A Simple Dip Coating Approach for Superhydrophobic TiO_2/Polystyrene Nanocomposite Coatings with Self-Cleaning Application

Rutuja A. Ekunde[1], Rajaram S. Sutar[2], Pradip P. Gaikwad[1], Sagar S. Ingole[1], Akshay R. Jundle[1], Sanjay S. Latthe[1]*

[1] Self-cleaning Research Laboratory, Department of Physics, Vivekanand College, Kolhapur (An Empowered Autonomous Institute), (Affiliated to Shivaji University, Kolhapur), Kolhapur – 416003, Maharashtra, India.

[2] School of Chemistry and Molecular Sciences, Henan University, Kaifeng, China.

*Corresponding author E-mail: latthes@gmail.com

Abstract

This study presents a facile and cost-effective strategy for fabricating superhydrophobic coatings using hydrothermally synthesized titanium dioxide (TiO_2) nanoparticles. TiO_2 nanoparticles were prepared via a hydrothermal method. A dip-coating technique was used to deposit the superhydrophobic layer on pre-cleaned glass substrates. The coating solution was formulated by dispersing unmodified TiO_2 nanoparticles in a polymethylhydrosiloxane (PMHS) and chloroform mixture, with polystyrene (PS) added as a binder to improve film uniformity and adhesion. The coating exhibited the highest superhydrophobic performance, achieving a static water contact angle of 164° and a sliding angle of 5°, indicating excellent water repellency. The mechanical robustness of the coated glass slide was evaluated through a muddy water resistance test. The prepared superhydrophobic coating revealed excellent self-cleaning performance against the muddy water. The developed coatings hold significant potential for applications in self-cleaning due to their simplicity, scalability, and superhydrophobic behavior.

Keywords: Superhydrophobic, TiO_2 nanoparticles, dip coating, self-cleaning

1. Introduction

Superhydrophobic surfaces have garnered significant interest due to their remarkable water-repellent property, which makes them ideal for preventing the accumulation of dirt [1]. Inspired by natural surfaces such as lotus leaves, which exhibit unique self-cleaning properties. The superhydrophobic surface is defined by its wetting character, which shows a static water contact angle (WCA) greater than 150° and a sliding angle (SA) smaller than 10° [2]. The superhydrophobicity on the lotus leaf surface occurs due to a thin waxy layer on micro-scale papillae [3]. Various strategies have been employed to fabricate such surfaces, primarily by introducing surface roughness and incorporating low surface energy materials [4]. Numerous bioinspired and synthetic approaches have been explored to develop multifunctional surfaces with micro/nano features for applications including self-cleaning [5], oil–water separation [6], corrosion protection [7], anti-icing [8] and etc. In previous studies, a wide range of materials including SiO_2, TiO_2, ZnO, Al_2O_3, candle soot, and various polymers, have been employed in the development of self-cleaning superhydrophobic coatings. Latthe et al. [2] applied a suspension of hydrophobic SiO_2 nanoparticles (NPs) to various substrates, including motorcycle bodies, building walls, mini boats, solar cell panels, window glass, cotton shirts, fabric shoes, cellulose paper, metal, wood, sponges, plastic, and marble. These coatings demonstrated excellent water repellency and outstanding self-cleaning properties. Ding et al. [9] developed a superhydrophobic fluorinated polysiloxane/TiO_2 nanocomposite coating applicable to substrates such as aluminum, glass, wood, paper, and polypropylene. The coating exhibited excellent durability across a wide pH range, varying temperatures, and UV exposure, and was recoverable after oil contamination. A FAS-TiO_2/PVDF composite formed hierarchical micro/nanostructures via electrostatic interactions, and when applied to a copper substrate, showed a water contact angle of 160° and a sliding angle of 5°. Kokare et al.

[10] developed a self-cleaning superhydrophobic coating using Octadecyltrichlorosilane(ODS)-modified TiO_2 nanoparticles through a dip coating method. TiO_2 nanoparticles were dispersed in ethanol with varying concentrations of ODS to enhance hydrophobicity. The coatings prepared with five deposition layers exhibited a water contact angle above 150° and a sliding angle below 10°. Increasing ODS concentration improved surface roughness, enhancing water repellency. The coatings demonstrated stability against water jet impact and effectively repelled colored and muddy water, making them suitable for self-cleaning applications. In this work, TiO_2 nanoparticles were synthesized via a hydrothermal method and utilized to fabricate a superhydrophobic coating through a simple dip coating process. The coating was developed by incorporating PMHS and PS as surface-modifying and binding agents. The influence of coating thickness was investigated by varying the number of dip-coating cycles. The coating shows excellent superhydrophobicity and self-cleaning performance. This facile approach offers a cost-effective route to prepare superhydrophobic coating with potential applications in self-cleaning technologies.

2. Experimental Section

2.1 Chemicals

Titanium tetraisopropoxide (TTIP) was procured from Spectrochem Pvt. Ltd., Mumbai, India. Polymethylhydrosiloxane (PMHS) and polystyrene (PS) were purchased from Sigma Aldrich. Ethanol, Chloroform ($CHCl_3$) were procured from Loba Chemie. Micro glass substrates (75× 25 × 1.35 mm) were obtained from Blue star, Polar Industrial Corporation, India.

2.2 Synthesis of TiO_2 Nanoparticles via Hydrothermal Method

Initially, 20 mL of ethanol was mixed with 30 mL of distilled water and stirred at 400 rpm for 20 min to form a homogeneous solution. Subsequently, 15 mL of titanium tetraisopropoxide (TTIP) dissolved in 25 mL of ethanol was added dropwise to the above mixture under continuous stirring. The resulting sol was further stirred at ambient temperature for 2 h to promote hydrolysis and condensation reactions, forming a uniform sol-gel system. The obtained sol-gel was transferred to a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 80 °C for 24 h. Upon completion, the product was collected and dried at 40 °C for 3 h to remove residual solvents. The dried material was ground using an agate mortar to reduce particle size and improve uniformity. Finally, the resulting powder was calcinated at 400 °C for 2 h to obtain TiO_2 nanoparticles.

2.3.Preparation of TiO_2-PS Superhydrophobic Coating

The glass substrates were sequentially cleaned using ultrasonic treatment in 0.1 M Hcl, 0.1 M NH_4OH, ethanol, and distilled water, each for 10 minutes. After cleaning, the substrates were dried in a hot air oven at 60 °C for 10 minutes before being utilized for the fabrication process. Initially by dissolving 0.16 mL of PMHS in 40 mL of chloroform. The mixture was stirred for 20 min using a magnetic stirrer at 100 rpm to ensure complete dissolution. Subsequently, 800 mg of unmodified TiO_2 nanoparticles were added to the PMHS solution, and the resulting suspension was stirred continuously for 1 h to achieve a homogeneous dispersion of nanoparticles. Simultaneously, in a separate beaker, 200 mg of PS was dissolved in 20 mL of chloroform. This PS solution was then added to the TiO_2-PMHS suspension under constant stirring. The combined mixture was stirred for an additional 30 min to obtain a uniform and stable coating solution suitable for deposition. Pre-cleaned glass slides were immersed in the prepared coating solution. The number of deposition cycles was varied as 1, 2, and 3, respectively, to study the influence of coating thickness. After deposition, the coated slides were dried in an oven at 100 °C for 30 min to ensure solvent evaporation and film formation.

3. Results and Discussion

3.1. Wettability

The wettability of the fabricated superhydrophobic glass surfaces was assessed by measuring the water contact angle using a contact angle goniometer. Samples were prepared with one, two, and three deposition cycles to evaluate the effect of deposition frequency on surface hydrophobicity. The results showed a clear trend of increasing WCA with the number of deposition cycles, indicating enhanced surface superhydrophobicity. Specifically, the WCA for the sample with one deposition cycle was measured at 154°, which increased to 159° after two deposition cycles. Further improvement was observed with three deposition cycles, where the WCA reached 164°. This progressive increase in WCA demonstrates that a greater number of deposition cycles contributes to the development of hierarchical surface roughness and reduced surface energy, two critical factors for achieving superhydrophobic behavior. Therefore, the surface coated with three deposition cycles exhibited the highest degree of water repellency, representing the optimal condition for superhydrophobic performance in this study.

3.2. Self-Cleaning Ability

The self-cleaning ability of the superhydrophobic coating was tested using a simple muddy water test. A stream of muddy water was poured onto the coated glass slide to observe its behaviour.

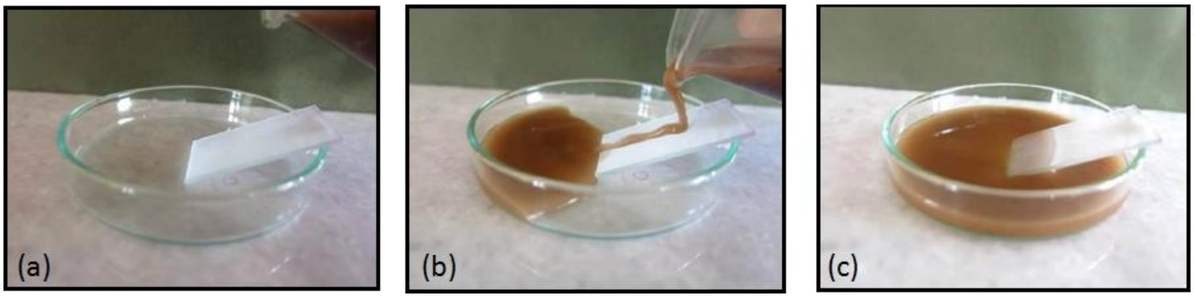

Fig. 1: Photograph showing muddy water rolling off the coated glass slide during the self-cleaning performance.

The muddy water was seen to roll off the surface without leaving any residues, indicating excellent self-cleaning performance. This property is attributed to the high water contact angle and low surface adhesion of the superhydrophobic surface.

3.3. Mechanical Durability

The mechanical durability of superhydrophobic coatings is a critical factor for their real-world applicability, particularly in outdoor environments where surfaces may be subjected to physical wear and environmental contaminants. In this study, the mechanical robustness of the coated glass slide was evaluated through a muddy water resistance test. Approximately 2 L of muddy water were continuously poured over the coated surface to simulate prolonged exposure to abrasive and wet conditions. Prior to the test, the WCA of the coated slide was measured at 164°, indicating excellent superhydrophobicity. However, after the durability test, a noticeable reduction in WCA was observed, decreasing to 154°, which suggests partial degradation of the surface coating due to mechanical stress. Despite this reduction, the surface maintained a contact angle above 150°, confirming that the coating still exhibited superhydrophobic behavior. These results indicate that while some loss in hydrophobic performance occurred, the coating retained moderate mechanical durability under harsh testing conditions.

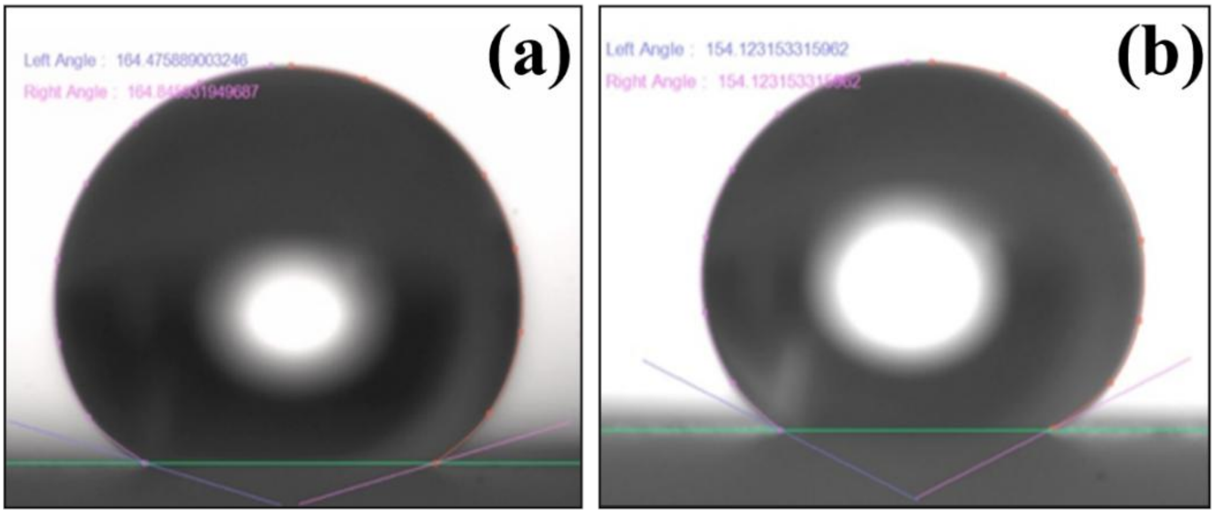

Fig. 2: Water contact angle of the coating (a) before durability test (164 °) and (b) after durability test (154°).

4. Conclusion

We have successfully fabricated superhydrophobic surface on a glass substrate using the simple dip coating technique. The method employed a mixture of PMHS, chloroform, and TiO_2 nanoparticles. The fabricated surface exhibited a water contact angle of up to 164° and a sliding angle of 5°. The coated glass slides demonstrated excellent self-cleaning behavior by repelling muddy water without residue. Moreover, the coating retained its superhydrophobic nature even after a mechanical durability test involving muddy water, although a slight reduction in contact angle was noted. Overall, the dip coating technique proved to be a simple and effective method for fabricating superhydrophobic coatings with promising practical applications.

Acknowledgements

One of the authors, SSL, is grateful for financial assistance received through the Seed Money Scheme from Vivekanand College, Kolhapur (Empowered Autonomous), Ref. No. VCK/3108/2023-24 dated 30/03/2024.

References:

[1] S. Wang, K. Liu, X. Yao, L. Jiang, Bioinspired surfaces with superwettability: new insight on theory, design, and applications, Chemical reviews, 115 (2015) 8230-8293.

[2] S.S. Latthe, R.S. Sutar, V.S. Kodag, A. Bhosale, A.M. Kumar, K.K. Sadasivuni, R. Xing, S. Liu, Self–cleaning superhydrophobic coatings: Potential industrial applications, Progress in Organic Coatings, 128 (2019) 52-58.

[3] Z. Liang, M. Geng, B. Dong, L. Zhao, S. Wang, Transparent and robust SiO2/PDMS composite coatings with self-cleaning, Surface Engineering, 36 (2020) 643-650.

[4] S.S. Latthe, C. Terashima, K. Nakata, M. Sakai, A. Fujishima, Development of sol–gel processed semi-transparent and self-cleaning superhydrophobic coatings, Journal of Materials Chemistry A, 2 (2014) 5548-5553.

[5] X. Wang, H. Ding, S. Sun, H. Zhang, R. Zhou, Y. Li, Y. Liang, J. Wang, Preparation of a temperature-sensitive superhydrophobic self-cleaning SiO2-TiO2@ PDMS coating with photocatalytic activity, Surface and Coatings Technology, 408 (2021) 126853.

[6] P. Xu, X. Li, Fabrication of TiO2/SiO2 superhydrophobic coating for efficient oil/water separation, Journal of Environmental Chemical Engineering, 9 (2021) 105538.

[7] X. Liu, T. Zhan, B. Zhang, Attapulgite-based superhydrophobic coating on aluminum alloy substrate with self-cleaning, anti-corrosion and robustness, Journal of Industrial and Engineering Chemistry, 130 (2024) 357-367.

[8] X. Zhou, S. Yu, S. Jiao, Z. Lv, E. Liu, Y. Zhao, N. Cao, Fabrication of superhydrophobic TiO2 quadrangular nanorod film with self-cleaning, anti-icing properties, Ceramics International, 45 (2019) 11508-11516.

[9] X. Ding, S. Zhou, G. Gu, L. Wu, A facile and large-area fabrication method of superhydrophobic self-cleaning fluorinated polysiloxane/TiO 2 nanocomposite coatings with long-term durability, Journal of Materials Chemistry, 21 (2011) 6161-6164.

[10] A.M. Kokare, R.S. Sutar, S. Deshmukh, R. Xing, S. Liu, S.S. Latthe, ODS–modified TiO2 nanoparticles for the preparation of self-cleaning superhydrophobic coating, in: AIP Conference Proceedings, AIP Publishing, 2018.