

REVIEW

on thesis of

Zuo Yong

On the topic «Stability of textured water-repellent surfaces (Стабільність текстурованих водовідштовхувальних поверхонь)»,
submitted for the degree of Doctor of Philosophy
field of knowledge 16 – Chemical and Bioengineering
specialty 161 – Chemical Technology and Engineering

Relevance of the dissertation topic.

The significance of the dissertation research stems from the growing demand for a deeper understanding of physicochemical processes occurring at solid–liquid and solid–gas interfaces, which govern the performance of modern functional coatings. The creation of surfaces exhibiting extreme water repellency remains an important challenge at the intersection of colloid chemistry, surface chemistry, polymer science, and corrosion science. Despite considerable progress in this field, many aspects related to the formation, stability, and degradation of superhydrophobic systems remain insufficiently understood.

The topic is also consistent with the strategic priorities of scientific and technological development in Ukraine, particularly those associated with advanced materials, environmentally responsible technologies, and the extension of service life of metallic structures operating under aggressive environmental conditions. From both scientific and practical perspectives, corrosion protection of aluminum alloys remains a relevant problem because the durability of such materials is controlled by a complex interplay of electrochemical reactions, interfacial phenomena, and environmental factors.

The dissertation addresses several fundamental questions concerning the relationship between surface chemistry, hierarchical morphology, and wetting behavior. Particular attention is devoted to the influence of surface free energy components on the stabilization of superhydrophobic states, the role of chemical modification in controlling interfacial interactions, and the mechanisms responsible for the deterioration of functional properties during environmental exposure. The study further examines the chemical transformations occurring within the polymer matrix under ultraviolet irradiation and their impact on coating performance. In addition, the work provides valuable insight into the coupling between surface wettability and electrochemical corrosion processes in coated aluminum systems.

The obtained results contribute to the advancement of fundamental knowledge in the fields of surface and colloid chemistry, physicochemistry of interfaces, and

corrosion science, while simultaneously providing a scientific basis for the rational design of multifunctional protective coatings with improved long-term stability.

Thus, the topic of Zuo Yong's work can be considered as relevant.

Assessment of the validity of the scientific results of the dissertation, their reliability and novelty.

The scientific novelty of the dissertation's findings lies in the following:

An important scientific achievement of the dissertation is the establishment of a comprehensive framework for the characterization of superhydrophobic surfaces based on the combined application of dynamic wetting analysis and surface free energy decomposition. The author convincingly demonstrates that static contact angle measurements alone are insufficient for describing wetting behavior and that the polar component of surface energy plays a decisive role in stabilizing the Cassie-Baxter state. This finding significantly expands the methodological basis for evaluating and designing superhydrophobic materials.

A further contribution of the work is the systematic investigation of wetting phenomena across textured surfaces covering an exceptionally broad range of characteristic dimensions. The obtained results provide new insight into the limitations of classical equilibrium wetting models and reveal the growing influence of contact line pinning effects at large texture periodicities. These findings contribute to a more complete understanding of the transition between different wetting regimes on structured surfaces.

Particularly noteworthy is the identification of the dominant degradation pathway of superhydrophobic composite coatings during environmental exposure. Through the combination of accelerated UV aging experiments and spectroscopic analysis, the author demonstrates that photo-oxidative transformations of the polymer matrix constitute the principal cause of performance deterioration. The reported changes in characteristic FTIR absorption bands provide convincing experimental evidence supporting the proposed degradation mechanism and clarify the chemical origin of the loss of hydrophobicity.

The dissertation further establishes a scientifically substantiated design concept for durable superhydrophobic coatings based on maximizing the density of the inorganic particle network while minimizing the amount of polymeric binder. The proposed formulation was experimentally validated and demonstrated substantial improvements in both wetting and electrochemical characteristics. The quantitative performance indicators reported by the author confirm the practical significance of this design strategy.

Another important element of novelty is the development and validation of a multiphysics computational model capable of reproducing electrochemical

polarization behavior and quantitatively separating the contributions of individual protection mechanisms. The model provides valuable mechanistic insight into the synergistic interaction between diffusion-controlled barrier effects and surface passivation processes, thereby strengthening the interpretation of the experimental observations.

Finally, the dissertation demonstrates that the dense inorganic framework within the optimized coating performs a dual function by simultaneously generating hierarchical surface roughness and acting as an effective barrier to ionic transport. The resulting mechanism-oriented design approach represents a meaningful advancement beyond traditional composition-based optimization strategies and contributes to the development of scientifically grounded principles for the creation of multifunctional protective coatings. The presented scientific results are sufficiently substantiated, supported by extensive experimental evidence, and fully justify the novelty claims formulated by the author.

The scientific research was performed by the applicant at the department of chemical technology of composite materials of Igor Sikorsky KPI within the framework of the scientific work plan approved by the Department of Chemical Technology of Composite Materials at Igor Sikorsky Kyiv Polytechnic Institute, taking into account the law of Ukraine "About priority directions of science and technics development" No. 2623-III dated 11.07.2001 on the relevance of the thesis topic to the direction "novel substances and materials" under the supervision of Head of Department of Chemical Technology of Composite Materials, doctor of technical sciences, associated professor Myronyuk Oleksiy Volodymyrovych.

The scientific objective set in the dissertation has been fully accomplished, and the candidate has fully mastered the methodology of scientific research.

Assessment of the content of the dissertation, its completeness, and compliance with the principles of academic integrity.

In terms of its content, the dissertation by candidate Zuo Yong fully complies with the Higher Education Standard for specialty 161, "Chemical Technologies and Engineering," and the research areas specified in the "Chemical Technologies and Engineering" educational program.

The dissertation is a complete scientific work and demonstrates the candidate's personal contribution to the research field of "New Substances and Materials."

Having reviewed the similarity report based on the results of the dissertation's text-matching check, it can be concluded that Zuo Yong's dissertation is the result of the candidate's independent research and contains no elements of falsification, compilation, fabrication, plagiarism, or borrowing. The ideas, results, and texts of

other authors that were used are properly cited with references to the corresponding sources.

Language and Style of Presenting Results

The dissertation is written in English.

The dissertation is well structured and logically organized, with all chapters consistently aligned with the stated research objectives. The material is presented in a coherent sequence, progressing from the theoretical background and literature review to the experimental results, their discussion, and the resulting conclusions.

The language and style are appropriate for a doctoral dissertation. The author correctly applies accepted terminology in the fields of materials science, surface chemistry, corrosion protection, and electrochemistry. Experimental methods and research findings are described clearly, while the figures and tables effectively support the presentation of the results.

The dissertation complies with the established academic requirements and provides an adequate and accessible presentation of the scientific and practical outcomes of the research. The dissertation consists of an introduction, six chapters, conclusions, a bibliography, and appendices. The total length of the dissertation is 154 pages.

The introduction substantiates the importance of the research topic, formulates the aim and objectives of the work, and presents the scientific novelty, practical significance, and personal contribution of the candidate. Information concerning the dissemination of the results and their connection with ongoing scientific research programs is also provided.

The first chapter presents a critical review of the current state of research in the field of superhydrophobic materials and protective coatings. Particular attention is devoted to the physicochemical principles of wetting, the role of surface morphology and chemistry in controlling interfacial phenomena, methods of chemical functionalization, and the use of inorganic particulate systems for the creation of hierarchical structures. The analysis of the literature enables the identification of unresolved scientific questions that form the basis of the dissertation.

The second chapter describes the materials employed in the study, including inorganic fillers, surface-modifying agents, and polymeric binders, together with the experimental and computational methods used. The chapter demonstrates the application of modern physicochemical, electrochemical, and spectroscopic techniques, providing a reliable foundation for the obtained results.

The third chapter investigates the relationship between surface topography and wetting behavior. The author analyzes textured surfaces over a broad range of characteristic dimensions, evaluates the applicability of classical wetting theories, and

examines the influence of structural parameters on contact line behavior and apparent hydrophobicity.

The fourth chapter focuses on the chemical aspects of superhydrophobic surface formation. Special attention is given to silane modification processes, changes in surface free energy, and the contribution of chemical composition to the stabilization of the Cassie–Baxter wetting regime. The results provide valuable insight into the physicochemical factors governing highly water-repellent surfaces.

The fifth chapter addresses the chemical and structural stability of superhydrophobic coatings under environmental exposure. Using accelerated aging and spectroscopic analysis, the author investigates degradation processes occurring within the coating and demonstrates the key role of photo-oxidative transformations of the polymer matrix in the deterioration of functional properties.

The sixth chapter presents the development of composite protective coatings based on inorganic particle networks and surface-functionalized fillers for corrosion protection of aluminum alloys. The relationships between composition, microstructure, electrochemical behavior, and protective performance are established. Experimental findings are complemented by multiphysics modeling, allowing the individual contributions of diffusion barrier effects and surface passivation processes to be quantitatively evaluated.

This dissertation is formatted in accordance with the requirements of Order No. 40 of the Ministry of Education and Science of Ukraine dated January 12, 2017, “On the Approval of Requirements for the Formatting of Dissertations.”

Presentation of dissertation results

The scientific findings of the dissertation are presented in four of the candidate’s scientific publications, including: two articles in scientific journals that were included in the list of Ukrainian scientific journals in their respective fields as of the date of publication; 2 articles in scientific journals indexed in the Web of Science Core Collection and/or Scopus databases, of which 2 articles appeared in journals classified in the first through third quartiles (Q1–Q3) according to the SCImago Journal and Country Rank or Journal Citation Reports classifications.

In addition, the results of the dissertation were presented at 5 scientific conferences.

The results obtained within the dissertation have been sufficiently communicated through the candidate’s scientific publications and presented to the professional community for evaluation and discussion. The published papers are directly related to the subject of the dissertation, contain its principal scientific outcomes, and adequately reflect the findings submitted for defense. A substantial

portion of the dissertation is founded on previously published peer-reviewed research, which enhances the reliability and traceability of the reported results.

The candidate's scientific contributions have been published in journals meeting the formal requirements for Doctor of Philosophy degree applicants. Examination of the publication portfolio confirms that the main concepts, experimental observations, and conclusions presented in the dissertation have been appropriately disseminated. The published works provide detailed methodological descriptions, experimental evidence, and scientific interpretation, thereby supporting the credibility and reproducibility of the research findings.

An assessment of the dissertation manuscript, abstract, and related publications did not reveal any indications of plagiarism, data fabrication, falsification, or other breaches of academic ethics. References to the work of other researchers are provided where appropriate, and all borrowed concepts and information are properly attributed. The dissertation constitutes an original piece of research based predominantly on the candidate's own scientific achievements and is consistent with the principles of academic integrity and accepted standards of scholarly conduct.

Thus, the scientific results described in the dissertation are fully reflected in the candidate's scientific publications.

Shortcomings and comments on the dissertation.

1. The dissertation places considerable emphasis on the morphology and functional performance of the developed composite coatings; however, the characterization of the inorganic fillers remains relatively limited. In particular, for the silane-functionalized calcium carbonate and fumed silica particles, no information is provided regarding specific surface area, particle size distribution after modification, degree of agglomeration, or grafted silane content. The absence of such data complicates the establishment of a direct relationship between filler characteristics and the resulting coating properties.
2. Many of the conclusions presented in the dissertation rely on the effectiveness of silane surface modification of both the particles and the aluminum substrate. However, the degree of surface functionalization is not quantitatively assessed. Although FTIR spectroscopy confirms the presence of organic functional groups, it does not provide a reliable measure of surface coverage or reaction completeness. Additional characterization by XPS, TGA, or surface elemental analysis would have strengthened the evidence supporting the proposed modification mechanism.
3. The proposed coating concept is based predominantly on the use of calcium carbonate particles; however, the dissertation contains little discussion regarding the rationale behind this choice compared to other widely used inorganic fillers

for superhydrophobic systems, such as alumina, titania, zinc oxide, talc, or diatomaceous earth. Consequently, it remains unclear whether the observed effects are specific to calcium carbonate or represent a more general behavior of particulate mineral fillers with similar morphology.

4. The author convincingly demonstrates an increase in carbonyl absorption and a decrease in aliphatic functional groups during UV exposure. Nevertheless, the mechanism of photo-oxidative degradation of the polymer matrix is discussed primarily on a qualitative basis. The work does not attempt to quantify oxidation kinetics, conversion of functional groups, or molecular weight changes within the polymer phase, which could have provided a more comprehensive understanding of the degradation processes involved.
5. For a number of experimental datasets, only average values are reported without confidence intervals, statistical significance testing, or detailed assessment of data variability. This is particularly relevant for wetting characteristics and electrochemical measurements, both of which can be highly sensitive to local surface heterogeneities. A more comprehensive statistical analysis would have increased confidence in the observed trends and strengthened the reliability of the conclusions.
6. The dissertation suggests that silane treatment contributes to increased charge-transfer resistance and improved corrosion protection through surface passivation. However, direct evidence regarding changes in the composition or structure of the native aluminum oxide layer is not provided. The absence of surface-sensitive analytical techniques such as XPS or Auger electron spectroscopy limits the ability to conclusively verify the proposed passivation mechanism.
7. The bifractional $\text{CaCO}_3/\text{SiO}_2$ system is presented as a key element of the optimized coating architecture; however, the contribution of silica nanoparticles is considered mainly from the perspective of hierarchical roughness generation. Their possible influence on suspension rheology, particle packing density, pore structure, mechanical stability of the inorganic network, and long-term coating durability is not examined in detail. A more thorough analysis of these effects would have enhanced the scientific depth of the study.
8. The corrosion resistance of the developed coatings was evaluated primarily in a 3 wt.% NaCl solution. While this electrolyte is widely used in laboratory studies, practical applications often involve environments with substantially different chemical compositions and pH values. Additional testing under acidic, alkaline, or mixed-ion conditions would have provided a more comprehensive assessment of the applicability and limitations of the proposed coating system.

I can assume that the comments made are not decisive, do not diminish the overall scientific novelty and practical significance of the results, and do not affect the positive evaluation of the dissertation.

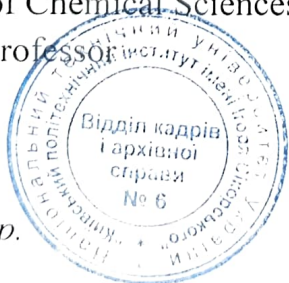
Conclusion on the Dissertation

I confirm that the doctoral dissertation by Zuo Yong, a candidate for the degree of Doctor of Philosophy, on the topic “Stability of Textured Water-Repellent Surfaces” has been carried out to a high scientific standard, does not violate the principles of academic integrity, and constitutes a complete scientific study, the combination of theoretical and practical results of which solves a scientific problem of significant importance for chemical and bioengineering. In terms of its relevance, practical value, and scientific novelty, the dissertation fully complies with the requirements of current Ukrainian legislation, as set forth in paragraphs 6–9 of the “Procedure for Awarding the Degree of Doctor of Philosophy and for Revoking the Decision of an Ad Hoc Specialized Academic Council of a Higher Education Institution or Research Institution on Awarding the Degree of Doctor of Philosophy,” approved by Resolution No. 44 of the Cabinet of Ministers of Ukraine dated January 12, 2022.

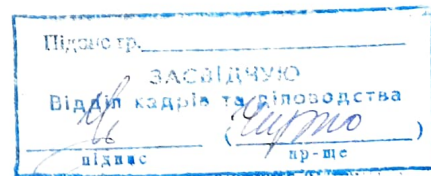
Candidate Zuo Yong is eligible to be awarded a Doctor of Philosophy degree in Field of Study 16, Chemical and Bioengineering, in the specialty 161, Chemical Technology and Engineering.

Reviewer:

Associate Professor of Chemical Technology
of Ceramics and Glass Department
of Igor Sikorsky Kyiv Polytechnic Institute,
Candidate of Chemical Sciences,
Associate Professor



Ihor PYLYPENKO



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