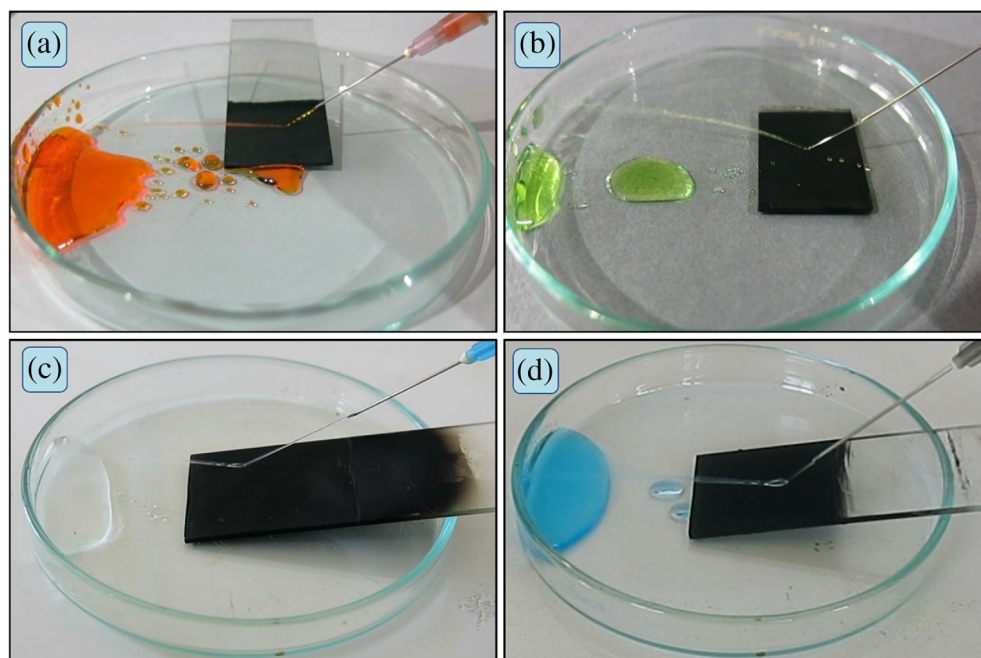
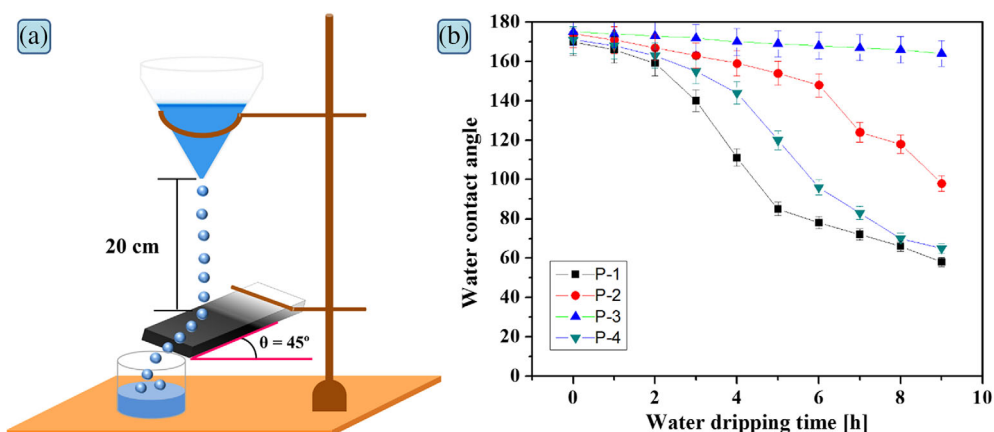


FIGURE 4 (a) the schematic set-up for water-drop impact test, (b) the relationship between water contact angle and water dripping time [Color figure can be viewed at wileyonlinelibrary.com]



allow impacting water-jet to wet the surface.^{45,46} The stable wetting properties of the water-jet impacted samples were confirmed further by checking the WCAs. We observed no substantial change in WCAs on the water-jet impacted samples confirming excellent mechanical durability of coating.

Superhydrophobic coatings can be subjected to the impact of water droplets (i.e., rainy season) and hence its effect should be studied. Water-drop impact test was conducted on the samples in order to prove its mechanical durability. A schematic set-up for water-drop impact test was shown in Figure 4(a). Water droplets were dripped at a rate of one drop per second on the sample located below 20 cm with tilting angle of 45°. Figure 4(b) shows the relationship between WCA and water dripping time. After exposing the samples to impacting water droplets for 9 h, the change in WCA was examined. A drastic decrease in WCAs was observed after 9 h of water dripping on the

P-1, P-2, and P-4 samples and that might be due to the damage prone to surface structure or elimination of trapped air from the rough structure. In contrast, a slight change in WCAs was observed for the P-3 sample after water-drop impact test (WCA ~ 164° and SA ~ 9°) which proves the mechanical robustness of the surface structure as well as preservation of trapped air inside the highly porous structure. Water-drop impact test also proved that P-3 sample showed excellent mechanical durability and maintained the superhydrophobicity as compared with other samples prepared by the similar approach.

3.4 | Self-cleaning property of the prepared superhydrophobic coating

Self-cleaning is the most important characteristic of the superhydrophobic coating. Inspired from lotus leaf, a

high water repellent coating with self-cleaning ability can be developed. The durable self-cleaning superhydrophobic coating plays a significant role in various industrial applications.⁴⁸ The air occupies about 99% of contact area between water droplet and the prepared superhydrophobic coating, which adequately helps in self-cleaning performance. Therefore, any dust present on coating can be easily picked-up by rolling water drops. Figure 5(a–d) reveals the optical images of self-cleaning performance by P-1, P-2, P-3, and P-4 samples, respectively. The chalk dust arbitrarily sprayed on P-1 sample (Figure 5(a)) and tilted by $\sim 10^\circ$. The water droplets

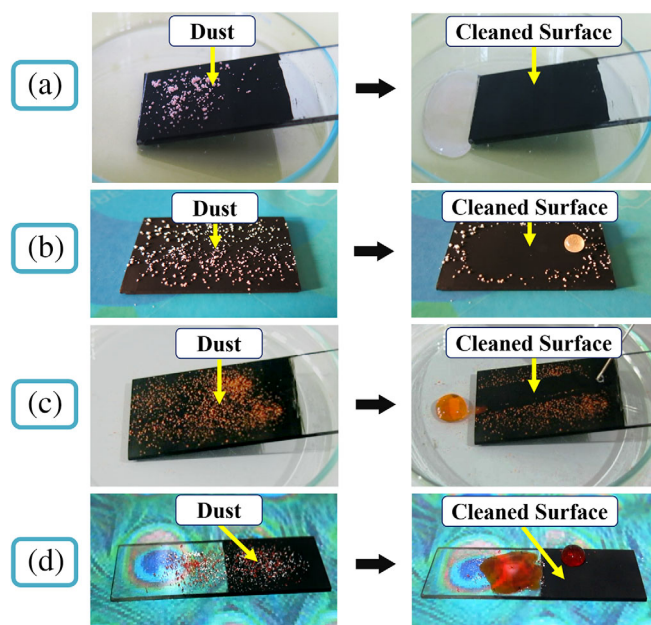


FIGURE 5 Self-cleaning behavior of prepared superhydrophobic coatings, (a) P-1, (b) P-2, (c) P-3, and (d) P-4 samples [Color figure can be viewed at wileyonlinelibrary.com]

dripped on sample, the rolling water droplets carried away the dust particles and left a clean superhydrophobic surface. The P-2 sample was kept horizontal and initially covered the entire surface of sample with chalk dust as shown in Figure 5(b). A water drop of volume $20\ \mu\text{l}$ was made rolled on the dust contaminated sample with the help of syringe needle tip. The rolling water drop adsorb the dust particles from the sample (Figure 5(b)). The dust adsorbed water drop shows spherical shape, which indicates that the adhesion between dust particle and water droplets is greater than adhesion between dust particles and coating. The orange color dye was sprinkled on P-3 sample and kept inclined at $\sim 10^\circ$ (Figure 5(c)). The water drops gently placed on coating by syringe, water drop rolled down from the coating and carried away the dust particles from its path is shown in Figure 5(c). Figure 5 (d) depicts the mixture of dye and chalk particles scattered on uncoated and coated sample (P-4 sample). On uncoated sample, water drop spreads and dust particles stick on it. Hence, it does not show self-cleaning property. Using syringe tip a water drop rolled on dust-contaminated sample. The freely rolling water drop catches the dust particles from coated sample keeping it clean and dust free (Figure 5(d)). In all these attempts, it was confirmed that the prepared P-1 to -P-4 samples show excellent self-cleaning ability. The corresponding videos of self-cleaning performance of the coatings are provided in the supporting information (Video S1(a–d)).

3.5 | Adhesive tape and sandpaper abrasion tests

The mechanical stability of the fabricated coating was also investigated further by adhesive tape and sandpaper

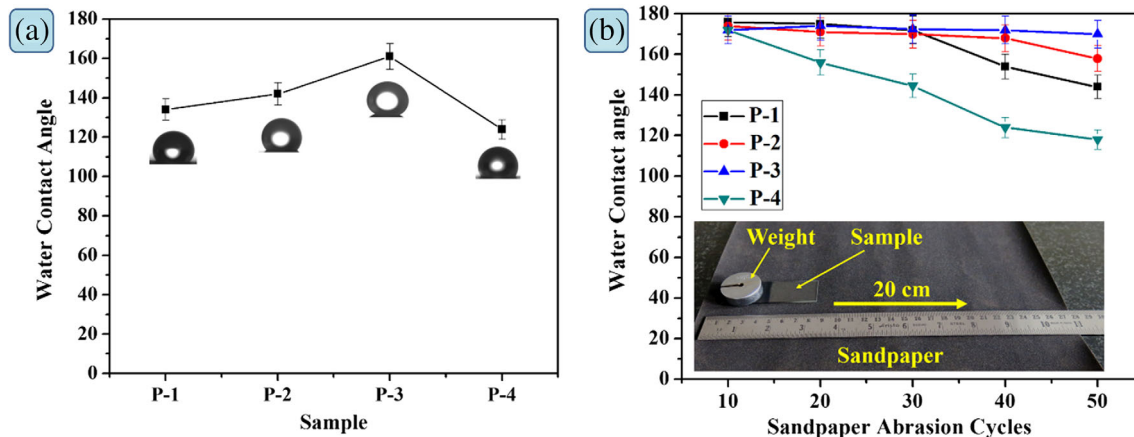


FIGURE 6 The relationship between (a) water contact angle (WCA) and polymer deposited candle soot surface after 20 adhesive tape cycles, and (b) WCA and sandpaper abrasion cycles [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Comparison between superhydrophobicity and durability tests of CS based coating

Materials	Method	WCA/SA (°)	Water-drop impact test from height/volume	Adhesive-tape test strength/peeling cycle	Sandpaper abrasion test load/distance	References
CS/EPF (expanded polystyrene foam)	Spray coating	161/4	—	—	—	36
CS/MTCS	Vapor deposition	161/3	1500 ml/20 cm	—	—	37
CS/PVDF/DMF	Casting	169/3	—	—	—	32
CS/PDMS	Dip coating	163/1	4500 ml/10 cm	—	—	31
CS/paraffin wax	—	162/1	10,000 drops/10 cm	—	—	28
CS/TEOS/PDMS	Dip coating and CVD	163/2	20 L	—	—	51
CS/TiO ₂ /1H,1H,2H,2H-perfluorodecyltriethoxysilane (FAS)	Template method	168/1	5 ml/s for 6 days/20 cm	—	—	52
CS/PDMS	CVD	157/3	330,800 drops/10 cm	—	—	53
CS/silver hydrogen fluoride	Spray coating	—	—	—	100 g/150 cm	41
Carbon nanoparticles-acetone	Spray coating	—	1000 drops/80 cm	—	—	35
CS-PS	Dip coating	170/2	7200 drops/20 cm	4 N/m/12 cycles	50 g/800 cm	Present study
CS-PE	Dip coating	174/1	18,000 drops/20 cm	4 N/m/17 cycles	50 g/1000 cm	Present study
CS-PP	Dip coating	175/1	32,400 drops/20 cm	4 N/m/20 cycles	50 g/1000 cm	Present study
CS-PVDF	Dip coating	171/3	10,800 drops/20 cm	4 N/m/8 cycles	50 g/400 cm	Present study

Abbreviations: CS, candle soot; MTCS, methyltrichlorosilane; PDMS, polydimethylsiloxane; PE, polyethylene; PP, polypropylene; PS, polystyrene; PVDF, polyvinylidene fluoride; SA, sliding angle; TEOS, tetraethoxysilane; WCA, water contact angle.

abrasion tests. Mostly, the industrial applications of superhydrophobic coating are ignored due to their poor mechanical stability. In superhydrophobic coating research, adhesive tape and sandpaper abrasion tests are used widely to study the mechanical stability.^{49,50} In this work, the adhesive tape having adhesion strength of 4 N/m was used to study the mechanical stability of coating. The tape was applied on the coating and confirmed good contact between tape and coating surface. After that, the tape was peeled off slowly to study the coating stability. This process was repeated for 20 cycles and then measured the WCAs on the coating surface. The variation of WCA with adhesive tape peeling cycles was shown in Figure 6(a). We observed that a small amount of coating material was stuck on tape for the P-3 sample and revealed the WCA value nearly 161° after 20 cycles. In contrast, WCAs found decreased for P-1, P-2, and P-4 samples due to more adhesion of coating material on the tape as compared with P-3 sample. This test results indicate that the CS particles strongly entangled in PP chain, and weakly in PS, PE, and PVDF, respectively.

The mechanical abrasion resistance is a key factor for superhydrophobic coating. In the day-to-day applications, hard and mechanical abrasion resistant coating directly effect on lifespan of superhydrophobicity. Generally, sandpaper abrasion test was used to study the mechanical abrasion resistance of the coating. The test was performed by placing a sandpaper (grit no. 320) on the coated glass slide with 50 g weight on it and dragged for 20 cm with speed of 5 mm/s for one cycle of abrasion. The WCA was measured after each 10 cycles of abrasion reveals the change in WCA as a function of number of abrasion cycles (Figure 6(b)). A pictorial abrasion test set-up was shown as an inset image of Figure 6(b). We observed that the WCA of P-3 sample was reduced by ~5° after 50 abrasion cycles, which indicates the prepared coating has stable under mechanical abrasion. This is due to the strong adherence of CS particles by PP on the substrate. The WCA of P-1, P-2, and P-4 samples were reduced by ~53, ~26, and 16°, respectively, which confirm that PS, PE, and PVDF weakly bind the CS particle on the substrate. The adhesive tape and sandpaper abrasion tests were also confirmed that PP is a good polymer for the fabrication of superhydrophobic coating with CS composition. Table 4 compares the durability of the superhydrophobic surfaces, which were fabricated using CS particles/polymer composition in the literature. The comparison table suggest that our developed superhydrophobic coating showed better performance and robustness with high mechanical stability.

4 | CONCLUSIONS

The robust self-cleaning superhydrophobic coating was fabricated by deposition of CS layer on glass slide followed by applying a thin layer of PP via dip coating method. The spherical water drop exhibit WCAs nearly 170, 174, 175, and 171° along with SAs nearly 2, 1, 1, and 3° on the CS coatings modified with PS, PE, PP, and PVDF, respectively. The rolling water droplets carried away the dust particles and left a clean superhydrophobic coating, which confirmed excellent self-cleaning ability of the fabricated coatings. A continuous water-jet hitting (more than 1 min) and water droplet dripping (9 h) on the PP-CS coating revealed no loss in superhydrophobicity and hence confirmed its good mechanical stability. The PP-CS coated glass slide remained floating on the water surface for 10 days and also showed stable plastron layer at the coating while immersing in water, which express an excellent water-repellent nature. The stable wetting property under sandpaper abrasion and adhesive tape tests also revealed high mechanical stability of the PP-CS coating. The above results indicate that, the PP layer applied CS surface has excellent stability and robustness than PS, PVDF, and PE covered CS surface.

An important highlights of this work is;

- The CS coated surface can maintain the superhydrophobicity on the coated glass substrate by the introduction of polymers.
- PP playing a pivotal role in enhancing the surface contact angle as compared to other polymers such as PS, PE, and PVDF.
- The PP coated substrate also showed better stability and robustness as compare to other polymer-coated substrate.
- A simple and faster fabrication of stable superhydrophobic coating can be obtained by applying PP on CS coated substrate, which also revealed the excellent self-cleaning ability.

All the obtained results suggest that our facile and inexpensive method for fabricating stable superhydrophobic coatings could find potential usage in industrial applications.

ACKNOWLEDGMENTS

This work is financially supported by DST – INSPIRE Faculty Scheme, Department of Science and Technology (DST), Govt. of India. (DST/INSPIRE/04/2015/000281). Sanjay S. Latthe acknowledges financial assistance from the Henan University, Kaifeng, China. We greatly appreciate the support of the National Natural Science Foundation of China (21950410531).

ORCID

Rajaram S. Sutar  <https://orcid.org/0000-0002-9184-5038>

REFERENCES

- [1] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.
- [2] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
- [3] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1.
- [4] F. Geyer, M. D'Acunzi, A. Sharifi-Aghili, A. Saal, N. Gao, A. Kaltbeitzel, T.-F. Slood, R. Berger, H.-J. Butt, D. Vollmer, *Sci. Adv.* **2020**, *6*, eaaw9727.
- [5] S. S. Latthe, R. S. Sutar, V. S. Kodag, A. K. Bhosale, A. M. Kumar, K. Kumar Sadasivuni, R. Xing, S. Liu, *Prog. Org. Coat.* **2019**, *128*, 52.
- [6] S. K. Samal, S. Mohanty, S. K. Nayak, in *Superhydrophobic Polymer Coatings* (Eds: S. S. Latthe, R. S. Sutar, A. K. Bhosale, K. K. Sadasivuni, S. Liu), Elsevier, Amsterdam, Netherlands **2019**, Chapter 15, p. 339.
- [7] S. S. Latthe, R. S. Sutar, T. B. Shinde, S. B. Pawar, T. M. Khot, A. K. Bhosale, K. K. Sadasivuni, R. Xing, L. Mao, S. Liu, *ACS Appl. Nano Mater.* **2019**, *2*, 799.
- [8] Y.-C. Liu, W.-J. Huang, S.-H. Wu, M. Lee, J.-M. Yeh, H.-H. Chen, *Corros. Sci.* **2018**, *138*, 1.
- [9] N. Ning, S. Wang, Z. Zhang, Z. Feng, Z. Zheng, B. Yu, M. Tian, L. Z. Ning, *Chem. Eng. J.* **2019**, *373*, 318.
- [10] S. S. Latthe, R. S. Sutar, A. K. Bhosale, S. Nagappan, C.-S. Ha, K. K. Sadasivuni, S. Liu, R. Xing, *Prog. Org. Coat.* **2019**, *137*, 105373.
- [11] C. Peng, Z. Chen, M. K. Tiwari, *Nat. Mater.* **2018**, *17*, 355.
- [12] C. Wang, F. Tang, Q. Li, Y. Zhang, X. Wang, *Colloids Surf. A* **2017**, *514*, 236.
- [13] A. Tripathy, A. Kumar, S. Sreedharan, G. Muralidharan, A. Pramanik, D. Nandi, P. Sen, *ACS Biomater. Sci. Eng.* **2018**, *4*, 2213.
- [14] P. Varshney, J. Lomga, P. K. Gupta, S. S. Mohapatra, A. Kumar, *Tribol. Int.* **2018**, *119*, 38.
- [15] D. Zhi, Y. Lu, S. Sathasivam, I. P. Parkin, X. Zhang, *J. Mater. Chem. A* **2017**, *5*, 10622.
- [16] S. S. Latthe, C. Terashima, K. Nakata, M. Sakai, A. Fujishima, *J. Mater. Chem. A* **2014**, *2*, 5548.
- [17] X. Gong, S. He, *ACS Omega* **2020**, *5*, 4100.
- [18] A. B. Gurav, Q. Xu, S. S. Latthe, R. S. Vhatkar, S. Liu, H. Yoon, S. S. Yoon, *Ceram. Int.* **2015**, *41*, 3017.
- [19] M. K. Meena, A. Sinhamahapatra, A. Kumar, *Colloid Polym. Sci.* **2019**, *297*, 1499.
- [20] M. M. Aljumaily, M. A. Alsaadi, R. Das, S. B. A. Hamid, N. A. Hashim, M. K. AlOmar, H. M. Alayan, M. Novikov, Q. F. Alsahy, M. A. Hashim, *Sci. Rep.* **2018**, *8*, 1.
- [21] H. Li, X. Wang, Y. He, L. Peng, *Cellulose* **2019**, *26*, 2055.
- [22] K. D. Esmeryan, C. E. Castano, Y. I. Fedchenko, R. Mohammadi, I. K. Miloushev, K. A. Temelkov, *Colloids Surf. A* **2019**, *567*, 325.
- [23] B. Gao, X. Du, Y. Liu, B. Song, S. Wei, Y. Li, Z. Song, *Vacuum* **2019**, *159*, 29.
- [24] R. M. Manasi, A. Chauhan, S. Patel, f V. Balakrishnan, A. Halder, R. Vaish, *Carbon* **2019**, *144*, 684.
- [25] C.-J. Liang, J.-D. Liao, A.-J. Li, C. Chen, H.-Y. Lin, X.-J. Wang, Y.-H. Xu, *Fuel* **2014**, *128*, 422.
- [26] B. N. Sahoo, B. Kandasubramanian, *Mater. Chem. Phys.* **2014**, *148*, 134.
- [27] X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, *Science* **2012**, *335*, 67.
- [28] K. seo, M. Kim, H. K. Do, *Carbon* **2014**, *68*, 583.
- [29] R. Höfer, A. S. Matharu, Z. Zhang, in *Green Chemistry for Surface Coatings, Inks and Adhesives: Sustainable Applications* (Eds: S. S. Latthe, K. Nakata, R. Höfer, A. Fujishima, C. Terashima), London, United Kingdom **2019**, Chapter 5, p. 92.
- [30] X. Lin, S. Park, D. Choi, J. Heo, J. Hong, *J. Ind. Eng. Chem.* **2019**, *74*, 79.
- [31] X. Liu, Y. Xu, K. Ben, Z. Chen, Y. Wang, Z. Guan, *Appl. Surf. Sci.* **2015**, *339*, 94.
- [32] B. N. Sahoo, K. Balasubramanian, *J. Colloid Interface Sci.* **2014**, *436*, 111.
- [33] P. Singh, S. S. Chauhan, G. Singh, M. Sharma, V. P. Singh, R. Vaish, *J. Appl. Polym. Sci.* **2020**, *137*, 48678.
- [34] Z. Yuan, J. Huang, C. Peng, M. Wang, X. Wang, J. Bin, S. Xing, J. Xiao, J. Zeng, X. Xiao, X. Fu, H. Gong, D. Zhao, H. Chen, *Appl. Phys. A* **2016**, *122*, 125.
- [35] T. F. Qahtan, M. A. Gondal, I. O. Alade, M. A. Dastageer, *Sci. Rep.* **2017**, *7*, 7531.
- [36] B. N. Sahoo, K. Balasubramanian, M. Sucheendran, *J. Phys. Chem. C* **2015**, *119*, 14201.
- [37] L. Xiao, W. Zeng, G. Liao, C. Yi, Z. Xu, *ACS Appl. Nano Mater.* **2018**, *1*, 1204.
- [38] R. Iqbal, B. Majhy, A. Sen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 31170.
- [39] B. N. Sahoo, S. Nanda, J. A. Kozinski, S. K. Mitra, *RSC Adv.* **2017**, *7*, 15027.
- [40] S. Wu, Y. Du, Y. Alsaaid, D. Wu, M. Hua, Y. Yan, B. Yao, Y. Ma, X. Zhu, X. He, *Proc. Natl. Acad. Sci.* **2020**, *117*, 11240.
- [41] K. D. Esmeryan, C. E. Castano, T. A. Chaushev, R. Mohammadi, T. G. Vladkovad, *Colloids Surf. A* **2019**, *582*, 123880.
- [42] D. Parbat, A. Das, K. Maji, U. Manna, *J. Mater. Chem. A* **2020**, *8*, 97.
- [43] L. Shen, W. Wang, H. Ding, Q. Guo, *Appl. Surf. Sci.* **2013**, *284*, 651.
- [44] T. Bharathidasan, S. Sathiyanyanan, *Prog. Org. Coat.* **2020**, *148*, 105828.
- [45] A. Kibar, H. Karabay, K. S. Yiğit, I. O. Ucar, H. Y. Erbil, *Exp. Fluids* **2010**, *49*, 1135.
- [46] S. S. Latthe, P. Sudhagar, C. Ravidhas, A. Jennifer Christy, D. David Kirubakaran, R. Venkatesh, A. Devadoss, C. Terashima, K. Nakataac, A. Fujishima, *CrstEngComm* **2015**, *17*, 2624.
- [47] R. S. Sutar, S. S. Latthe, A. K. Bhosale, R. Xing, S. Liu, *Macromol. Symp.* **2019**, *387*, 218.
- [48] P. D. Sanjeev, M. A. S. Aly, S. S. Latthe, R. Xing, R. S. Sutar, S. Nagappan, C.-S. Had, K. K. Sadasivuni, S. Liu, *Prog. Org. Coat.* **2020**, *138*, 5381.
- [49] S. S. Latthe, P. Sudhagar, A. Devadoss, A. Madhan Kumar, S. Liu, C. Terashima, K. Nakataa, A. Fujishima, *J. Mater. Chem. A* **2015**, *3*, 14263.
- [50] M. Satapathy, P. Varshney, D. Nanda, A. Panda, S. S. Mohapatra, A. Kumar, *Cellul.* **2017**, *24*, 4405.
- [51] Y. Wang, Y. Zhu, C. Zhang, J. Li, Z. Guan, *ACS Appl. Mater. Interfaces* **2017**, *9*, 4142.

- [52] S. Liu, M. Sakai, B. Liu, C. Terashima, K. Nakata, A. Fujishima, *RSC Adv.* **2013**, 3, 22825.
- [53] X. Liu, Y. Xu, Z. Chen, K. Ben, Z. Guan, *RSC Adv.* **2015**, 5, 1315.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Sutar RS, Latthe SS, Nagappan S, et al. Fabrication of robust self-cleaning superhydrophobic coating by deposition of polymer layer on candle soot surface. *J Appl Polym Sci.* 2020;e49943. <https://doi.org/10.1002/app.49943>