



Durable Self-Cleaning Superhydrophobic Coating of SiO₂–Cyanoacrylate Adhesive via Facile Dip Coat Technique

Rajaram S. Sutar, Sanjay S. Latthe, A. K. Bhosale, Ruimin Xing,* and Shanhu Liu*

The hydrophobic silica nanoparticles have been widely used in the fabrication of superhydrophobic surfaces. In this study, we prepared superhydrophobic coating using hydrophobic SiO₂ nanoparticles by facile dip coat technique. After that, a layer of cyanoacrylate adhesive was applied to improve the durability of the superhydrophobic coating. Finally, the coating was annealed at 200 °C for 10 min. A water drop on prepared superhydrophobic coating showed contact angle $\approx 173^\circ$ and sliding angle $\approx 1^\circ$. The prepared superhydrophobic coating revealed self-cleaning behavior for more than 2 years. This approach can be useful for fabrication of superhydrophobic coating for practical industrial application including solar panel, windows glass, vehicle glass and fabrics, and so on.

separation and drag-reduction.^[5–9] The research on self-cleaning superhydrophobic solid surfaces is currently a hot topic in materials science.

Ogihara et al.^[10] sprayed the suspension of SiO₂ in alcohol on paper and confirmed dependency of superhydrophobicity on the aggregation states of nanoparticles, which are determined by the type of alcohol used in the suspensions. Latthe et al.^[11] have applied the suspension of hydrophobic silica nanoparticles on various types of industrial objects including the body of motorcycle, building wall, mini boat, solar cell panel, window glass, cotton shirt, fabric shoes, paper (currency notes), metal, wood, sponges, plastic and marble, and so on. This work

1. Introduction

The self-cleaning concept originates from *N. nucifera* lotus leaf. Lotus leaf surface is self-cleaning surface because water drops easily roll off the leaf surface by adopting dust particles. At first, Barthlott and Neinhuis studied the surface structure of the lotus leaves using a scanning electron microscope, which revealed the coexistence of micro and nanostructures.^[1] That enables the trapping of air underwater droplets so the contact area of a water droplet on it consequently reduces. The low surface energy wax on lotus leaf leads to water repellent property.^[2] The Wenzel^[3] and Cassie-Baxter^[4] proposed a theory to explain the wetting phenomenon on a rough surface. The superhydrophobic surfaces are generally prepared by creating a rough surface using low surface energy materials. The superhydrophobicity of the surface characterized by high water contact angle (higher than 150°) and low sliding angle (less than 10°), have tremendous applications in self-cleaning, anti-corrosive, antifouling, anti-adhesion, oil-water

reports that such coated surfaces exhibit water contact angle nearly 160° and sliding angle less than 6° with excellent and durable self-cleaning performance. Kokare et al.^[12] have prepared self-cleaning superhydrophobic surface by applying a multiple layer of octadecyltrichlorosilane (ODS) and TiO₂ mixture using ethanol as a solvent. Liu et al.^[13] have obtained hydrophobic silica particles from fluoroalkoxysilane (17FTMS) and these silica particles embedded into the sol–gel processed silica matrix and deposited on glass plates. The dirt particles accumulated on this deposited surface of superhydrophobic coating was efficiently cleaned by quickly sliding water drops. Gurav et al.^[14] have prepared self-cleaning superhydrophobic coating by depositing silica particles modified with methyl groups using methyltrichlorosilane as a modifying agent via dip coating. Latthe et al.^[15] have developed sol–gel processed semi-transparent, durable and self-cleaning superhydrophobic coatings on glass using a silica–PMMA composite. Satapathy et al.^[16] prepared porous and non-porous linear low-density polyethylene (LLDPE) and SiO₂ coatings on glass substrates using solution-casting and dip-coating technique, respectively. They have achieved superhydrophobicity by increasing amount of silica nanoparticles in non-porous LLDPE matrix and found increased porosity in porous LLDPE and porous LLDPE/SiO₂ coatings. Lin et al.^[17] prepared self-cleaning superhydrophobic cotton fabric by immersing in SiO₂/fluoropolymer solution and dried at 160° for 5 min. Guo et al.^[18] prepared the superhydrophobic surface by dropping SiO₂ and polymer (Polyvinyl chloride [PVC], polymethylmethacrylate [PMMA], polyethylene [PE]) nanocomposite solution on a glass substrate and dried at 40 °C. Chen et al.^[19] deposited nanocomposite of SiO₂ and polymer (PS and PVC) on a glass substrate using the spin-coating technique. They have reported that the surface water repellency and roughness increases

S. S. Latthe, R. Xing, S. 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, P. R. China
E-mail: rmxing@henu.edu.cn; liushanhu@vip.henu.edu.cn

R. S. Sutar, S. S. Latthe, A. K. Bhosale
Self-cleaning Research Laboratory
Department of Physics
Raje Ramrao College
Shivaji University
Jath 416 404, Maharashtra, India

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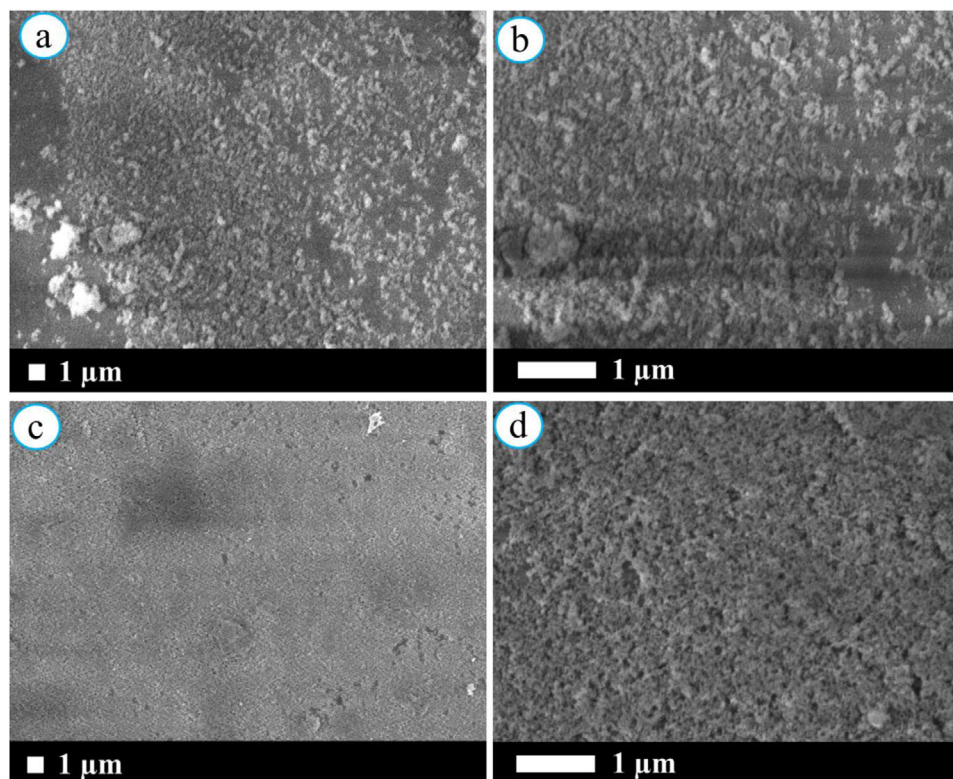


Figure 1. a and b) SEM images for sample S1, and c and d) for sample S3.

by the addition of hydrophobic SiO₂ nanoparticles, avoiding the use of any low-energy surface modification reagents. The coatings exhibited sustainable stability in wide pH range and can prevent metal from corrosion. Latthe et al.^[20] have decorated leaf mesh by SiO₂-polystyrene nanocomposite using dip coating method and achieve water contact angle nearly 162°. Liu et al.^[13] prepared a self-cleaning superhydrophobic silica coating using fluoroalkoxysilane (17FTMS). Chang et al.^[21] applied the superhydrophobic coating on a wood substrate by dipping it in silica nanoparticles loaded polydimethylsiloxane (PDMS). Wang et al.^[22] prepared self-cleaning superhydrophobic coating by spraying paint-like suspension of biopolymer castor oil-based polyurethane and fused SiO₂ nanoparticles. Latthe et al.^[23] prepared semi-transparent and self-cleaning superhydrophobic coating on the glass from poly(methylmethacrylate) (PMMA) in sol-gel processed silica sol. Pawar et al.^[24] prepared self-cleaning superhydrophobic silica-polystyrene composite coating by spin deposition technique. Yoon et al.^[25] fabricated self-cleaning, optically transparent, and robust superhydrophobic coatings using organosilane-coated alumina particles on glass plates by a simple electro-spray technique.

In this paper, we present a facile method to prepare highly durable self-cleaning superhydrophobic coating on the glass. A layer of SiO₂ nanoparticles was applied on the glass by dip coating and dried at room temperature. This procedure was repeated for 15 times to achieve desired surface roughness. Then this 15 layer deposited silica coating was dip coated with a single layer of cyanoacrylate adhesive. After annealing at 200 °C for 10 min,

the coated glass exhibit water contact angle $\approx 173^\circ$ and sliding angle $\approx 1^\circ$.

2. Experimental Section

2.1. Materials

Hydrophobic SiO₂ nanoparticles (AEROSIL RX 300-5, Surface area $\approx 210 \text{ m}^2 \text{ g}^{-1}$, Nippon AEROSIL Co. Ltd, Japan), hexane, and ethyl acetate (Spectrochem Private Limited, Mumbai India), cyanoacrylate adhesive (Pidilite Industries Ltd. Mumbai India) and micro slide glasses (Blue Star, India) were purchased.

2.2. Deposition of Silica Nanoparticles

The glass slides were cleaned by detergent and tap water. After that rinsed by ethanol and distilled water and dried at room

Table 1. Chemical composition of coated glass surface by EDS analysis.

Elements	C	O	Si
Weight percentage	67.24	29.99	2.77
Atom percentage	73.61	24.65	1.74

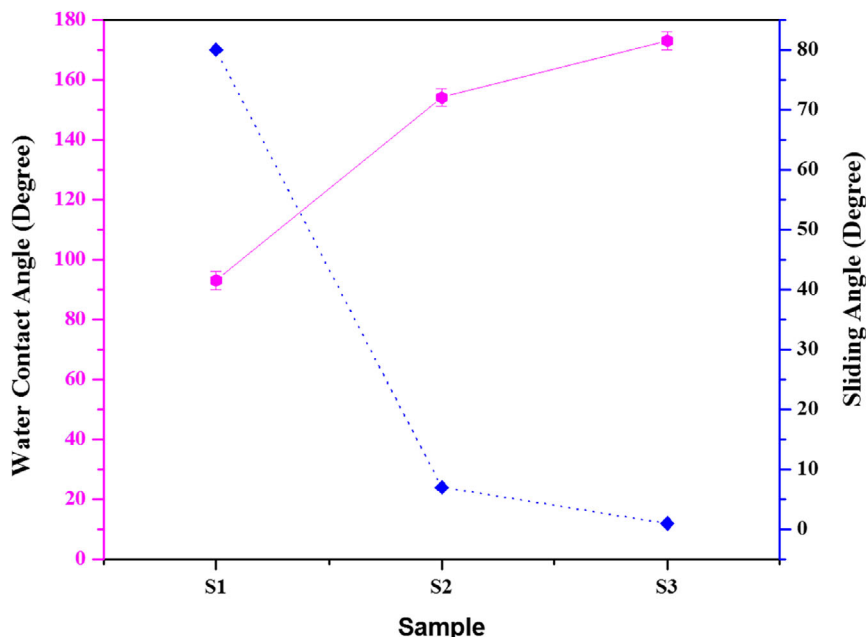


Figure 2. The water contact angle increases with increasing concentration of SiO₂ nanoparticles.

temperature. The different amount of hydrophobic silica nanoparticles (1, 5, and 10 mg mL⁻¹) were dispersed in hexane and labeled as samples S1, S2, and S3, respectively. These mixtures were continuously stirred by a magnetic stirrer at 200 rpm. The 15 layers of SiO₂ nanoparticles were deposited on a glass slide by dip coating with dipping and withdrawing rate of 5 mm s⁻¹.

2.3. Modification of Silica Nanoparticles Film

A 5 mL cyanoacrylate adhesive was added in 20 mL ethyl acetate and kept for stirring for 1 min. The above silica nanoparticles deposited glass slides were immersed in cyanoacrylate adhesive solution and taken out with dipping and withdrawal rate of 5 mm s⁻¹. Finally, the deposited film was annealed at 200 °C for 10 min.

2.4. Surface Characterization

The surface morphology of prepared superhydrophobic coating was analyzed by using Field Emission Scanning Electron Microscopy (JEOL, JSM-7610F, Japan), energy dispersive spectroscopy (EDS, Oxford Instruments X-Max, England) was used to analyze the elemental composition of prepared coatings. The wettability of the coating was examined by contact angle meter (HO-IAD-CAM-01, Holmarch Opto-Mechatronics Pvt. Ltd, India). The durability and mechanical stability were investigated by water jet impact test, adhesive tape test, and water drop impact test. The self-cleaning property was analyzed by

cleaning the dust through water drops on the superhydrophobic coating.

3. Result and Discussion

3.1. Surface Morphology and Chemical Composition of the Coating

The study of surface morphology is one of the most needed and important characterizations of the superhydrophobic coating. The surface morphology of the coated surface can be analyzed by SEM images. The micro/nanoscale rough surface can exhibit significant non-wetting property as compared to the smooth surface. The deposition of multiple SiO₂ nanoparticles layers affects on surface roughness. The SEM images of sample S1 and S3 are shown in **Figure 1a,b** and **c,d**, respectively. The S1 sample reveals a smooth surface structure. At low amount of SiO₂ nanoparticles, coating is non-uniform and pores are not well interconnected.

In coatings, roughness and pores were increased with amount of SiO₂ nanoparticles. The air filled micro/nanoscale rough structure was achieved by increasing amount of SiO₂ nanoparticles. In higher magnification, SEM image of S3 sample, rough and porous structure is observed (**Figure 1d**). The uniform, rough and porous structure of S3 sample support to increase water contact angle.

The chemical composition of SiO₂—cyanoacrylate adhesive superhydrophobic coating was confirmed by EDS. The result is shown in **Table 1**. It is revealed that the superhydrophobic coating is composed of Carbon (C), Oxygen (O), and Silicon (Si) elements. The Si arises from SiO₂ nanoparticles, C from



Figure 3. Optical image of colored water drops on the superhydrophobic coating.

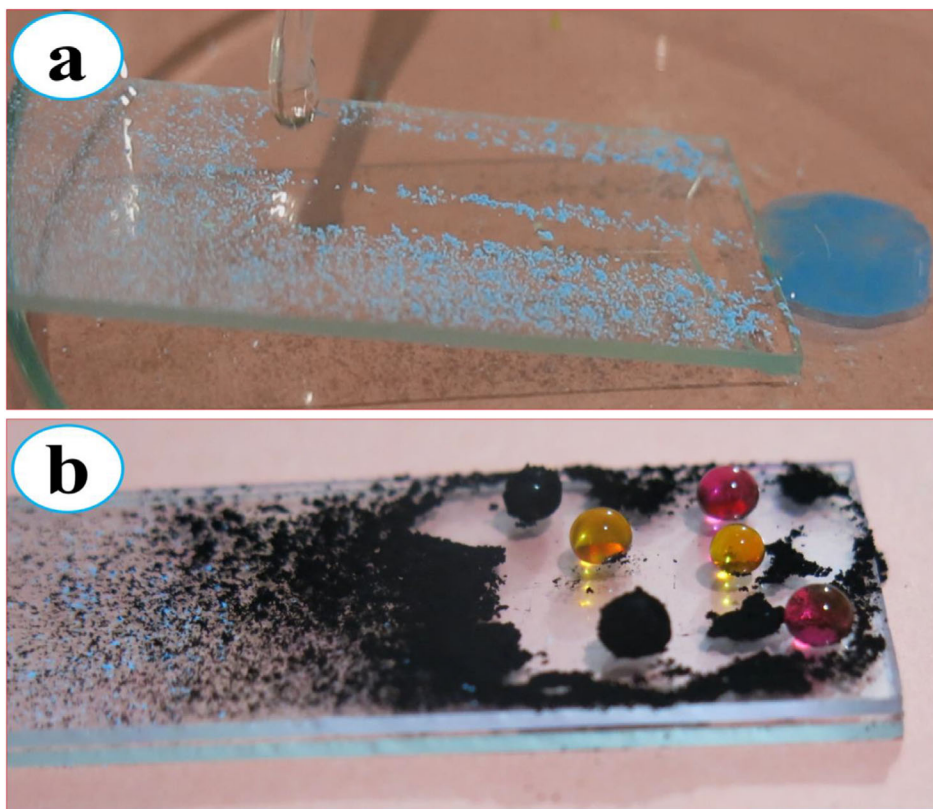


Figure 4. Optical image of a) self-cleaning behavior and b) self-cleaned surface of the superhydrophobic S3 sample.

cyanoacrylate and hydrophobic silica nanoparticles, and O from SiO₂ and cyanoacrylate.

3.2. The Wetting and Self-Cleaning Nature Coating

The wettability of the prepared coating was tested by measuring the static and dynamic water contact angle. The cyanoacrylate adhesive modified coating showed increasing contact angle with increasing amount of SiO₂ nanoparticles. At cyanoacrylate adhesive modified S2 coating the wettability changes from Wenzel state to Cassie-Baxter state. The sliding angle significantly changes from samples S1 to S3. The samples S1–S3 without modification with

cyanoacrylate adhesive showed water contact angle 79°, 150°, and 170°, respectively. Whereas after applying a layer of cyanoacrylate adhesive on S1, S2, and S3 samples, mechanical durability significantly improved and the water contact angle was slightly increased. Figure 2 illustrates that the water contact angle increases whereas the sliding angle decreases with increasing amount of SiO₂ nanoparticles. S3 sample revealed the highest water contact angle 173° and low sliding angle 1°. The contact angle and sliding angle of S1 was 93° and 80°, respectively, which indicated that the water adhesion is high. But for sample S2, the contact angle and sliding angle were changed notably. S2 sample showed contact angle ~154° and sliding angle ~3°. Figure 3 depicts an optical image of 10 µL colored water drops on the superhydrophobic

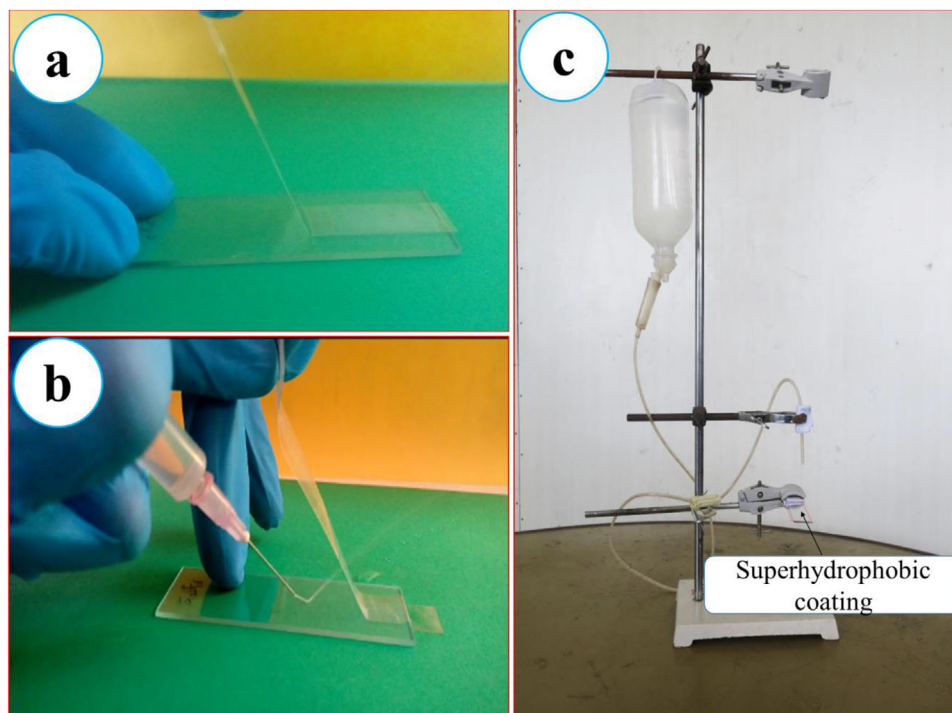


Figure 5. Optical images of a) adhesive tape peeling test, b) water jet impact test after the adhesive tape test, and c) setup of water drop impact test.

S3 sample. The water drop achieves perfectly spherical shape and hardly rests on a superhydrophobic coating.

Generally, the superhydrophobic surfaces are self-cleaning because it cleans itself by the flow of water. In daily life, layers of dust particles grow continuously on the surface of the vehicle body, industrial machinery, solar panels, building walls and many. The detergent and manpower are needed to clean such surfaces. The self-cleaning superhydrophobic coating is the best option to solve such problems. The dust particles were sprayed on the superhydrophobic S3 sample. When water was dropped on the dusted superhydrophobic surface, they roll off adopting dust particles and clean the surface. **Figure 4a** depicts an optical image of the self-cleaning performance of the superhydrophobic coating. The water drops easily collect dust particles, which confirms that the superhydrophobic coating was able to self-clean (**Figure 4b**).

3.3. Mechanical Durability and Stability Tests

The adhesive tape test was carried out using 4 N m^{-1} adhesion strength tape. The adhesive tape was applied on the superhydrophobic S3 coating and normally pressed by a finger to make good contact between tape and coating.^[26] The tape was peeled off slowly ($\approx 2 \text{ mm s}^{-1}$). This process was repeated for ten times (**Figure 5a**). The minor change in water contact angle ($\approx 171^\circ$) and stability for water jet hitting after adhesive tape test indicates that prepared coating is adherent and mechanically stable. **Figure 5b** shows water jet rebounding after adhesive tape peeling off. In water drop impact testing, water droplets are dropped on the pre-

pared superhydrophobic surface from the height 40 cm at rate of one drop per second.^[27] The setup for the water drop impact test is shown in **Figure 5c**. After 5 h water drop impact test, the contact angle change with a small value ($\approx 169^\circ$). This small change in contact angle confirms that the coating is stable against water drop impact test. The superhydrophobic S3 sample was kept in a lab in the open air. The wettability and self-cleaning behavior were unchanged after 2 years. The superhydrophobicity and self-cleaning behavior of coating was not diminished, indicating long-term durability of the superhydrophobic S3 coating.

4. Conclusion

Durable self-cleaning superhydrophobic silica coating was successfully prepared by simple dip coat technique. A layer of cyanoacrylate adhesive helps to enhance the durability of SiO_2 nanoparticle coating. In this work, we achieved a water contact angle $\approx 173^\circ$ and sliding angle $\approx 1^\circ$. The SEM study of S3 sample indicates uniform and porous structure of the superhydrophobic coating. The prepared superhydrophobic coatings are not only mechanically durable but also revealed long-term self-cleaning behavior.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

adhesive, durable, self-cleaning, SiO₂ nanoparticles, superhydrophobic

- [1] C. Neinhuis, W. Barthlott, *Ann. Bot.* **1997**, *79*, 667.
- [2] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1.
- [3] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.
- [4] A. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
- [5] Z. Chen, G. Li, L. Wang, Y. Lin, W. Zhou, *Mater. Des.* **2018**, *141*, 37.
- [6] Y. Wang, G. He, Y. Shao, D. Zhang, X. Ruan, W. Xiao, X. Li, X. Wu, X. Jiang, *Sep. Purif. Technol.* **2018**.
- [7] J. Xie, J. Hu, X. Lin, F. Liang, F. Wu, X. Liao, H. Luo, L. Shi, *Appl. Surf. Sci.* **2018**, *457*, 870.
- [8] D.-Y. Kim, J.-G. Lee, B. Joshi, S. S. Latthe, S. Al-Salem, S. S. Yoon, *J. Mater. Chem. A* **2015**, *3*, 3975.
- [9] H. Yoon, S.-H. Na, J.-Y. Choi, S. S. Latthe, M. T. Swihart, S. S. Al-Deyab, S. S. Yoon, *Langmuir* **2014**, *30*, 11761.
- [10] H. Ogihara, J. Xie, J. Okagaki, T. Saji, *Langmuir* **2012**, *28*, 4605.
- [11] S. S. Latthe, R. S. Sutar, V. S. Kodag, A. K. Bhosale, A. M. Kumar, K. K. Sadasivuni, R. Xing, S. Liu, *Prog. Org. Coat.* **2019**, *128*, 52.
- [12] A. M. Kokare, R. S. Sutar, S. G. Deshmukh, R. Xing, S. Liu, S. S. Latthe, *ODS-Modified TiO₂ Nanoparticles for the Preparation of Self-Cleaning Superhydrophobic Coating*, AIP Conference Proceedings, AIP Publishing **2018**, vol. 1953. No. 1.
- [13] S. Liu, S. S. Latthe, H. Yang, B. Liu, R. Xing, *Ceram. Int.* **2015**, *41*, 11719.
- [14] A. B. Gurav, Q. Xu, S. S. Latthe, R. S. Vhatkar, S. Liu, H. Yoon, S. G. Yoon, *Ceram. Int.* **2015**, *41*, 3017.
- [15] S. S. Latthe, C. Terashima, K. Nakata, S. Munetoshi, A. Fujishima, *J. Mater. Chem. A* **2014**, *2*, 5548.
- [16] M. Satapathy, P. Varshney, D. Nanda, S. S. Mohapatra, A. Behera, A. Kumar, *Surf. Coat. Technol.* **2018**, *341*, 31.
- [17] J. Lin, C. Zheng, W. Ye, H. Q. Wang, D. Y. Feng, Q. Y. Li, B. W. Huan, *J. Appl. Polym. Sci.* **2015**, *132*.
- [18] Y. Guo, Q. Wang, *Appl. Surf. Sci.* **2010**, *257*, 33.
- [19] H. Chen, X. Zhang, P. Zhang, Z. Zhang, *Appl. Surf. Sci.* **2012**, *261*, 628.
- [20] 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**.
- [21] H. Chang, K. Tu, X. S. Wang, J. Liu, *RSC Adv.* **2015**, *5*, 30647.
- [22] Q. Wang, G. Chen, J. Tian, Z. Yu, Q. Deng, M. Yu, *Mater. Lett.* **2018**, *230*, 84.
- [23] S. S. Latthe, C. Terashima, K. Nakata, M. Sakai, A. Fujishima, *J. Mater. Chem. A* **2014**, *2*, 5548.
- [24] P. G. Pawar, R. Xing, R. C. Kambale, A. M. Kumar, S. Liu, S. S. Latthe, *Prog. Org. Coat.* **2017**, *105*, 235.
- [25] H. Yoon, H. Kim, S. S. Latthe, M. Kim, S. Al-Deyab, S. S. Yoon, *J. Mater. Chem. A* **2015**, *3*, 11403.
- [26] S. S. Latthe, P. Sudhagar, A. Devadoss, A. M. Kumar, S. Liu, C. Terashima, K. Nakata, A. Fujishima, *J. Mater. Chem. A*, **2015**, *3*, 14263.
- [27] J. Ryu, K. Kim, J. Park, B. G. Hwang, Y. Ko, H. Kim, J. Han, E. Seo, Y. Park, S. J. Lee, *Sci. Rep.* **2017**, *7*, 1981.