coatings

Editorial

Superhydrophobic and Superoleophobic Surfaces: Key Points, Challenges and Applications

Ioannis Karapanagiotis

Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; karapana@chem.auth.gr

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1. Introduction: Terminology and Key Points

Non-wettable surfaces have been uninterruptedly studied during the 20th century [1] but they have attracted increasing scientific interest in the last two decades, as is evident in Figure 1, due to their numerous potential technological applications. The goal of this short Editorial is twofold: (i) to provide a critical discussion on the relevant terminology and key points which are used to describe the non-wetting state (Section 1) and (ii) to describe the nine research articles which are included in this Special Issue, titled "Superhydrophobic and Superoleophobic Surfaces" (Section 2).

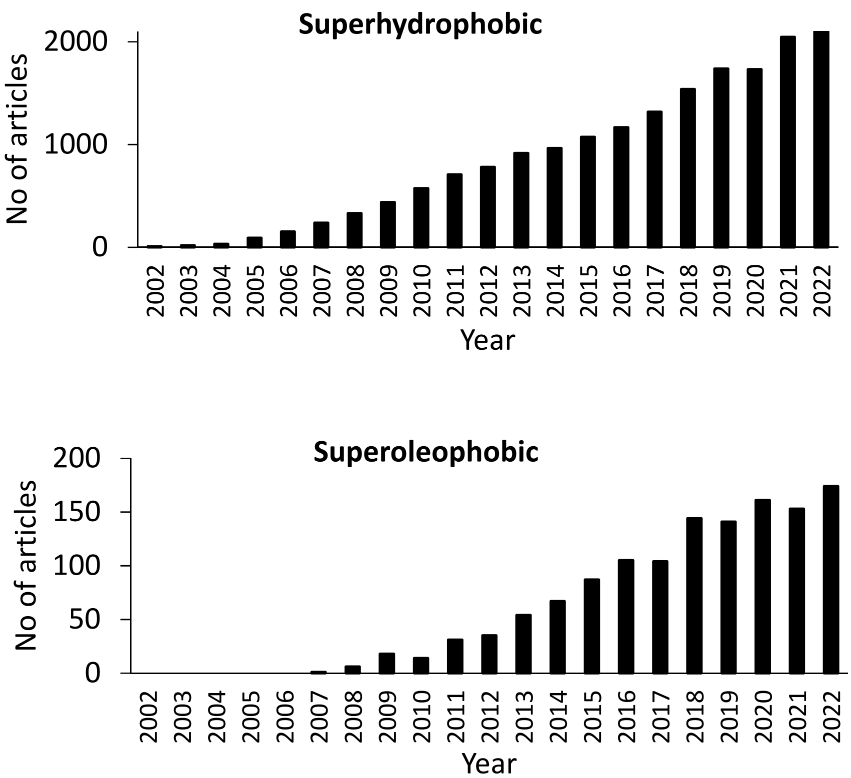

Figure 1. Number (No.) of published articles per year which include the words "superhydrophobic" and "superoleophobic" in their titles, abstracts or keywords. Data were obtained from Scopus (February 2023).

In Figure 2, the four wetting regimes which describe the interaction of a water drop with a solid, passive surface are defined, according to the value of the static water contact angle (WCA). The standard terms "hydrophobicity" and "hydrophilicity" originate from the Greek roots "hydro" (water), "phobia" (fear) and "philia" (friendship) and they have been widely used in textbooks to describe surfaces which correspond to a WCA > 90° and a WCA < 90°, respectively. By the beginning of the 21st century, the terms "superhydrophobicity" and "superhydrophilicity" became popular to describe surfaces which correspond to very large (typically, >150°) and very low (typically, <5°) WCAs, respectively. Therefore, a superhydrophobic surface is defined exclusively by the very large static WCA. A superhydrophobic surface is not necessarily a water repellent surface. For example, a water drop is adhered by the superhydrophobic surface (WCA > 150°) of a rose petal [2]. In contrast, a water drop is repelled by the superhydrophobic surface (WCA > 150°) of a lotus leaf [3]. The water drop remains pinned on the rose petal surface, implying drop adhesion, and easily rolls off the lotus leaf surface, implying drop repellency [2,3]. Both, repellent and adhesive, superhydrophobic surfaces have attracted considerable attention as summarized in several review articles [4,5]. To test the repellent/adhesive character of a surface, dynamic contact angles should be measured such as the roll off angle, the sliding angle or the contact angle hysteresis. For adhesive rose-like surfaces, the dynamic angles are practically not defined (i.e., theoretically are infinite) implying that a water drop does not move even if the surface is titled by 90° degrees. For lotus-like surfaces the dynamic angles take very small values (typically, <10°).

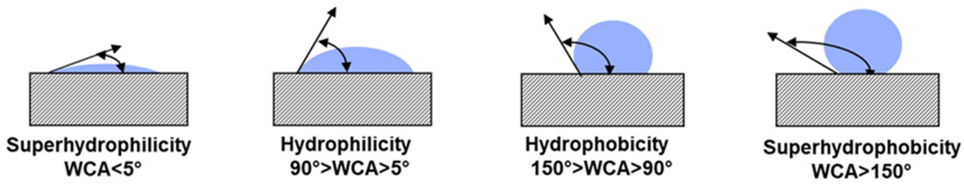

Figure 2. Wetting regimes, defined by the water contact angle (WCA) of a static drop on a solid, passive surface.

The interaction of an oil drop with a solid surface is described using similar terms as above. Therefore, a superoleophobic surface is defined by the large contact angle (typically, >150°) of a static oil drop (OCA) on the surface whereas small dynamic angles (typically, <10°) of oil drops are reported for oil-repellent surfaces.

The interdependence between wettability and surface roughness was mathematically expressed by Wenzel [6] and Cassie and Baxter [7] in the 1930–1940s and was experimentally revealed by Neinhuis and Barthlott in 1997 [3,8]. Since then, numerous experimental studies have tried to correlate the wetting properties and roughnesses of non-wettable surfaces. Roughness measurements are usually carried out using either atomic force microscopy (AFM) or optical profilometry. AFM is an excellent technique to scan relatively small areas, typically no larger than 100 × 100 μm. However, the contact diameter of a water drop (8 μL) with a superhydrophobic surface is of the order of 1–2 mm, roughly an order of magnitude larger than the maximum AFM scan size. Therefore, AFM images can only be used with confidence to measure the roughnesses of micro-patterned surfaces, with structural features which are repeated within the maximum scan size of the technique (roughly 100 × 100 μm). The roughness of a micro-patterned surface is independent of the area which is selected to scan by AFM and, moreover, independent of the size of the selected area. Optical profilometry provides the surface morphology on a much larger scale (typically several mm) and is therefore advantageous to measure the roughnesses of surfaces which exhibit structures that are randomly distributed in large scales, e.g., of the order of several mm. AFM measurements on randomly rough surfaces include a considerable degree of uncertainty as the results are affected by the areas which are selected to measure roughness. Both techniques, AFM and optical profilometry, can be used to make qualitative observations regarding the structure of any surface. Nevertheless, reporting quantitative roughness measurements should be carefully considered, taking into account the limitations of the instrumentations with respect to the size of the contact area between a water/oil drop and the solid surface.

Superhydrophobicity and superoleophobicity are usually observed on rough surfaces of low-surface-energy materials. For example, it was shown that the superhydrophobic character of the lotus leaf surface originates from micro/nano-sized features and the hydrophobic character of epicuticular waxes [3,8]. In practice, both conditions, surface structure combined with low-surface-energy agents, should be satisfied to achieve superoleophobicity. Producing a superoleophobic surface is a challenging task, as it is difficult to impede the wetting of oil which has a very-low surface tension (~32 mN/m). However, water corresponds to a much larger surface tension (~72 mN/m) and therefore it is easier to achieve superhydrophobicity than superoleophobicity. Consequently, low-surface-energy (hydrophobic) agents are not always necessary to achieve superhydrophobicity which can originate exclusively from the contribution of the special surface structure. Hence, superhydrophobicity was observed in the past on rough surfaces of inherently hydrophilic materials [9], which correspond to a Young's contact angle < 90°. The same message was reported by Muslimov et al. [10], whose article is included in the present Special Issue and it is briefly discussed in the following section. These experimental results [9,10] are supported by the Cassie–Baxter model which suggests that superhydrophobicity can be induced on an inherently hydrophilic material, provided that the solid fraction contacted by the liquid is very small [7].

2. Challenges and Applications

As mentioned, superhydrophobic surfaces can have numerous potential applications. The wide range of applications is reflected in the research articles of this Special Issue, as shown in Table 1. In particular, micro/nano-structured materials were designed, produced and tested for microdevices and implantology [10], anti-corrosion [11–13], packaging and textiles [14,15], aluminum microplastic removal [16], conservation of cultural heritage [17] and the protection of wood [18]. The improvement of the poor durability of the structured, superhydrophobic and superoleophobic coatings is probably the most important challenge which needs to be addressed. Depending on the targeted application, priority is given to different aspects of durability such as, for instance, chemical stability [11], mechanical stability [13,16] and durability in outdoor conditions [17]. In the following, the articles included in this Special Issue [10–18] are briefly described.

Table 1. Structured materials and applications, described in the articles which are included in the present Special Issue, titled "Superhydrophobic and Superoleophobic Surfaces".

Treated Substrate Material	Application	Reference
ZnO	Microelectronics, gas sensors	[10]
TiO_2	Implantology, photocatalysis	[10]
Co–Ni	Anti-corrosion	[11]
65Mn steel	Anti-corrosion	[12]
Aluminum	Anti-corrosion	[13]
PET	Packaging, textiles	[14]
Various fabrics	Textiles	[15]
Aluminum	Microplastic removal	[16]
Calcarenite stone	Cultural heritage protection	[17]
Wood	Wood protection and self-healing	[18]

Muslimov et al. [10] used gold (Au) and hematite (Fe_2O_3) to coat microrods of zinc oxide (ZnO). A very high WCA (168°) was obtained on the Au–ZnO surfaces which was attributed to the surface structure and specific interaction of the water molecules with the Au atoms. However, the observed superhydrophobicity was not accompanied by water repellency as significant hysteresis was observed on the Au–ZnO surfaces. On the contrary, a small roll off angle (9°) was reported for the superhydrophobic (WCA = 173°) Fe_2O_3–ZnO surfaces due to the specific microstructure of the coating and the non-polar layer of Fe_2O_3. In the same study, the wetting properties of titanium oxide (TiO_2) coatings were tuned from hydrophilicity (WCA = 73°) to superhydrophobicity (WCA = 150°) using nitrogen plasma in an open atmosphere with different compositions. In particular, a high content of molecular nitrogen and atomic nitrogen in the plasma were used to produce the hydrophilic and superhydrophobic coatings, respectively. The superhydrophobic ZnO-based coatings produced in this work [10] can be used in microdevices. Moreover, hydrophilic and superhydrophobic TiO_2 coatings are important in implantology and photocatalysis, respectively.

Three reports, included in the Special Issue, describe methods to produce coatings for anti-corrosion. Wang et al. [11] produced two kinds of Cobalt (Co)–Nickel (Ni)-based superhydrophobic coatings following an electrodeposition process and modification of the rough surfaces with perfluorooctyltrichlorosilane (PFTEOS). Tungsten carbide (WC) powder was added in one of the two prepared coatings. Apart from superhydrophobicity, the two coatings also showed water repellency, which was evidenced by the low sliding angles. Moreover, the coatings showed long-term chemical durability, as they maintained their extreme non-wetting properties after being immersed for more than 10 days in a 3.5 wt.% NaCl solution. The coatings offered good protection against corrosion even after the loss of their superhydrophobic character [11]. Zhang et al. [12] produced coatings of enhanced hydrophobicity (140° < WCA < 150°) on 65Mn steel by direct current electrodeposition, carried out involving stearic acid in the solution. The influence of deposition time on the corrosion resistance of the coatings was studied. It was shown that the best corrosion resistance was obtained for the coating which was deposited for 30 min, as it corresponded to the highest WCA and high coating thickness [12]. Sebastian et al. [13] produced a superhydrophobic (WCA = 162°) coating using hydrophobic functionalized silica (SiO_2) nanoparticles and an epoxy resin. The coating was deposited on aluminum alloy substrates and showed very good mechanical durability according to the results which were obtained by sandpaper and Taber abrasion tests. Moreover, the nanocomposite coating offered very good protection against corrosion [13].

The packaging and textile industries are particularly interested in the interaction of water with their products. Afonso et al. [14] were able to produce superhydrophobic polyethylene terephthalate (PET) through solvent-induced crystallization, which generated roughness, followed by a fluorination step. The best structure was achieved using dichloromethane which was selected among several tested solvents. Attention was focused on the removal of an unexpected smooth and thin polymer skin which was generated on top of the structured material. Low contact angle hysteresis was achieved (15–20°) implying that the treated PET material showed significant water repellency. The method has the potential to be used in several applications, particularly by the packaging and textile industries in which PET is extensively used [14]. Kim [15] investigated the interaction of water, in liquid and vapor forms, with twelve types of laminated and coated woven fabrics following standards tests for textiles (JIS L 1092 and JIS L 1099). Superior waterproof, breathable and water-repellent characteristics were achieved by treatment with a hydrophilic laminated finish using a nylon woven fabric [15].

Water harvesting and cleaning, including water–oil separation, are apparently very important potential applications of superhydrophobic surfaces. Within this context, Rius-Ayra et al. [16] produced a superhydrophobic and superoleophilic coating for microplastic (high-density polyethylene) removal by combining electrodeposition and electrophoresis. The coating was deposited on an aluminum substrate and consisted of zinc laurate ($Zn(C_{11}H_{20}COO)_2$) hierarchical structures and titanium oxide (TiO_2) nanoparticles. Superhydrophobicity and water repellency were evidenced by the large WCA (153°) and small contact angle hysteresis (1°), respectively. Moreover, the coating showed high durability against abrasion [16].

Hydrophobization of natural stone is a strategy in conservation science and practiced to impede water-induced degradation of buildings of cultural heritage. The potential of this strategy has been promoted by the recent development of advanced, highly hydrophobic and superhydrophobic materials. A commercial fluorine-based polymer dispersed in water (PROTECT IT R 100/HBG) was evaluated by Lettieri et al. [17] for the protection of porous calcarenite (Lecce) stone. After optimizing the amount of the deposited protective coating, the treated stone became highly hydrophobic (WCA = 141°). The coating offered good protection against water penetration by capillarity and graffiti staining. Furthermore, the treatment produced only slight reductions in the water vapor transport properties and had practically no effect on the color of the treated stone. Finally, the short-term durability of the coating was evaluated after outdoor exposure for four weeks [17].

Wood is very sensitive to the degradation effects induced by water or other liquids. Yan and Peng [18] produced a coating for the protection of wood. In particular, microcapsules were added to a waterborne primer and brushed on Basswood. Several coatings were produced by varying the core–shell ratio and the mass fraction of the microcapsules. The liquid resistance of the coatings was tested against 15% NaCl and, moreover, against ethanol, a detergent and red ink. The resistance of the coatings against NaCl was excellent, as no marks were left on the treated Basswood samples. The resistance of the coatings against the other liquids depended on the core–shell ratio and the mass fraction of the microcapsules. Several other parameters were evaluated including, color change, mechanical properties and coating adhesion. Based on the comprehensive analysis, the best performance was achieved when the content of the microcapsules of a 0.67:1 core–shell ratio was 10.0%. Interestingly, the coating had a certain self-healing property for microcracks [18].

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References

1. Ollivier, H. Recherches sur la capillarité. *J. Phys. Theor. Appl.* **1907**, *6*, 757–782. [CrossRef]
2. Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal effect: A superhydrophobic state with high adhesive force. *Langmuir* **2008**, *24*, 4114–4119. [CrossRef] [PubMed]
3. Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, *202*, 1–8. [CrossRef]
4. Khan, M.Z.; Militky, J.; Petru, M.; Tomková, B.; Ali, A.; Tören, E.; Perveen, S. Recent advances in superhydrophobic surfaces for practical applications: A review. *Eur. Polym. J.* **2022**, *178*, 111481. [CrossRef]
5. Xu, P.; Zhang, Y.; Li, L.; Lin, Z.; Zhu, B.; Chen, W.; Li, G.; Liu, H.; Xiao, K.; Xiong, Y.; et al. Adhesion behaviors of water droplets on bioinspired superhydrophobic surfaces. *Bioinspir. Biomim.* **2022**, *17*, 041003. [CrossRef] [PubMed]
6. Wenzel, R.N. Resistance of solid surfaces to wetting by water. *Eng. Chem.* **1936**, *28*, 988–994. [CrossRef]
7. Cassie, A.B.D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546–951. [CrossRef]
8. Neinhuis, C.; Barthlott, W. Characterization and distribution of water-repellent, self-cleaning plant surfaces. *Ann. Bot.* **1997**, *79*, 667–677. [CrossRef]
9. Ntelia, E.; Karapanagiotis, I. Superhydrophobic Paraloid B72. *Prog. Org. Coat.* **2020**, *139*, 105224. [CrossRef]
10. Muslimov, A.E.; Gadzhiev, M.K.; Kanevsky, V.M. New Approaches to increasing the superhydrophobicity of coatings based on ZnO and TiO_2. *Coatings* **2021**, *11*, 1369. [CrossRef]
11. Wang, S.; Xue, Y.; Xue, Y.; Lv, C.; Jin, Y. Long-term durability of robust super-hydrophobic Co–Ni-based coatings produced by electrochemical deposition. *Coatings* **2022**, *12*, 222. [CrossRef]
12. Zhang, Y.; Du, Q.; Lin, T.; Tang, S.; Hu, J. A study on the corrosion resistance of hydrophobic coatings on 65Mn steel. *Coatings* **2021**, *11*, 1399. [CrossRef]
13. Sebastian, D.; Yao, C.-W.; Nipa, L.; Lian, I.; Twu, G. Corrosion behavior and mechanical properties of a nanocomposite superhydrophobic coating. *Coatings* **2021**, *11*, 652. [CrossRef]
14. Afonso, E.; Martínez-Gómez, A.; Huerta, A.; Tiemblo, P.; García, N. Facile Preparation of hydrophobic PET surfaces by solvent induced crystallization. *Coatings* **2022**, *12*, 137. [CrossRef]
15. Kim, H.-A. Water repellency/proof/vapor permeability characteristics of coated and laminated breathable fabrics for outdoor clothing. *Coatings* **2022**, *12*, 12. [CrossRef]
16. Rius-Ayra, O.; Biserova-Tahchieva, A.; Llorca-Isern, N. Durable superhydrophobic coating for efficient microplastic removal. *Coatings* **2021**, *11*, 1258. [CrossRef]
17. Lettieri, M.; Masieri, M.; Aquaro, M.; Dilorenzo, D.; Frigione, M. Eco-friendly protective coating to extend the life of art-works and structures made in porous stone materials. *Coatings* **2021**, *11*, 1270. [CrossRef]

18. Yan, X.; Peng, W. Effect of microcapsules of a waterborne core material on the properties of a waterborne primer coating on a wooden surface. *Coatings* **2021**, *11*, 657. [CrossRef]