Macromolecular Symposia
www.ms-journal.de

Octadecyltrichlorosilane-Modified Superhydrophobic-Superoleophilic Stainless Steel Mesh for Oil-Water Separation

Rajaram S. Sutar, Narayan P. Kulkarni, Saravanan Nagappan, Akshay R. Jundle, P. G. Pawar, Nikhil N. Pargaonkar, Nilam B. Gharge, Prashant S. Yadav, Shrutika S. Kshirsagar, Susmita S. Kanchankoti, Akshata S. Sawant, Snehal G. Kodag, S. S. Mahajan, V. S. Shinde, Kang Hyun Park, Kishor Kumar Sadasivuni, Appasaheb K. Bhosale, and Sanjay S. Latthe**

Recently, oil-water separation has become an important topic due to its increasing commercial demand. Here, in this study, a simple technique to prepare superhydrophobic-superoleophilic mesh for oil-water separation is reported. The pre-cleaned stainless steel mesh is modified by octadecyltrichlorosilane (ODS) through solution immersion method. The modified mesh shows the water contact angle (WCA) of 158 ± 2° and oil contact angle (OCA) of 0°. The prepared superhydrophobic-superoleophilic mesh effectively separates various oils, including petrol, kerosene, diesel, vegetable oil, and coconut oil from oil–water mixtures with separation efficiency greater than 95%, and stable recyclability up to 10 cycles. In case of low viscosity oil (petrol), the modified mesh shows permeation flux of 2086.95 ± 104.34 L/(m^2.h), which is higher than high viscosity oils.

1. Introduction

Superhydrophobic and superoleophilic surfaces have demonstrated excellent water-repellant with contact angle (CA) over 150° and oil absorption properties with CA $< 10°$ due to superior water hesitant and oil loving behaviors.[1–3] The superhydrophobic surface property was inspired from Lotus leaf due to the presence of micro-nano hierarchical structure. Generally, superhydrophobic surfaces were fabricated by developing a highly rough surface with micro-nano hierarchical surface by covering a thin layer of hydrophobic material on the surface to develop an excellent superhydrophobic property. Several researchers have developed superhydrophobic surfaces by depositing a layer of sol-gel processed hydrophobic silica particles. [4–9] Kokare et al. have prepared superhydrophobic surface by applying layer of suspension of TiO_2 particles and ODS. [10] In the recent days, porous materials along with special wetting properties have attracted considerable attentions in the separation of oil from polluted ocean water, industrial wastewater, and oil-water mixtures.[1–3] Many efforts have been done for the fabrication

---

R. S. Sutar, N. P. Kulkarni, A. R. Jundle, N. N. Pargaonkar, N. B. Gharge, P. S. Yadav, S. S. Kshirsagar, S. S. Kanchankoti, A. S. Sawant, S. G. Kodag, A. K. Bhosale, S. S. Latthe
Self-cleaning Research Laboratory
Department of Physics
Raje Ramrao College, Jath 416404
(Affiliated to Shivaji University, Kolhapur)
Maharashtra, India
E-mail: akbhosale1@gmail.com; latthes@gmail.com

S. Nagappan, K. H. Park
Department of Chemistry
Chemistry Institute for Functional Materials
Pusan National University
Busan 46241, Republic of Korea

K. K. Sadasivuni
Center for Advanced Materials
Qatar University
Doha, P. O. Box 2713, Qatar

P. G. Pawar
Shivaji Polytechnic College
Sangola, Maharashtra 413307, India

S. S. Mahajan
Jaysingpur College
Jaysingpur, Maharashtra 416101, India

V. S. Shinde
Baburao Patil College of Arts and Science
Angar, Dist- Solapur, Maharashtra 413214, India

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/masy.202100096

DOI: 10.1002/masy.202100096

of superhydrophobic-superoleophilic membrane,[2] mesh,[1] sponge, [3] and cotton fabric [11] to separate oil and water from oil-water mixture. Zhu et al.[12] have developed porous superhydrophobic materials including polyester fabric, copper mesh, and sponge by immersing in the suspension of hydrophobic SiO_2 and polyfluorowax. These porous materials can separate oils from oil-water mixture up to 10 cycles of oil-water separation test. On the other hand, Nanda et al.[13] have synthesized superhydrophobic and superoleophilic coating on stainless steel mesh via chemical etching using a mixture of ferric chloride ($FeCl_3$) and hydrochloric acid (HCl) followed by hydrophobic treatment with hexadecyltrimethoxysilane for oil-water separation. Whereas, Ke et al.[14] have fabricated superhydrophobic and superoleophilic sponges by dipping in an ethanol solution of octadecyltrichlorosilane (ODTS). Wang et al. [10] have immersed filter paper into the OTS/MTS (methyltrichlorosilane) solution in n-hexane at temperature of 25 ± 2°C for different periods of time (from 1 to 8 min) to fabricate superhydrophobic filter paper. Various routes were also performed by several researchers by simply modifying the porous structure with hydrophobic agents to develop superhydrophobic and superoleophilic properties. So that, these porous superhydrophobic and superoleophilic surfaces can be applied for oil-water separation because the porous surface easily separate the oil through the pore channels.

The present work describes a facile method for the fabrication of superhydrophobic/superoleophilic stainless steel mesh for oil-water separation. The superhydrophobicity was achieved by optimizing the immersion period of time in hexane solution of octadecyltrichlorosilane (ODS). The prepared superhydrophobic mesh delivered an excellent mechanical, thermal, and chemical stability and also showed excelled self-cleaning and oil-water separation ability.

2. Result and Discussion

2.1. Surface Structure and Wettability of Superhydrophobic Mesh

The surface wettability of stainless steel was measured by contact angle measurement using water and oil droplet. The surfaces with CA higher than 150° can deliver the superhydrophobic state due to the complete water repellant behavior of the substrate. The pristine stainless steel mesh have superhydrophilic as well as superoleophilic properties, so that the surface can completely wet for water and oil droplets. The immersion of cleaned stainless steel mesh in hexane solution of ODS showed the development of hydrophobic surface property and further enhanced with immersion period. The WCA of the mesh substrate immersed for 1 h showed ∼ 116° due to the formation of thin layer of closely packed ODS. The presence of CH_3-terminated groups and the self-assembly of monolayer that changes surface from hydrophilic to hydrophobic. [15,16] Long chain of ODS react with hydroxyl group on the surface and form a densely packed monolayer due to cross-link with neighboring silane molecules. Wang et al.[17] stated that the reaction time significantly alter the surface wettability. In this work, we get similar results, hydrophobicity has been enhanced by 2 h of immersion. We also found that 2 h immersion period of time is an optimal condition to obtain superhydrophobic surface with WCA of $158 \pm 2°$ and SA of $< 5°$. The color dyed water droplets exhibited spherical shape on superhydrophobic stainless steel mesh, as shown in **Figure 1**(A). Inset of Figure 1 (A) and (B) are the optical CA images of water drop and oil drop on superhydrophobic mesh. This superhydrophobic mesh was used for further characterization. Superhydrophobicity may be attributed to developing hierarchical rough structure during reaction between chain of alkyltrichlorosilanes and hydroxyl group. It was clearly confirmed by SEM micrograph of 2 h immersed stainless steel mesh in ODS. In Figure 1 (C) and (D), it is clearly seen that silane form of closely packed layer on the mesh surface with micro-/nano-scale hierarchical rough structure. This hierarchical rough structure responsible for the superhydrophobic state that mean the ability to trap air between the rough structures. [18] In general, the surface with more rough structure and hierarchical morphology covered with a thin layer of hydrophobic organic functional group coating can deliver excellent superhydrophobic property. The superhydrophobic property was altered by changing the surface roughness and morphology. The WCA was reduced to 138° by further increasing the immersion time (reaction time), this is might be due to the formation smooth surface during the reaction. The mesh surface has remains superoleophilic with oil contact angle of about 0°.

2.2. Mechanical, Thermal, and Chemical stability of Superhydrophobic Mesh

The mechanical stability, thermal stability, chemical stability, and self-cleaning ability of superhydrophobic mesh are highly important in various applications, because these properties are most desirable properties for commercial products. So, we investigated these properties on the ODS modified stainless steel substrate. The coated substrate illustrated excellent thermal stability that can maintain the surface property at higher temperature, which is much needed for the commercial usage. The thermal stability of superhydrophobic mesh was checked by heating the mesh for 1 h in oven at different temperature 100°C, 150°C, and 200°C. The superhydrophobic mesh has thermally stable up to 150°C temperature. At 200°C, superhydrophobic mesh lost their superhydrophobicity because degradation of OTS molecules takes place and it breaks the physisorption bonding from the mesh surface. [19] Due to thermal aging, the color of coating turned into brown color (**Figure 2** (A)). Furthermore, heating the mesh was turned to hydrophilic in nature due to the loss of organic functional groups from the coated substrate. These results suggest that the coated substrate have better stability of maintaining the superhydrophobicity up to 150°C. Nagappan et al.[20] also reported an excellent thermal stability of the coated hybrid substrates, which maintains the thermal stability up to 500°C. The stability of superhydrophobicity against hot water droplet also much important in various coatings. They also studied the stability against various droplet temperatures and the coated substrate which shown an excellent stability against hot and cold water. [20] On the other hand, Wan et al.[21] reported that superhydrophobic surfaces loss their property when it was exposed to hot water. This is due to an easier penetration of water droplet beneath the surface due to loss of some surface hydrophobicity. We also checked the ability of hot water repellency of superhydrophobic mesh was carried out by examining WCA and SA with water at

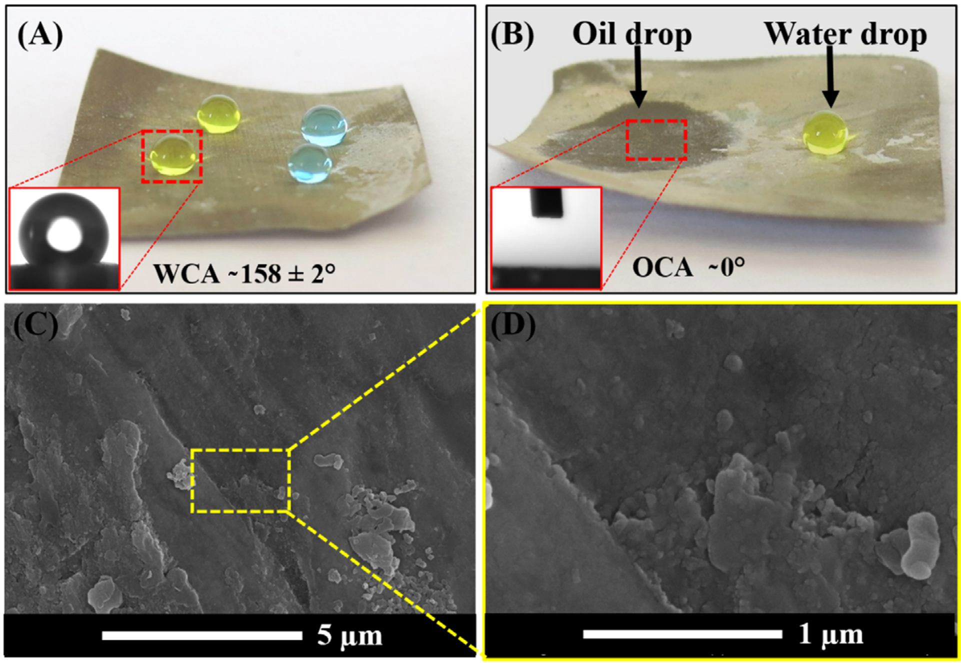

Figure 1. A) The photograph of color dyed water droplets on superhydrophobic mesh (ODS-2 sample). B) The photograph of oil and water drop on superhydrophobic mesh (ODS-2 sample). C) and (D) the SEM images of ODS-2 sample at different magnifications.

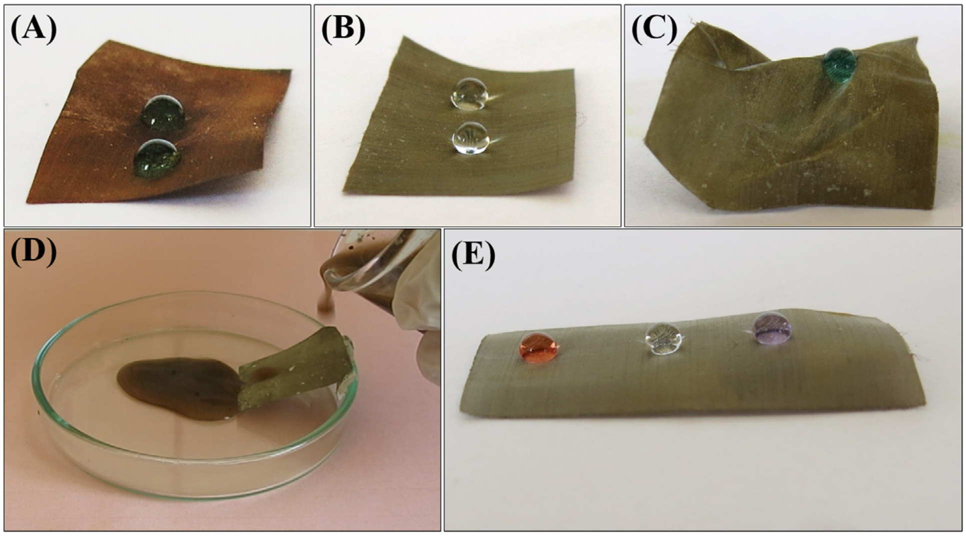

Figure 2. A) Water droplets on ODS-2 sample after heat treatment. B) Hot water droplets on ODS-2 sample. C) After twisting/bending the ODS-2 sample. D) Self-cleaning behavior of ODS-2 sample. E) Water (middle), Acidic (left), and basic (right) liquid droplets on ODS-2 sample.

controlled temperatures. The prepared superhydrophobic mesh exhibited WCA 151 ± 2° and SA 8 ± 2° when dealing with water temperature of 78 ± 5°C. The optical photograph of hot water droplet on mesh was shown in Figure 2 (B). These results suggest the maintenance of excellent stability against hot water on the coated substrate. Furthermore, the mechanical durability of superhydrophobic mesh was also tested by twisting and bending of mesh. This test was repeated until mesh loss their superhydropobicity. Figure 2 (C) reveals after 15 times twisting and bending of mesh, which confirms that prepared superhydrophobic mesh has good mechanical durability. Sometimes, the mesh can come in contact with dirty and solid contaminated water in the process of oil-water separation. The dirt easily sticks to mesh and consequently reduces the life of mesh. Therefore, to avoid this problem, it required self-cleaning character on the superhydrophobic mesh. Muddy water was prepared by adding 5 g of fine soil in 20 mL water. To test self-cleaning ability of superhydrophobic mesh, muddy water was poured on it at tilting angle nearly

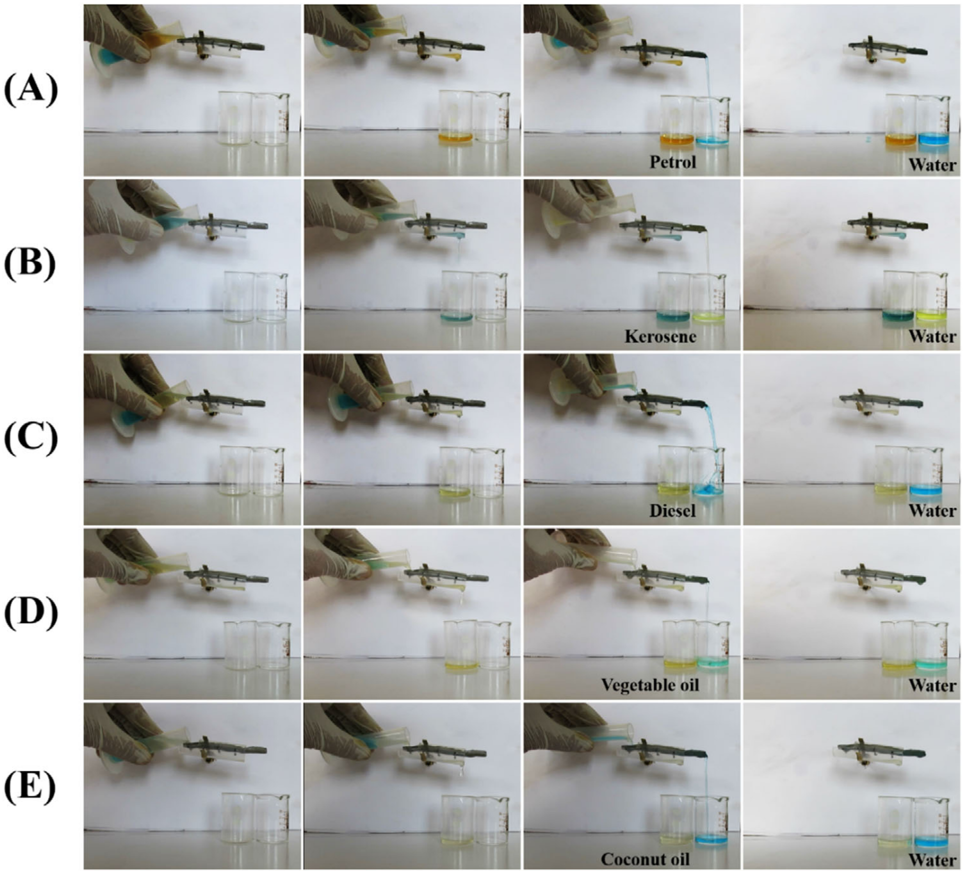

Figure 3. The process of oil-water separation of (A) petrol, (B) kerosene, (C) diesel, (D) vegetable oil, and (E) coconut oil from oil-water mixture.

30° (Figure 2 (D)). The muddy water was repelled on the mesh surface due to high water repellent property. This test confirms that prepared superhydrophobic mesh has excellent self-cleaning property. Chemical stability test was also performed on the superhydrophobic mesh by measuring the CA using aqueous acidic and basic droplets.[22] The mesh can sustain its CA greater than 150° under acidic and basic droplets (Figure 2 (E)), which propose an excellent chemical stability of the fabricated superhydrophobic mesh.

2.3. Oil-water Separation Ability of Superhydrophobic Mesh

The oil-water separation ability of the prepared superhydrophobic mesh was evaluated using gravity-driven oil-water separation process. A homemade flow tube-type oil–water separator was installed at an angle 45°.[23] The oil-water mixture was prepared by adding 5 mL oil in 5 mL water. Oil float on water surface when added into the water. The oil-water mixture was poured to the separator tube in order to evaluate oil-water separation ability. At the beginning, oil quickly permeated through mesh and was collected in the beaker underneath, later on the remaining water was collected in another beaker (**Figure 3**). Oils having different viscosities such as petrol, kerosene, diesel, vegetable oil, and coconut oil were used to examine oil-water separation. The process of separation of petrol, kerosene, diesel, vegetable oil, and coconut oil from oil-water mixture as shown in Figure 3(A) – (E), respectively.

The separation efficiency and permeation flux are an important data in the study of oil-water separation. The separation efficiency (γ) was calculated by using followed formula: Separation efficiency $(\gamma) = \frac{V_1}{V_0} \times 100$, where V_0 and V_1 are represent volume of the oil, after and before the separation process.[24] The low viscosity oil revealed separation efficiency 97 ± 1% due to their high flow rate though mesh. Conversely, high viscous vegetable and coconut oil could not completely pass out through mesh, which showed low separation efficiency (**Table 1**). For low viscous oil, the prepared superhydrophobic mesh has showed higher than 90% separation efficiency after 10 cycles of oil-water separation and is significantly reduced for high viscous oil after 5 cycles. Permeation flux (J) was calculated by using followed formula, $J = V/St$, where V is volume of the permeated oil (L), S is the active area (m^2) of mesh, and t is time (h) for the separation.[25] Table 1 reveals the values of viscosity of different oils including petrol, kerosene, diesel, vegetable oil, and coconut oil. The value of permeation flux depends on viscosity of oil. Low viscous oil (petrol) exhibited permeation flux of 2086.95 ± 104.34 L/(m^2.h) and high viscous oil (coconut oil) showed 968.01± 48.4 L/(m^2.h). The variation of values of permeation flux with different type of oils are shown in Table 1.

Table 1. The absolute viscosity of different oils, permeation flux, and separation efficiency for different oil/water mixture.

Oils	Petrol	Kerosene	Diesel	Vegetable oil	Coconut oil
Absolute Viscosity (cP) at ~ 25°C	0.5	2.0	2.4	34	55
Permeation Flux (J) [L/(m^2.h)]	2086.95 ± 104.34	2020.49± 101.02	1814.81 ± 104.34	1318.74 ± 90.74	968.01± 48.4
Separation efficiency [γ]	97 ± 1	97 ± 1	96 ± 1	94 ± 1	93 ± 1

3. Conclusion

Superhydrophobic/superoleopholic stainless steel mesh was prepared by a facile immersion technique. At optimal immersion period of time of mesh in hexane solution of ODS revealed high water contact angle of 158 ± 2° and sliding angle < 5°. In surface analysis, observed that the long chain of silane formed closely packed structure which is responsible to superhydrophobicity by forming hierarchical rough structure. The prepared superhydrophobic stainless steel mesh has exhibited highly mechanical, thermal, chemical stability, hot water repellency, and self-cleaning ability. Also, showed excellent oil-water separation ability with separation efficiency higher than 95% and permeation flux of 2086.95 ± 104.34 L/(m^2.h) for low viscous oil up to 10 separation cycles. These findings suggest that highly robust superhydrophobic/superoleophilic mesh was fabricated by this approach and can be used for selective oil-water separation in practical applications.

4. Experimental Section

Materials: Octadecyltrichlorosilane was purchased from Sigma Aldrich, USA. Hexane was obtained from Spectrochem, PVT, Mumbai, India. Petrol, diesel, and kerosene collected from Bharat petroleum, India. Vegetable oil and coconut oil were collected from local market. Stainless steel mesh (diameter of the wire~ 40 μm with pore size~ 50 μm) was procured from Taitong Metal Mesh Ltd., China.

Preparation of Superhydrophobic Coating on Mesh: The stainless steel mesh was cleaned ultrasonically by acetone, ethanol, and distilled water for 5 min, respectively, then dried in an oven at 60°C for 10 min. The coating solution was prepared by adding 1 mL of ODS into 5 mL of hexane and kept in ultrasonication bath for 15 min to mix well. The cleaned mesh was immersed in coating solution for 1 h. The deposition setup enclosed in closely packed container. The deposition process carried out at room temperature (25°C -30°C). Thereafter, ODS-deposited mesh was placed in hexane to remove residual ODS from the mesh surface and dried at room temperature. Finally, ODS-deposited mesh was dried at 80°C in an oven for 1 h. Coatings were prepared by immersing for 2 and 3 h in coating solution. Thereafter, the mesh coated by dipping in coating solution for 1, 2, and 3 h were named as ODS-1, ODS-2, and ODS-3 sample, respectively.

Characterizations: The measurements of water contact angle (WCA), water sliding angle, and oil contact angle were performed by using contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India). The surface structure of prepared superhydrophobic mesh was examined by scanning electron microscope (SEM). Mechanical stability was checked by bending and twisting the mesh. Thermal stability was examined by applying heat treatment to superhydrophobic mesh and depositing hot water droplets on it. Self-cleaning test was carried out by pouring muddy water on prepared superhydrophobic mesh. The chemical stability was analyzed by depositing acidic and basic droplets. The gravity-driven oil-water separation was performed by set-up installing at nearly 45° using petrol, diesel, kerosene, coconut oil, and vegetable oil.

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]. S.S.L. 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.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hot water repellent, ODS coating, oil-water separation, stainless steel mesh, superhydrophobic-superoleophilic

Received: April 10, 2021
Revised: June 6, 2021

[1] 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.
[2] M. W. Lee, S. An, S. S. Latthe, C. Lee, S. Hong, S. S. Yoon, *ACS Appl. Mater. Interfaces* **2013**, *5*, 10597.
[3] R. S. Sutar, et al. in *Macromolecular Symposia*, **2020**. Wiley Online Library.
[4] 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.
[5] S. A. Mahadik, M. S. Kavale, S. K. Mukherjee, A. V. Rao, *Appl. Surf. Sci.* **2010**, *257*, 333.
[6] S. A. Mahadik, et al., *J. Sol-Gel Sci. Technol.* **2012**, *63*, 580.
[7] S. A. Mahadik, V. Parale, R. S. Vhatkara, D. B. Mahadik, M. S. Kavale, P. B. Wagh, S. Gupta, J. Gurav, *Appl. Surf. Sci.* **2013**, *277*, 67.
[8] V. G. Parale, D. B. Mahadik, S. A. Mahadik, M. S. Kavale, P. B. Wagh, S. C. Gupta, A. V. Rao, *Ceram. Int.* **2013**, *39*, 835.
[9] V. G. Parale, K.-Y. Lee, H.-H. Park, *J. Korean Ceram. Soc.* **2017**, *54*, 184.
[10] A. M. Kokare, et al. ODS–modified TiO2 nanoparticles for the preparation of self-cleaning superhydrophobic coating. in AIP Conference Proceedings. **2018**, AIP Publishing LLC.
[11] S. A. Mahadik, F. D. Pedraza, B. P. Relekar, V. G. Parale, G. M. Lohar, S. S. Thorat, *J. Sol-Gel Sci. Technol.* **2016**, *78*, 475.
[12] X. Zhu, Z. Zhang, B. Ge, X. Men, X. Zhou, Q. Xue, *J. Colloid Interface Sci.* **2014**, *432*, 105.

[13] D. Nanda, A. Sahoo, A. Kumar, B. Bhushan, *J. Colloid Interface Sci.* **2019**, *535*, 50.
[14] Q. Ke, Y. Jin, P. Jiang, J. Yu, *Langmuir* **2014**, *30*, 13137.
[15] Q. He, C. Ma, X. Hu, H. Chen, *Anal. Chem.* **2013**, *85*, 1327.
[16] J. X. H. Wong, H.-Z. Yu, *J. Chem. Educ.* **2013**, *90*, 1203.
[17] J. Wang, J. X. H. Wong, H. Kwok, X. Li, H.-Z. Yu, *PLoS One* **2016**, *11*, e0151439.
[18] A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546.
[19] D. Nanda, P. Varshney, M. Satapathy, S. S. Mohapatra, A. Kumar, *Colloids Surf. A* **2017**, *529*, 231.
[20] M. Cao, X. Luo, H. Ren, J. Feng, *J. Colloid Interface Sci.* **2018**, *512*, 567.
[21] F. Wan, D.-Q. Yang, E. Sacher, *J. Mater. Chem. A* **2015**, *3*, 16953.
[22] Y. Zhang, X. Wang, C. Wang, J. Liu, H. Zhai, B. Liu, X. Zhao, D. Fang, *RSC Adv.* **2018**, *8*, 35150.
[23] C. Yeom, Y. Kim, *J. Ind. Eng. Chem.* **2016**, *40*, 47.
[24] Y. Li, Q. Yu, X. Yin, J. Xu, Y. Cai, L. Han, H. Huang, Y. Zhou, Y. Tan, L. Wang, H. Wang, *Cellulose* **2018**, *25*, 6691.
[25] V. Singh, Y.-J. Sheng, H.-K. Tsao, *J. Taiwan Inst. Chem. Eng.* **2018**, *87*, 150.