



# Superhydrophobic Nanocomposite Coatings of Hydrophobic Silica NPs and Poly(methyl methacrylate) with Notable Self-Cleaning Ability

Rajaram S. Sutar, Sima S. Gaikwad, Sanjay S. Latthe,\* Vishnu S. Kodag, S. B. Deshmukh, L. P. Saptal, S. R. Kulal, and Appasaheb K. Bhosale\*

The present paper describes a facile and inexpensive dip coating method for preparation of hierarchical superhydrophobic nanocomposite coating. The hydrophobic silica nanoparticles (NPs) are synthesized via sol-gel technique. The superhydrophobicity of the coating is controlled by adjusting the concentration of silica NPs in poly (methyl methacrylate) (PMMA). After optimization, the coating exhibited water contact angle of 165° and sliding angle of 4°. The surface morphology of the superhydrophobic coatings revealed hierarchical rough structure formed on the glass substrate, which enable air trapping. The prepared superhydrophobic coating showed wetting stability under water jet impact with notable self-cleaning performance. The mechanical stability of the superhydrophobic coating is studied using sandpaper abrasion and adhesive tape peeling test. Such highly non-wettable and self-cleaning coatings have potential in various practical applications.

city of the coatings can be evaluated by water contact angle (WCA) higher than 150° with negligible flow resistance, i.e., rolling angle less than 10°. Such coatings are attracting great interest because of their potential applications in self-cleaning<sup>[4-7]</sup> anti-icing,<sup>[8]</sup> anti-corrosion,<sup>[9]</sup> and so on.<sup>[10-12]</sup>

Manoudis et al.<sup>[13]</sup> have found that the static WCA of the coating increases rapidly with concentration of hydrophilic silica NPs and reached maximum value of 154° while spraying suspension of hydrophilic silica NPs and PMMA on glass substrate. Pan et al.<sup>[14]</sup> have sprayed a mixture of PMMA and silica NPs on steel surface and achieved WCA ~150° and sliding angle ~2°. Kavale et al.<sup>[15]</sup> have obtained optically transparent, superhydrophobic uniform coatings by simple dip coating method using PMMA

## 1. Introduction

Notable anti-wetting and self-cleaning property of lotus leaf inspired many researchers to work in the field of superhydrophobic coating research. It is well known that the superhydrophobic coating is rough at nano/microscale level and composed of low surface energy hydrophobic material.<sup>[1-3]</sup> The rough structure able to trap air pocket underneath of liquid and hydrophobic material allows mobility of water droplets. The superhydrophobi-

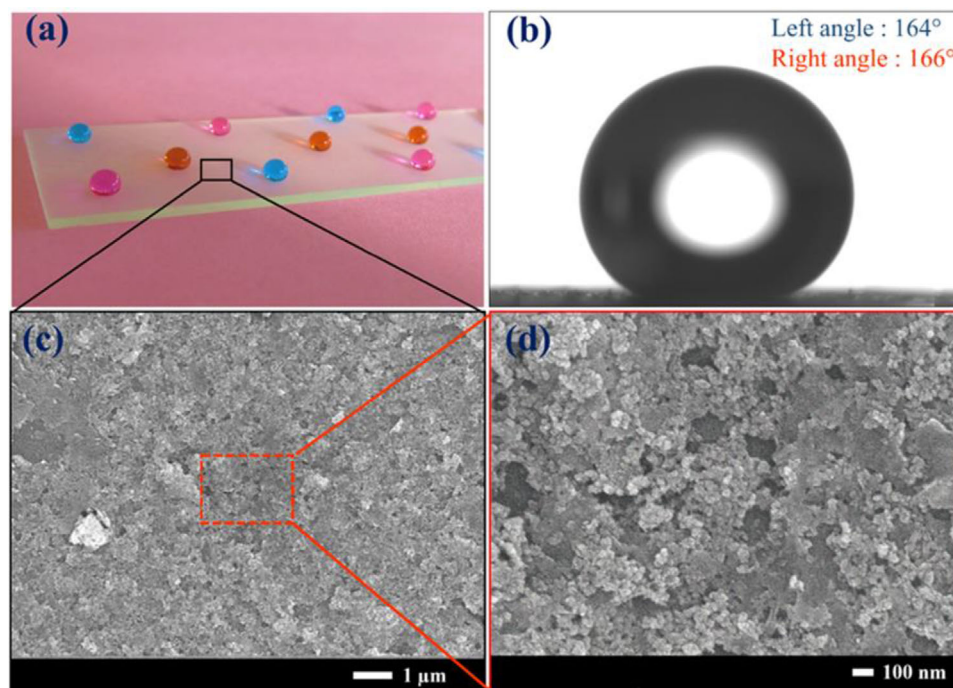
city of the coatings, which enhanced the hydrophobicity and durability of the coatings. Parale et al.<sup>[16]</sup> have fabricated superhydrophobic coating on different metal substrates by sol-gel dip coating method at room temperature. The addition of PMMA in MTMS sol helped to achieve adherent coatings on different substrates. Mahadik et al.<sup>[17]</sup> have fabricated transparent and superhydrophobic silica coating on glass substrates using spray deposition method followed by surface modification with trimethylchlorosilane. Suwan et al.<sup>[18]</sup> have fabricated the dip-coated PMMA/SiO<sub>2</sub> film, which exhibited WCA of 160° and transmittance of 95%, while spray-coated film exhibited WCA 140° and 85% of transparency. These durable and optically transparent superhydrophobic films exhibited an excellent self-cleaning property. Latthe et al.<sup>[19]</sup> have prepared semi-transparent and self-cleaning superhydrophobic coatings from the nanocomposite of silica-PMMA. The concentration of PMMA affects the mechanical durability as well as the optical transparency of the superhydrophobic coating. Xu et al.<sup>[20]</sup> have fabricated superhydrophobic coatings on glass substrates via dip-coating from the suspension of hydrophobically modified hollow silica NPs – PMMA. After modification of the coatings by chemical vapor deposition perfluorooctyltrimethoxysilane, the coatings not only showed excellent superhydrophobicity but also significant antireflection property in the visible/near-IR spectral range. Wang et al.<sup>[21]</sup> have prepared superhydrophobic PMMA-SiO<sub>2</sub> nanocomposite films on glass slide via spin coating. In the investigation of relation to the dosage of SiO<sub>2</sub> NPs dispersion in

R. S. Sutar, S. S. Gaikwad, S. S. Latthe, V. S. Kodag, A. K. Bhosale  
Self-cleaning Research Laboratory  
Department of Physics  
Raje Ramrao College  
(Affiliated to Shivaji University, Kolhapur)  
Jath, Maharashtra, India  
E-mail: latthes@gmail.com; akbhosale1@gmail.com

S. B. Deshmukh, L. P. Saptal  
Department of Zoology  
Raje Ramrao College  
(Affiliated to Shivaji University, Kolhapur)  
Jath, Maharashtra, India

S. R. Kulal  
Department of Chemistry  
Raje Ramrao College  
(Affiliated to Shivaji University, Kolhapur)  
Jath, Maharashtra, India

DOI: 10.1002/masy.202001116



**Figure 1.** a) Photograph of color-dyed water drops on P3 sample, b) digital photograph of water drop on P3 sample. SEM image of P3 sample at c) low and d) high magnifications.

PMMA solution, it was found that hydrophilic PMMA film transferred to superhydrophobic PMMA–SiO<sub>2</sub> nanocomposite films when hydrophobic SiO<sub>2</sub> NPs were introduced into the PMMA solution at a high concentration.

In this study, hydrophobic silica NPs were prepared by sol–gel technique using methyltrimethoxysilane (MTMS). A suspension of hydrophobic silica NPs and PMMA was deposited on glass slides at controlled dipping and withdrawing speed. The coating showed self-cleaning performance along with WCA of 165° and the water droplets easily rolled off the coating surface.

## 2. Results and Discussion

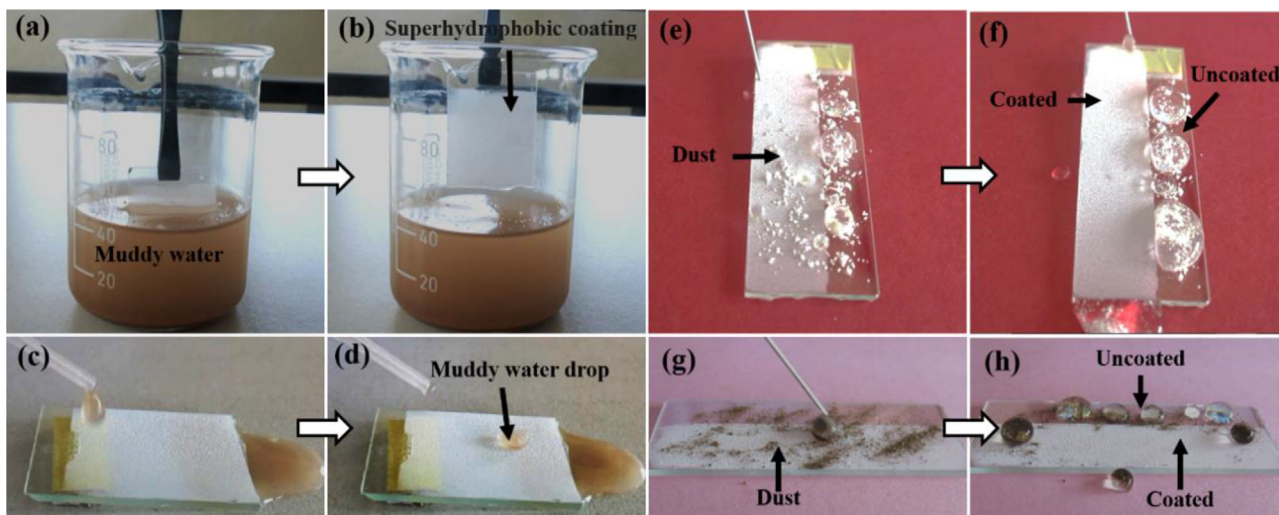
### 2.1. Surface Microstructure and Wettability of the Coating

The surface wettability of any solid surface depends on its chemical and morphological structure. As shown in **Figure 1a**, the different colored water drops kept on P3 sample acquired ball-like shape with WCA of ~ 165° (Figure 1b) with merely 1° difference between right and left WCA, which confirms the homogeneity of the coating surface. Also, the water drops roll off quickly at very low SA of 4°. Such highly nonwetting property of the P3 sample might be due to its porous and rough surface morphology. From **Figure 1c,d**, it is clear that the nanocomposite of silica NPs – PMMA was uniformly deposited on the substrate with rough and porous morphology. The hydrophobic silica NPs (size ~40–50 nm) were found aggregated and embedded in PMMA structure by creating rough structure. Xu et al.<sup>[22]</sup> have also found the similar surface morphology for the superhydrophobic coating prepared with nanocomposite of hollow silica NPs and PMMA. The air pockets get trapped in the rough structure, and hence

when the water drop sits on the P3 sample, it sits on air – solid composite structure. The air pockets could not allow the water drop to enter the rough structure with minimum solid contact area and hence the coating surface show high WCA and low SA. For less concentrations of silica NPs in nanocomposite structure, P1 and P2 samples exhibited WCA of 113° and 137°, respectively. Since the concentration of silica NPs is less, the P1 and P2 samples fail to achieve desired surface roughness, and hence, the anticipated air trapping cannot be achieved. Whereas, with increasing silica NPs concentration, P4 sample exhibited superhydrophobic state with WCA of 167°. Xu et al.<sup>[22]</sup> and Wang et al.<sup>[23]</sup> have also found the similar trend of increase in WCA with increasing concentrations of silica NPs in PMMA.

### 2.2. Self-cleaning Property of Coating

Environmental contaminants such as inorganic/organic and various types of dust particles may degrade or damage the superhydrophobicity of the coating. The self-cleaning behavior of superhydrophobic coating is a typical property for their practical application. The water drop exhibited spherical shape, low adhesion with coating, and quickly roll off the coating. While rolling off water drops picked away dust particles present on the surface, this is called as self-cleaning phenomenon.<sup>[24]</sup> The self-cleaning performance of superhydrophobic coating was studied in different ways such as by impacting water jet<sup>[25]</sup> and rolling water drop<sup>[7]</sup> on contaminated surface, immersing in muddy water,<sup>[26]</sup> and pouring muddy water on it.<sup>[5]</sup> The muddy water was prepared by adding 5 g soil in 40 mL water. The P3 sample immersed in this muddy water and ejected slowly from muddy water. It was observed that,



**Figure 2.** Optical photographs of a-b) P3 sample immersed in muddy water, c-d) muddy water droplets roll off P3 sample, e-h) self-cleaning performance of P3 sample.

the coating remained clean without any impression of muddy water drops as shown in **Figure 2a,b**. Subsequently, muddy water was poured on P3 sample kept at inclination angle  $10^\circ$ . In this experiment, droplets of muddy water were rolled off similar to normal water drops as depicted in **Figure 2c,d**. As shown in **Figure 2e-h**, a special P3 sample was prepared by coating half of the substrate with nanocomposite of silica NPs – PMMA and half part was kept uncoated. As depicted in **Figure 2e,g**, the different dust particles such as soil and chalk particles were spread on the special P3 sample. The water jet was impacted on the coated part from height of 5 cm, as shown in **Figure 2e**. The flowing water jet carried out dust contaminant from the coating and left behind a clean coating surface. On uncoated glass, water drops with dust particles heavily stuck on it. A water drop was gently placed with the help of syringe needle on the coated side, as shown in **Figure 2g**. The water drops adsorb dust particles from coating and roll off towards the uncoated part by efficiently cleaning the coated part. These experiments indicate that the prepared superhydrophobic coating was highly stable during self-cleaning tests.

### 2.3. Mechanical Durability

The mechanical durability of the superhydrophobic coating was inspected by water jet, adhesive tape, and sandpaper abrasion test.<sup>[9,27]</sup> The water jet produced by syringe and impacted on both uncoated and coated glass substrate. The water jet spreads over on glass substrate due to its hydrophilic nature. On the contrary, when the water jet hits on P3 sample, it bounces off the coating due to high water repellency as shown in **Figure 3**. The hierarchical structure entangled with air pockets may not allow jet to enter in the coating structure.<sup>[28]</sup> A water jet was kept hitting continuously on one position of coating surface for more than 2 min and continuous bouncing off of the water jet confirms high mechanical strength of the P3 sample.

The adhesive property of superhydrophobic coatings was examined by adhesive tape peeling test. An adhesive tape was gen-

tly applied on P3 sample and slowly peeled off from coating to investigate adhesiveness of coating. The superhydrophobicity of coating was checked by performing multiple cycles of adhesive tape peeling test. It was found that WCA value was remained unchanged after 10 cycles, showing good adhesive strength of the coating. After 18 cycles, wettability of the coating turned into sticky superhydrophobicity, where WCA showed  $150^\circ$ ; however, a water drop remains adhered on the coating surface even after upside down tilting of the sample. After 26 cycles, the WCA decreased to  $130^\circ$ , due to loss of the nanocomposite material during adhesive tape peel off process. Hence, after 30 cycles, coating showed hydrophilic nature and WCA was found less than  $72^\circ$ . The sandpaper abrasion test was used to characterize the mechanical durability of superhydrophobic coating. In this work, superhydrophobic coating (P3 sample) was rubbed with sandpaper (grit no. 400) by putting 100 g weight on it. It was observed that, after moving for 70 cm on sandpaper, P3 sample showed WCA of  $160^\circ$ , revealing good abrasive strength of the coating. Whereas, after 170 cm abrasion, the coating surface got damaged and WCA found decreased to  $123^\circ$ . The coating was completely damaged after 200 cm and turned to hydrophilic nature with WCA of  $55^\circ$ .

### 3. Conclusion

In summary, a facile and inexpensive dip coating method was used for the preparation of superhydrophobic coating, which showed notable self-cleaning ability. The wettability of the silica NPs–PMMA nanocomposite coating was controlled by optimizing the concentration of silica NPs in PMMA. The as-prepared superhydrophobic coating exhibited WCA of  $165^\circ$  with sliding angle  $\sim 4^\circ$ . The wettability of the superhydrophobic coating was found stable for continuous water jet impact. Particularly, this coating was stable for abrasion with sandpaper for 70 cm distance and 10 cycles of adhesive tape peeling test. This superhydrophobic coating showed excellent self-cleaning ability in different situations and hence promising for practical applications.

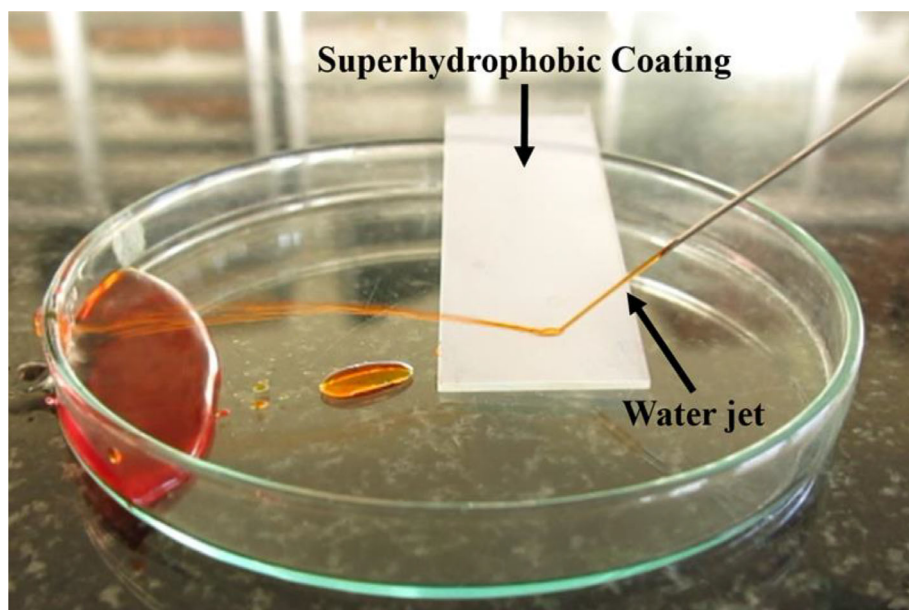


Figure 3. Optical image of water jet hitting on P3 sample.

#### 4. Experimental Section

**Materials:** MTMS was purchased from Sigma-Aldrich, USA. Methanol, ammonia, and chloroform were bought from Spectrochem PVT. LTD., India. Micro-glass slides (75 × 25 × 1.35 mm) were obtained from Blue star, Polar Industrial Corporation, India.

**Preparation of Hydrophobic SiO<sub>2</sub> NPs:** The hydrophobic silica NPs were prepared by sol-gel method.<sup>[29]</sup> In typical synthesis, the mixture of 4 mL MTMS, 40 mL methanol, and 8 mL distilled water was stirred for 20 min. Ammonia solution was added dropwise in the mixture and stirring was further continued for 30 min. The gel formed, which was aged overnight and dried at 80°C for 5 h. Finally, dried gel was grinded well using mortar and pestle to earn fine silica powder.

**Preparation of Superhydrophobic Coating:** At first, glass substrates were cleaned with tap water and laboratory reagent (Molyclean 02 Neutral, from Molychem, India). Thereafter, cleaned ultrasonically with distilled water and ethanol for 10 min. A 20 mg ml<sup>-1</sup> PMMA was completely dissolved in chloroform. The nanocomposites were prepared by adding hydrophobic silica nanoparticles in PMMA solution and stirred magnetically for 6 h. The cleaned glass substrate was dipped for 5 min and dried at 150°C for 3 h in oven. The coatings were prepared using varying concentrations of hydrophobic silica NPs in PMMA such as 20, 30, 40, and 50 mg ml<sup>-1</sup> and labeled as P1, P2, P3, and P4 samples, respectively.

**Characterizations:** The microstructure of coating was observed by field emission scanning electron microscopy (SEM, JEOL, JSM-7610F, Japan). The WCAs of coatings were measured on contact angle meter (HO-IAD-CAM-01; Holmarc Opto-Mechatronics Pvt. Ltd., India). For roll-off angle measurement, coated slide placed on substrate holder of contact angle meter and holder inclined slowly with adjusting screw. The water jet impact study was characterized by producing water jet on coating from 15 mL syringe. The water droplets were dropped on the coating placed at 30° inclination from height ~ 10 cm. The adhesive tape peeling and sandpaper abrasion tests were used to check mechanical stability of coating. The self-cleaning behavior was observed by pouring muddy water on coating and spreading artificial dust particles.

#### 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

coatings, lotus leaf, nanocomposite, self-cleaning, superhydrophobic

- [1] W. Barthlott, M. Mail, B. Bhushan, K. Koch, *Nano-Micro Lett.* **2017**, *9*, 23.
- [2] R. Fürstner, W. Barthlott, C. Neinhuis, P. Walzel, *Langmuir* **2005**, *21*, 956.
- [3] P. G. Pawar, R. Xing, R. C. Kambale, A. M. Kumar, S. Liu, S. S. Latthe, *Prog. Org. Coat.* **2017**, *105*, 235.
- [4] S. P. Dalawai, M. A. Saad Aly, S. S. Latthe, R. Xing, R. S. Sutar, S. Nagappan, C.-S. Ha, K. Kumar Sadasivuni, S. Liu, *Prog. Org. Coat.* **2020**, *138*, 105381.
- [5] A. M. Kokare, et al., *AIP Conference Proceedings*. AIP Publishing, **2018**.
- [6] 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.
- [7] R. S. Sutar, et al., *Macromolecular Symposia*, Wiley Online Library, **2019**.
- [8] 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.
- [9] 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.
- [10] S. S. Latthe, V. S. Kodag, R. S. Sutar, A. K. Bhosale, S. Nagappan, C.-S. Ha, K. K. Sadasivuni, S. R. Kulal, S. Liu, R. Xing, *Mater. Chem. Phys.* **2020**, *243*, 122634.

- [11] S. S. Latthe, et al., *Superhydrophobic Polymer Coatings*, Elsevier, **2019** p. 339.
- [12] 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.
- [13] P. N. Manoudis, I. Karapanagiotis, A. Tsakalof, I. Zuburtikudis, C. Panayiotou, *Langmuir* **2008**, 24, 11225.
- [14] S. Pan, N. Wang, D. Xiong, Y. Deng, Y. Shi, *Appl. Surf. Sci.* **2016**, 389, 547.
- [15] M. S. Kavale, D. B. Mahadik, V. G. Parale, P. B. Wagh, S. C. Gupta, A. V. Rao, H. C. Barshilia, *Appl. Surf. Sci.* **2011**, 258, 158.
- [16] V. Parale, et al., *Int. J. Mater. Sci. Eng* **2016**, 4, 60.
- [17] S. A. Mahadik, D. B. Mahadik, M. S. Kavale, V. G. Parale, P. B. Wagh, H. C. Barshilia, S. C. Gupta, N. D. Hegde, A. V. Rao, *J. Sol-Gel Sci. Technol.* **2012**, 63, 580.
- [18] M. Suwan, S. Supothina, *J. Ceram. Processing Res* **2017**, 18, 521.
- [19] S. S. Latthe, C. Terashima, K. Nakata, M. Sakai, A. Fujishima, *J. Mater. Chem. A* **2014**, 2, 5548.
- [20] L. Xu, L. Gao, J. He, *RSC Adv.* **2012**, 2, 12764.
- [21] J. Wang, X. Chen, Y. Kang, G. Yang, L. Yu, P. Zhang, *Appl. Surf. Sci.* **2010**, 257, 1473.
- [22] L. Xu, L. Gao, J. He, *RSC Adv.* **2012**, 2, 12764.
- [23] J. Wang, X. Chen, Y. Kang, G. Yang, L. Yu, P. Zhang, *Appl. Surf. Sci.* **2010**, 257, 1473.
- [24] W. Barthlott, C. Neinhuis, *Planta* **1997**, 202, 1.
- [25] P. Wang, B.o. Sun, T. Yao, M. Chen, X. Fan, H. Han, L. Li, C. Wang, *Chem. Eng. J.* **2017**, 326, 1066.
- [26] P. Xu, et al., *Mater. Des.* **2018**, 160, 974.
- [27] B. K. Tudu, A. Kumar, B. Bhushan, *Philos. Trans. Royal Soc. A* **2019**, 377, 20180272.
- [28] S. S. Latthe, P. Sudhagar, C. Ravidhas, A. Jennifer Christy, D. David Kirubakaran, R. Venkatesh, A. Devadoss, C. Terashima, K. Nakata, A. Fujishima, *CrystEngComm* **2015**, 17, 2624.
- [29] S. S. Latthe, A. V. Rao, *Surf. Coat. Technol.* **2012**, 207, 489.