IRSTI 29.19.22 https://doi.org/10.26577/ijmph.2024v15i1a9

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Obtaining hydrophobic coatings from AR+HMDSO u sing radiofrequency discharge at atmospheric pressure

Abstract. Hydrophobic coatings have attracted much attention due to their wide applications in various industries including electronics, textiles, and automotive. This study deals with the process of creating nanoscale coatings on a substrate achieved by plasma polymerization using plasma flow (jet) using radiofrequency discharge together with the precursor c6h18osi2 and the carrier gas Ar. In this work, we investigate the production of hydrophobic coatings using radiofrequency (RF) discharge at atmospheric pressure using a mixture of argon (Ar) and hexamethyldisiloxane (HMDSO). RF discharge is a versatile and efficient method of plasma generation that allows the deposition of thin films with defined properties. Here we investigate the influence of process parameters such as gas flow rate, discharge power, and substrate temperature on the morphology, chemistry, and hydrophobicity of the deposited coatings. The formation of these coatings was carefully studied under atmospheric pressure conditions, varying the number of cycles of experiments while maintaining optimal plasma parameters. The properties and elemental composition of the coatings were thoroughly studied using scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). In addition, the obtained coatings were found to possess hydrophobic properties. The hydrophobicity of these coatings was evaluated by measuring the contact angle with a goniometer with respect to cycles of experiments and long-term durability. This study contributes to a better understanding of the synthesis, structure, and hydrophobic characteristics of nanoscale coatings, opening promising perspectives for various applications. The results show that the hydrophobicity of the coatings can be optimized by tuning the process parameters, resulting in coatings with water contact angles greater than 160 degrees. Additionally, the durability and stability of the hydrophobic coatings are evaluated under different environmental conditions, allowing an assessment of their potential for practical applications.
Key words: plasma polymerization, atmospheric pressure, superhydrophobic coatings.

Introduction

Hydrophobic coatings, which repel water due to their low surface energy, find wide applications in various industries ranging from electronics to textiles [1], automotive [2], and medical devices [3]. Among the methods for producing hydrophobic coatings, the radiofrequency (RF) discharge at atmospheric pressure offers a promising avenue [4]. This technique involves the deposition of hydrophobic coatings from a precursor gas mixture of argon (Ar) and hexamethyldisiloxane (HMDSO) under the influence of RF discharge. The use of RF discharge at atmospheric pressure presents several advantages over conventional methods such as chemical vapor deposition (CVD) [5] and plasma-enhanced chemical vapor deposition (PECVD) [6]. Firstly, operating at atmospheric pressure eliminates the need for vacuum systems, simplifying the setup and reducing production costs. Secondly, the RF discharge process allows for precise control over the deposition parameters, resulting in coatings with tailored properties [7.8].

Certain techniques, such as acquiring coatings through chemical processes and under atmospheric pressure, offer superior cost efficiency and enhanced efficacy for large-scale manufacturing. Through the utilization of chemical procedures, it is possible to procure hydrophobic and superhydrophobic coatings characterized by exceptional stability [9]. Nonetheless, the chemical approach for obtaining superhydrophobic coatings necessitates the use of hazardous liquids and diverse solvents, presenting a notable drawback that can endanger human health and the environment. Moreover, the aforementioned techniques entail multiple stages for achieving superhydrophobic coatings, rendering the process of uniformly dispersing coatings intricate and time-intensive. Hence, the imperative of employing economical and eco-friendly methods across expansive surfaces emerges as a pressing concern.

Hydrophobic coatings obtained from Ar+HMDSO using RF discharge exhibit excellent water-repellent properties, making them suitable for applications requiring protection against moisture [10], corrosion [11], and fouling [12]. These coatings demonstrate high durability [13], thermal stability [14], and chemical resistance [15], making them ideal for outdoor and harsh environment applications [16.17].

We delve into the mechanisms underlying the formation of hydrophobic coatings through RF discharge at atmospheric pressure using Ar+HMDSO precursor gas mixture. We explore the influence of process parameters such as gas composition, discharge power, and substrate temperature on the properties of the resulting coatings. Additionally, we highlight the potential applications and future prospects of these hydrophobic coatings in various industries.

The results obtained may be of significant practical importance for the development of new materials with improved characteristics and expansion of their application area.

Experimental section

The scheme of an experimental installation aimed at studying the coating obtained using a plasma jet based on RF discharge at atmospheric pressure is shown in Figure 1. The plasma flux (jet) was generated using an RF generator between a copper wire wrapped in quartz glass and a grounded copper plate. Glass tube length: 100mm, inner diameter: 3mm and outer diameter: 10mm. Seren-R 301 with a high frequency of 13.56 MHz was used as a power source. Inert gas Ar and precursors HMDSO were used as the main gas flow. HMDSO is in liquid form at room temperature and therefore has a small volume poured into a barbotter. The flow of the prequels is controlled by the mass flow controller. The resulting coating samples settle on a glass substrate measuring 2x2 centimetre. Before starting the experiment, glass samples used as substrates are cleaned in an ultrasonic bath for 10 minutes. First, the concentration of gas mixtures Ar and HMDSO is sent to the quartz glass tube, and then, when a high-frequency voltage is applied to the electrode located outside the tube, atmospheric pressure plasma ignition occurs. As a result of coagulation of atoms in a plasma medium, the process of chemical reactions takes place, at a certain moment of time the coating grows to the nanoscale [10]. The experiment was carried out for the following parameters of the plasma: power magnitude 100-200 Watts, HMDSO/Ar fraction (Ar fraction 98%, HMDSO fraction 2%, respectively)

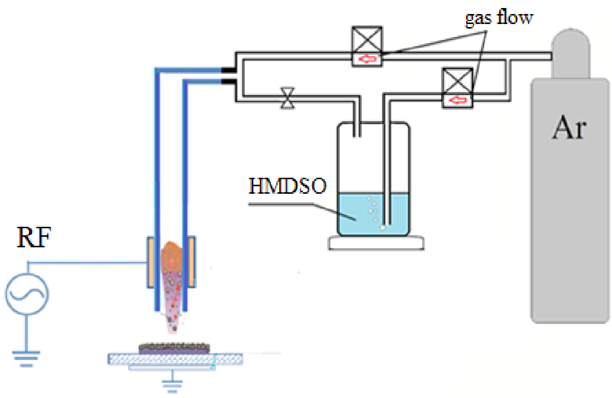


Figure 1 – Scheme of experimental setup

Main provision

In this study, a nanoscale coating was applied to the glass surface using RF discharge at atmospheric pressure. The coating exhibits hydrophobic properties. The hydrophobicity was tested under various experiment cycles while maintaining constant power, as well as assessing its durability over time.

Results and discussion

The following analyses were carried out to determine the properties of the coating formed as a result of the reaction of precursors with plasma flow on the surface of a glass sample.

- Morphological properties

The morphological properties of the synthesized samples were studied using a Quanta 3D 200i scanning electron microscope (SEM). The results of the analysis showed that the obtained particles have a variety of shapes, including spherical. The surface of the particles is heterogeneous and their sizes vary from 20 nm to 0.1 µm (Fig. 2).

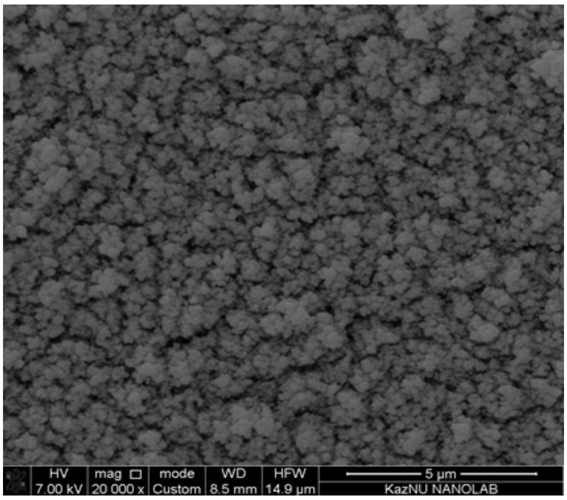


Figure 2 – SEM-micrographs of synthesized superhydrophobic particles formed on the glass surface

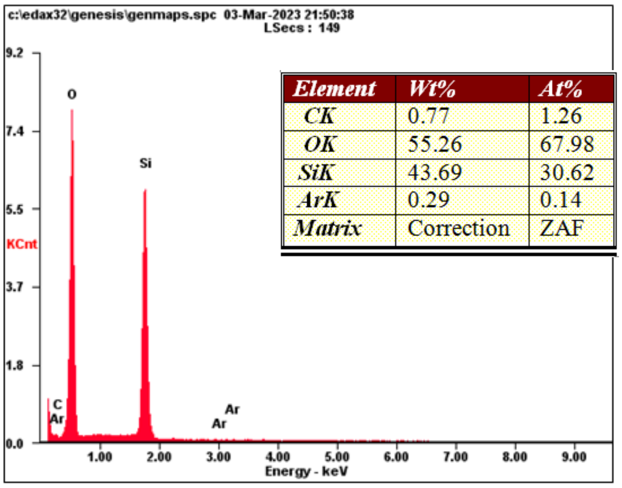
- Chemical composition

EDS spectroscopy (Electron Dispersive Spectroscopy) was used to determine the chemical composition of the synthesized coatings. The results of the analysis showed that the obtained coatings consist of the precursors component elements (Fig. 3)

- Hydrophobic properties

The morphological analysis of the obtained sample showed that the surface presents a water repellent property, i.e. hydrophobic character. To confirm this, the angle of contact with water was evaluated. Figure 4 shows a graph showing the relationship between the contact angle and the number of cycles of the experiment.

When analyzing the graph, it becomes evident that the contact angle undergoes minimal changes when the number of cycles is changed (Fig. 5).



Element	Wt%	At%
CK	0.77	1.26
OK	55.26	67.98
SiK	43.69	30.62
ArK	0.29	0.14
Matrix	Correction	ZAF

Figure 3 – Chemical composition of obtained coatings

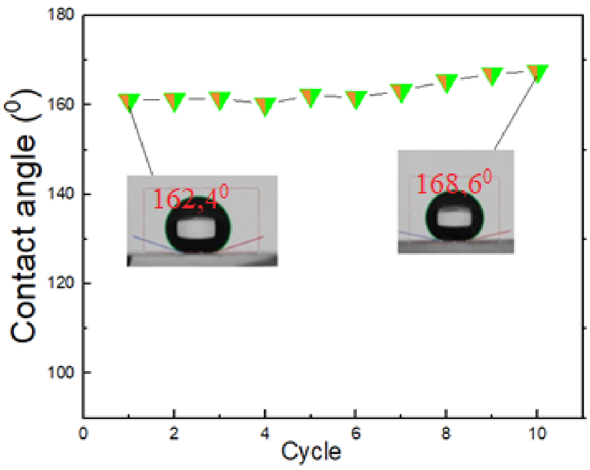


Figure 4 – Hydrophobic properties of the obtained samples proving through contact angle from the cycle of experiment

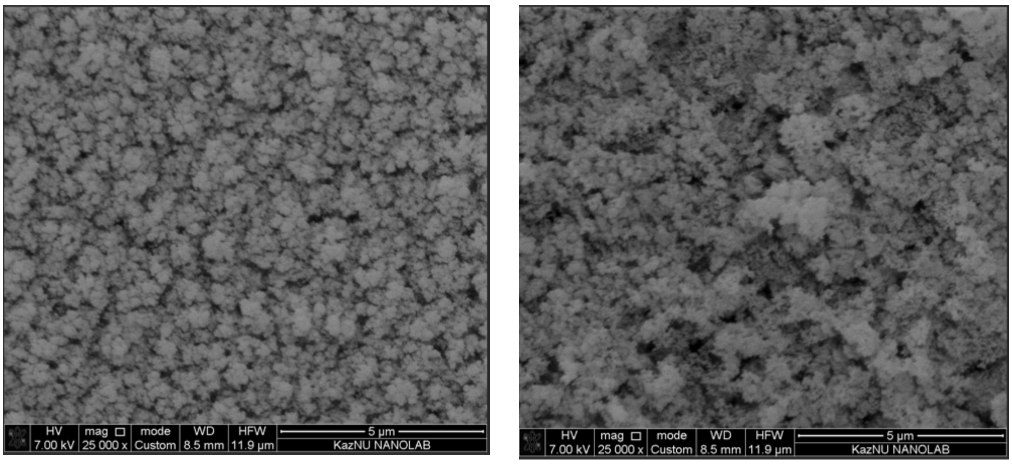


Figure 5 – Change of coating surface with increasing cycle of the experiment

This indicates that the experimental cycles have a negligible effect on the contact angle of the film because the process reached an equilibrium state relatively quickly, where further cycles have less and less effect on the surface properties. Also for further characterization, the contact angle with a long time course was measured (Figure 6). A trend is shown that the contact angle decreases over time which indicates a loss of superhydrophobicity i.e. the surface becomes less water repellent. The samples were stored under room conditions. However, when exposed to environmental factors such as UV radiation, humidity or chemical contaminants, the surface may undergo degradation. As a result of degradation, the surface structure may change, i.e., the chemical composition of the surface changes resulting in an uneven surface that will reduce its ability to effectively repel water.

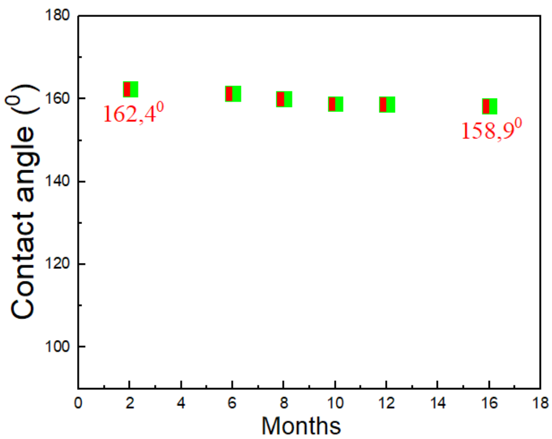


Figure 6 – Hydrophobic properties of the obtained samples proving through contact angle from the over time (0-18 months)

Conclusion

In conclusion, this study successfully demonstrated the formation and characterization of nanoscale coatings on a substrate through plasma polymerization, utilizing the precursor C6H18OSi2 and Ar carrier gas under radiofrequency discharge. The investigation focused on optimizing plasma parameters and assessing the coatings' properties under atmospheric pressure conditions, with particular attention to the number of experiment cycles. Through thorough analysis using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), we gained insights into the structural morphology and elemental composition of the coatings. Furthermore, the observed hydrophobicity of the coatings suggests their potential utility in applications requiring water repellency.

The results presented herein contribute to advancing our understanding of nanoscale coating synthesis and performance, with implications for various fields such as surface engineering, materials science, and functional coatings. Future research may delve deeper into optimizing coating parameters and exploring additional characterization techniques to further enhance our understanding and potential applications of these coatings.

Acknowledgements

All authors are grateful to the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP13067865 and Program No. BR21882187)

References

1. Wensheng Li, Zhenting Yin, Liangyuan Qi, Bin Yu, Weiyi Xing. "Scalable production of bioinspired MXene/black phosphorene nanocoatings for hydrophobic and fire-safe textiles with tunable electromagnetic interference and exceeding thermal management. ". *Chemical Engineering Journal* 460 no 15 (2023):141870– (In China). https://doi.org/10.1016/j.cej.2023.141870

2. Xiaodi Dong, Baoquan Wan, Yang Feng, Daomin Min, Ming-Sheng Zheng, Haiping Xu, Zhi-Min Dang, George Chen, Jun-Wei Zha. "Ultra-low-permittivity, high hydrophobic, and excellent thermally stable fluoroelastomer/polyimide composite films employing dielectric reduction ". *European Polymer Journal* 181 no 5 (2022): 111667– (In China), https://doi.org/10.1016/j.eurpolymj.2022.111667

3. Jiaojiao Du, Pengfei Wu, Haijiang Kou, Pengfei Gao, Yang Cao, Lingling Jing, Shengyu Wang, Peter Rusinov, Chao Zhang. "Self-healing superhydrophobic coating with durability based on EP + PDMS/SiO2 double-layer structure design". *Progress in Organic Coatings* 190 (2024): 108359–(In China) https://doi.org/10.1016/j.porgcoat.2024.108359

4. Chuanlong Ma, Lei Wang, Anton Nikiforov, Yuliia Onyshchenko, Pieter Cools, Kostya (Ken) Ostrikov, Nathalie De Geyter, Rino Morent. "Atmospheric-pressure plasma assisted engineering of polymer surfaces: From high hydrophobicity to superhydrophilicity". *Applied Surface Science* 535 (2021):147032–(In Ghent, Belgium) https://doi.org/10.1016/j.apsusc.2020.147032

5. Yawen Yuan, Yishi Wang, Shasha Liu, Xuxue Zhang, Xinzheng Liu, Changhui Sun, Dong Yuan, Yan Zhang, Xiaorong Cao. "Direct chemical vapor deposition synthesis of graphene super-hydrophobic transparent glass" *Vacuum* 202 ., (2022): 111136–(In China) https://doi.org/10.1016/j.vacuum.2022.111136

6. A. Orazbayev, M. N. Jumagulov, M. K. Dosbolayev, M. Silamiya, T. S. Ramazanov, L. Boufendi,. "Optical spectroscopic diagnostics of dusty plasma in rf discharge". *In Dusty/Complex Plasmas: Basic and Interdisciplinary Research*, Vol. 1397 (2020): pp. 379-380–(In Kazakhstan) https://doi.org/10.1063/1.3659852

7. Sagi Orazbayev, Rakhymzhan Zhumadilov, Askar Zhunisbekov, Maratbek Gabdullin, Yerassyl Yerlanuly, Almasbek Utegenov, Tlekkabul Ramazanov. "Superhydrophobic carbonous surfaces production by PECVD methods". *Applied Surface Science* 515 (2020): 146050–(In Kazakhstan). https://doi.org/10.1016/j.apsusc.2020.146050

8. S.A. Orazbayev, A.U. Utegenov, A.T. Zhunisbekov, M. Slamyiya, M.K. Dosbolayev, T.S. Ramazanov, "Synthesis of carbon and copper nanoparticles in radio frequency plasma with additional electrostatic field " *Contrib. Plasma Phys.* 58 (10) (2018): 961–966–(In Kazakhstan). https://doi.org/10.1002/ctpp.201700146

9. S.A. Orazbayev, M.M. Muratov, T.S. Ramazanov, M.K. Dosbolayev, M. Silamiya, M.N. Jumagulov, and L. Boufendi. "The Diagnostics of Dusty Plasma in RF Discharge by Two Different Methods" *Contrib. Plasma Phys*. 53 (2013): 436–(In Kazakhstan). https://doi.org/10.1002/ctpp.201200123

10. Zheng, S., Li, C., Fu, Q., Li, M., Hu, W., Wang, Q., Chen, Z. "Fabrication of self-cleaning superhydrophobic surface on aluminum alloys with excellent corrosion resistance". *Surf. Coat. Technol*. 276 (2015): 341–348–(In China) . https://doi.org/10.1016/j.surfcoat.2015.07.002

11. Genzer, J., and Efimenko, K. "Recent developments in superhydrophobic surfaces and their relevance to marine fouling: a review". *Biofouling* 22 (5-6) (2006): 339-360–(In China). https://doi.org/10.1080/08927010600980223

12. Zixiao Hong, Yuxin Xu, Daiqi Ye, Yun Hu. "One-step fabrication of a robust and transparent superhydrophobic self-cleaning coating using a hydrophobic binder at room temperature: A combined experimental and molecular dynamics simulation study". *Surface and Coatings Technology* 472 (2023): 129943–(In China) https://doi.org/10.1016/j.surfcoat.2023.129943

13. Jiaojiao Du, Pengfei Wu, Haijiang Kou, Pengfei Gao, Yang Cao, Lingling Jing, Shengyu Wang, Peter Rusinov, Chao Zhang. "Self-healing superhydrophobic coating with durability based on EP + PDMS/SiO2 double-layer structure design". *Progress in Organic Coatings* 190 (2024): 108359–(In China) https://doi.org/10.1016/j.porgcoat.2024.108359

14. Shih-Hsien Yang, Chi-Hung Liu, Chun-Hsien Su, Hui Chen. "Atmospheric-pressure plasma deposition of SiOx films for super-hydrophobic application". *Thin Solid Films*, Pages 517 no (17) (2009): 5284-5287–(In Taiwan ROC) https://doi.org/10.1016/j.tsf.2009.03.083

15. Jizhou Sun , Jian Wang, Weichen Xu, Binbin Zhang. "A mechanically robust superhydrophobic corrosion resistant coating with self-healing capability". *Materials & Design* 240 (2024): 112881–(In China) https://doi.org/10.1016/j.matdes.2024.112881

16. K.B. Golovin, J.W. Gose, M. Perlin, S.L. Ceccio, A. Tuteja. "Bioinspired surfaces for turbulent drag reduction". *Phil. Trans. Math. Phys. Eng. Sci.* 374 (2016): 20160189–(In China) https://doi.org/10.1098/rsta.2016.0189.

17. S. Brown, J. Lengaigne, N. Sharifi, M. Pugh, C. Moreau, A. Dolatabadi, L. Martinu, J.E. "Klemberg-Sapieha, Durability of superhydrophobic duplex coating systems for aerospace applications*". Surface and Coatings Technology* 401 (2020): 126249–(In Canada) https://doi.org/10.1016/j.surfcoat.2020.126249.

18. K. Gotoh, E. Shohbuke, G. Ryu. "Application of atmospheric pressure plasma polymerization for soil guard finishing of textiles" *Textil. Res. J.* 88 (2018): 1278–1289, https://doi.org/10.1177/0040517517698988.

19. Asadollahi, S., Profili, J., Farzaneh, M., & Stafford, L. "Multi-pass deposition of organosilicon-based superhydrophobic coatings in atmospheric pressure plasma jets". *Thin Solid Films* 714 (2020): 138369–(In Canada) https://doi:10.1016/j.tsf.2020.138369

20. L. Wang, S. Guo and S. Dong. "Facile Electrochemical Route to Directly Fabricate Hierarchical Spherical Cupreous Microstructures: Toward Superhydrophobic Surface". *Electrochemistry Communications*, Vol. 10 no 4 (2008), , pp. 655-658–(In China) . https://doi.org/10.1016/j.elecom.2008.01.034

21. Sultan S. Ussenkhan, Baglan A. Kyrykbay, Yerassyl Yerlanuly, Askar T. Zhunisbekov, Maratbek T. Gabdullin, Tlekkabul S. Ramazanov, Sagi A. Orazbayev, Almasbek U. Utegenov, "Fabricating durable and stable superhydrophobic coatings by the atmospheric pressure plasma polymerisation of hexamethyldisiloxane". *Heliyon*,Volume 10, Issue 1, (2024): e23844–(In Kazakhstan) . https://doi.org/10.1016/j.heliyon.2023.e23844

22. Orazbayev S., Gabdullin M., Ramazanov T., Askar, Z., Rakhymzhan Z. "Obtaining hydrophobic surfaces in atmospheric pressure plasma". *Mater. Today Proc.* 20 (2020):335–341–(In Kazakhstan).. https://doi.org/10.1016/j.matpr.2019.10.071

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Received 29 April 2024
Accepted 03 June 2024