Substrate-Independent Design of Liquid-Infused Slippery Surfaces via Mussel-Inspired Chemistry

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Self-cleaning and repellent coatings ensure enduring performance of surfaces in many areas of technology and everyday life. An ideal repellent coating is efficient in removing contaminations, yet easy to apply on a wide range of surface materials. To devise such a coating, two bioinspirations are combined that show opposing interfacial properties: the peristome of a pitcher plant and the versatile mussel-inspired chemistry of polydopamine (PDA). The possibility of PDA to bind to different surface materials is taken to provide a material-independent coating strategy. Its reactivity toward amines to cofunctionalize the coating with monoaminopropyl-polydimethylsiloxane is utilized to control the surface chemistry. This process, in effect, adheres silicone polymer chains to any desired surface material. Finally, inert silicone oil is added to the reaction mixture to provide in situ lubrication of the coating. Together, the process creates lubricant-infused surfaces in a one-step process independent of the underlying substrate. It is shown that the reaction mixture can be deposited by dip or spray coating, providing procedures to coat large surfaces and complex samples such as textiles and wood. The combination of the mussel-inspired chemistry with the pitcher plant-inspired control of wettability provides an experimentally simple coating process to impart efficient repellency and self-cleaning characteristics to virtually any surface material.

1. Introduction

Liquid-infused slippery surfaces (LISs) inspired by the pitcher plant's peristome are a remarkable approach to tailor surface wettability and impart repellency.^[1–7] Such surfaces operate by the confinement of a thin liquid layer on a solid substrate. If the

interactions in such composite systems are properly controlled,^[1,8–9] a second, impinging liquid is prevented from making direct contact with the underlying solid and slides off the substrate with ease. Besides the liquid repellency properties,^[2] LISs provide self-healing capabilities,^[2] pressure stability,^[2] and present a potential solution for a range of challenging contamination scenarios, such as medical biofouling,^[10–13] marine biofouling,^[14,15] or anti-icing.^[16–18]

The design of LISs can be divided into three general strategies: slippery liquid-infused porous surfaces (SLIPS),^[2,4,7] organogels,^[3,6,19,20] and polymer brushes.^[21,22] SLIPS rely on two main factors: maximizing the affinity of the lubricant to the surface by matching surface chemistry, and the introduction of surface roughness to enhance the adhesion of the lubricant to the substrate by capillary forces.^[5] There has been tremendous progress in the development of techniques to create such SLIPS systems.^[5,13,23–27] Typically, however, the design requires multiple

steps to introduce surface roughness, surface functionalization, and lubricant. So far, only few studies showed the fabrication of SLIPS in a one-step method, for example by electrospraying both a perfluorosilane and perfluoropolyether.^[28]

A second approach to create LISs are polymer brushes that are bound to a solid surface.^[21,22,29–34] Typically, alkylsiloxanes such as polydimethylsiloxane (PDMS) brushes are used to provide a liquid-like, low surface energy surface. The liquid-like molecule chains can be coupled via silane chemistry,^[32] via π -electron interactions after surface silanization,^[33] from acidic sol–gel chemistry^[21,29] or by partial thermal decomposition.^[30,34] Such surfaces show very low contact angle hysteresis (CAHs) and efficient repellency, but typically require oxidic substrates with surface hydroxyl groups to induce chemical binding.

Organogels consist of thin films of crosslinked, low surface energy polymers, such as polyalkylsiloxanes like PDMS,^[20,35] or perfluorinated polymers.^[20] The polymer network is subsequently swollen with a suitable lubricant (e.g., silicone oil^[20,35] or perfluorinated oils^[20]) to form a LIS. The fabrication process of organogels can be simplified by incorporating the lubricant directly during the polymerization,^[36–38] by solvent evaporation-induced phase separation,^[39] or by tethering chains in a PDMS network.^[40] The high number of functional groups

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within a polymer network creates a strong affinity to the lubricant and provides very stable and efficient repellent coatings.^[15]

Despite the tremendous progress in LISs coatings, the design of substrate-independent coating processes remains challenging due to the need of specific anchor groups that are able to modify the surface chemistry or bind polymeric groups onto the substrate. In addition, an ideal coating process should be experimentally simple and applicable in a single-step procedure without relying on complex equipment.

Mussel-inspired adhesives, containing dopamine groups provide a potential solution toward versatile substrate functionalization as they are able to bind to virtually any kind of surface material.^[41–45] Mimicking mussel-foot protein inspired surface chemistry,^[46,47] dopamine adheres to surfaces by a synergistic combination of hydration layers removal induced by the amine group,^[47,48] and the versatile interaction of catechols with surfaces,^[47,48] such as hydrogen bonding, π - π interactions, π -cation interactions, coordination bonding, or further hydrophobic interactions, such as coarcevation.^[43,47,49] Besides the efficient binding to different substrates, these catecholamines undergo an oxidative polymerization to form thin and homogeneous polydopamine layer on surfaces to enhance the coating efficiency.^[41,45,50]

Polydopamine coatings can be combined with different functional molecules to control the surface properties by various strategies, including prefunctionalization, codeposition, or postfunctionalization.^[45,51–54] In a prefunctionalization strategy, functional groups are implemented either in the catechol molecule,^[43] or in catechol-containing polymers^[55,56] before being applied to a substrate. In a postfunctionalization strategy, the remaining reactive groups of an already formed polydopamine layer can be further reacted with functional groups containing electron-donating groups, e.g., amines or thiols^[51–53] or electron-withdrawing groups like acid chlorides.^[57–60] Similarly, molecules containing amino or thiol groups can be codeposited together with dopamine during the coating formation process and will be directly incorporated into the polydopamine coating.^[45,51,61] This approach allows a facile one-step surface functionalization method based on mussel-inspired adhesive groups.^[61]

Polydopamine-based coatings have been used to design bioinspired, superhydrophobic surface coatings on a range of materials, including oxidic surfaces, metals, or polymers.^[41,50] To this end, hydrophobic moieties are incorporated into the polydopamine layer, using either prefunctionalized catechol-containing molecules^[62–65] or polymers,^[55,66–68] co-reactions of dopamine with hydrophobic thiols or amines,^[69] or a postfunctionalization of preformed polydopamine.^[42,58,70]

Polydopamine or catechol-containing moieties in general have been applied in the fabrication of LISs as intermediate layer for SLIPS,^[71] to facilitate the formation of silver nanoparticles in SLIPS^[27,72] and to enhance self-healing capacities by introduction of reversible coordination bond with Fe₃O₄ nanoparticles.^[35] In addition, polydopamine layers have been functionalized with specialized mussel-inspired dendritic polyglycerols, which form surface coatings with hierarchical roughness,^[57,72,73] to impart superhydrophobicity by postmodification. These coatings can be subsequently converted into environmentally friendly LISs coating by the infiltration with sunflower oil.^[73]

Here, we take advantage of the versatile adhesion and functionalization possibilities provided by the mussel-inspired catechol chemistry to develop an experimentally simple, substrate-independent one-step LISs fabrication method. We combine dopamine with commercially available amino-functionalized PDMS and silicone oil, which, upon drying, infuses the PDMS/polydopamine coating to form a LIS in a single process step. We first explore in detail the individual steps required to form a stable LIS coating and subsequently demonstrate how all individual steps can be combined to form, substrate-independent LIS coatings in an experimentally simple, one-step approach.

2. Results and Discussion

Figure 1 schematically illustrates our double-bioinspiration approach to create substrate-independent repellent surface coatings. We first separate all individual steps required to form such coatings to elucidate the reaction conditions and characterize the resulting change in surface properties (Figure 1a). In this multistep process, we first coat a substrate with a polydopamine (PDA) layer, in which the catechol serves simultaneously as a versatile anchor to the substrate by different interfacial interactions,^[43,47,49] as a crosslinker of the coating, and as a source of reactive functional groups at the surface of the formed layer (Figure 1b, left). Subsequently, the remaining reactive catechol groups are functionalized with monoaminopropyl-terminated-polydimethylsiloxane (MAP-PDMS), which reacts with the PDA coating presumably through a Michael type addition or a Schiff base reaction^[47] (Figure 1b, right). In a third step, a LIS is formed by addition of silicone oil as lubricant to the functionalized PDA surface, which wets the surface due to the high chemical affinity between the silicone oil and the MAP-PDMS-functionalities on PDA (Figure 1a,b).

The direct incorporation of functional moieties into the PDA coating is only possible for methanol and ethanol-soluble moieties, due to the low dopamine solubility in nonpolar solvent and the reduced dopamine reactivity in aprotic solvents.^[69] For a one-pot approach that combines all process steps (Figure 1c), the challenge therefore is the identification of an adequate solvent mixture, which dissolves all involved species, i.e., the polar dopamine and the nonpolar MAP-PDMS as functional group and silicone oil as lubricant. We identified a 1:1 v/v mixture of methanol (MeOH), responsible for the dissolution of dopamine, and tetrahydrofuran (THF), which dissolves the alkylsiloxane moieties. This mixture is then allowed to react in solution and subsequently applied to a substrate via spray or dip coating to form a substrate-independent LIS coating in a single step.

We first investigated and characterized the different process steps individually. Glass substrates were coated with a PDA layer by immersing a substrate into a solution of dopamine HCl and tris(hydroxymethyl)aminomethane (TRIS) at pH 8.5 for 24 h at room temperature, following the method developed by Lee et al.^[41] (**Figure 2a**). We monitored the formation of the PDA layer on the glass substrate by a change in contact angle. In addition, we transferred the system to MeOH as an organic solvent and tested triethylamine (TEA), 2,6-lutidine and piperidine as organic bases to initiate the reaction (Figure 2b). The

Figure 1. Double-bioinspiration strategy to form repellent surface coatings. (a) Schematic illustration of the LISs fabrication via a three-step mussel inspired PDA coating. (b) Simplified representation of the different reaction pathways of the catechol group in the crosslinked PDA coating: anchoring to the substrate, presenting reactive groups, functionalization via Schiff base reaction or Michael type addition and lubricant impregnation. (c) Schematic illustration of the one-step method that combines all individual process steps.

latter is important for the subsequent transfer of the reaction to a one-pot system described below. The significantly higher hydrophobicity of the PDA layer formed in the presence of piperidine might be caused by the covalent incorporation of piperidine in the PDA as proposed by You et al.^[69] We therefore used TEA in all following experiments to avoid potential problems arising from the presence of piperidine in the process. Next, we immersed the PDA layer into a solution of MAP-PDMS (20×10^{-3} M) in THF and let the reaction proceed for 10 days at room temperature. An increase in contact angle from $31.1 \pm 4.5^\circ$ to $100.4 \pm 3.8^\circ$ indicated a successful incorporation of the MAP-PDMS into the PDA layer (Figure 2c). The PDA/MAP-PDMS coating formed a homogeneous layer with a nanoscale roughness, as evidenced by scanning electron microscopy (SEM) (Figure 2d) and atomic force microscopy (AFM) (Figure S1, Supporting Information). In a final step, we infused the formed coating with $7.6 \mu\text{L cm}^{-2}$ silicone oil to form a LIS system. The low sliding angle (SA $3.5^\circ \pm 0.7^\circ$) and the CAH ($2.0^\circ \pm 1.5^\circ$) of the PDA/MAP-PDMS/silicone oil system indicates a low degree of pinning of the water droplet,^[20] and thus the successful formation of a LIS (Figure 2c).

We used X-ray photoelectron spectroscopy (XPS) analysis to investigate the change in chemical surface composition after each process step by averaging three measurements and showing the standard deviation as a filled area (Figure 2e–g). After the first step, an increase in signals of carbon and

nitrogen (C 1s, N 1s) are indicative of the PDA layer formation (Figure 2e,f). Simultaneously, the decrease of oxygen and silicon peak intensities (O 1s and Si 2p) corroborates the formation of a homogeneous organic layer covering the surface (Figure 2g). The N/C ratio of 0.133 is close to the theoretical ratio for PDA of 0.125.^[41] The N 1s peak of the PDA coating subsequently decreases after the MAP-PDMS functionalization (Figure 2f). In addition, we observe a strong increase in the Si 2p signal (Figure 2g). Together, these changes in surface chemistry indicate the formation of a surface-bound PDMS layer on top of the PDA coating, corroborating the contact angle and wetting experiments.

We subsequently combined all three process steps to provide a one-step methodology to form substrate-independent LIS coatings (Figure 3a). To this end, we mixed dopamine HCl, MAP-PDMS, and silicone oil in MeOH/THF and allowed the mixture to react for 96 h until it changed its color to black. We then spray coated the solution onto a substrate and varied both the number of spray cycles as well as the amount of (inert) silicone oil lubricant added to the reaction mixture to investigate the required amount to form a LIS coating in situ (Figure 3b). These results suggest that a minimum of two spray cycles and 20×10^{-3} M silicone oil are required to form a coating with a CAH below 10° , which is indicative of a stable coating.^[75] Note that even in the absence of inert silicone oil (0×10^{-3} M), some substrates seem to present a slippery surface with an apparent sliding angle below

Figure 2. Polydopamine-based formation of lubricant-infused coatings. (a) Schematic illustration of the three-step fabrication of LIS via mussel inspired PDA chemistry. (b) CA of the PDA coated substrates both in aqueous and organic solvents with various organic bases. (c) CA and CAH change after the functionalization of PDA with MAP-PDMS and the silicone oil infusion. The red arrows represent data points for the CAH off the scale bar, i.e., above 30°. (d) Scanning electron microscopy (SEM) micrograph of the PDA coated surface. (e–g) X-ray photoelectron spectroscopy (XPS) spectra of the pristine glass slide, after the PDA coating and after the surface functionalization of the PDA with MAP-PDMS.

5°. We attribute this phenomenon to the possibility that excess MAP-PDMS, which remains unbound after coating formation, may act as a lubricant layer itself. However, in our experiments, such coatings did not exhibit a stable and reliable repellency and failed more readily compared to the coatings with added, inert lubricants. The presence of nanoscale surface features in SEM images indicates the successful formation of a surface coating (Figure 3c). The stain-free removal of a dyed water droplet on a glass slide coated with seven spray cycles of the dispersion with 100×10^{-3} M silicone oil at a sliding angle (SA) of 5° shows the efficient liquid-repellency properties of the coating (Figure 3d; and Movie S1, Supporting Information). The same coating was able to repel Ketchup as an example of a sticky, non-Newtonian fluid (Figure 3e; and Movie S2, Supporting Information). The water repellent characteristics of the coating was also preserved when the applied dispersion was diluted up to 100 times (Figures S3a and S4, Supporting Information).

In literature, the codeposition of PDA and functional molecules is typically performed as a dip coating process in which the substrate is placed in a reaction vessel containing either aqueous systems with water soluble functional moieties^[45,51] or organic systems with alkyl- or perfluorinated thiols.^[69] We followed the same method but added free lubricant molecules to the solution to simplify the LISs fabrication process. We subsequently compared the results with the spray coating process introduced above. Together, we tested four different

approaches: Spray coating of the reacted PDA/MAP-PDMS, spray coating of the unreacted solution directly after mixing, as well as dip coating of the reacted dispersion and unreacted solution. For the reacted dispersion, the dip coating process was performed by immersing a substrate for 180 s into the preformed dispersion, while the dip coating process for the unreacted solution involved immersing the substrate for 96 h to allow the reaction to take place in the presence of the substrate. The latter corresponds to typical protocols in literature, however, with the addition of an inert lubricant to form the LIS coating.

All tested processes, involving both reacted and unreacted dispersions allowed the fabrication of liquid repellent LISs as the CAH values below 10°, as shown in Figure 4.

The dip coating method with both reacted or unreacted PDA, MAP-PDMS, and silicone oil mixture still requires a 96 h reaction time for the conversion of the components. The spraying process, in contrast, can significantly speed up the coating process as the reaction mixture forms a solid coating on the substrate within seconds. This process therefore provides two interesting strategies: using a prereacted dispersion allows separation of reaction and coating process, beneficial where a coating needs to be applied on demand. The possibility to form repellent LIS coatings by spray coating of unreacted mixtures allows the formation of LIS coating on very short time scales. The reaction occurs directly on the substrate, which

Figure 3. Mussel-inspired one-step process to form lubricant-infused coatings. (a) Schematic representation of the surface-independent one-step LISs fabrication process with reacted mussel-inspired PDA dispersions. CAH measurements of spray coated glass slides with (b) different lubricant concentrations and with (c) SEM micrograph of the surface after 7 spray cycles and after removal of the silicone oil. (d) Time-lapse images of a dyed water droplet sliding down a liquid-infused PDA coated glass slide with 100 mM silicone oil and 7 spray cycles at a tilt angle $<5^\circ$. (e) Time-lapse images of the stain-free removal of ketchup from the same sample using a tilt angle of approx. 45° .

increases the oxidative polymerization by efficient oxygen diffusion into the coating.^[76] We investigated the surface properties of the coatings prepared by the two one-step methods via the elemental composition of the topmost surface using XPS (Figure S5, Supporting Information). The measurements did not show a significant difference in the silicon content of dip-coated and spray-coated samples, indicating that their surface properties are similar, at least within the accuracy of the experiments. In all samples prepared in the presence of MAPDMS, the interfacial analysis shows a strong increase in the silicon (Si 2p) signal, while the nitrogen (N 1s) signal is largely suppressed compared to a plain PDA coating. We therefore conclude that in both types of coatings the PDMS chains preferentially bind to the surface of the coating. This stratification is an important prerequisite for the formation of stable coating since the PDMS chains minimize the interfacial energy with the free silicone oil used as lubricant.

Using spray coating of the unreacted solution allowed the design of LIS coatings with efficient repellency, as shown by the CAH (Figures S3c and S6b, Supporting Information) and SA (Figure S4c,d, Supporting Information) and the stain free removal of dyed water or ketchup (Figure S6d,e, Supporting Information).

The broadband absorption properties of polydopamine^[77,78] generally affect the optical properties of the coating and can lead to a brownish appearance of the material and loss of transmitted light. Spray coating of the unreacted solutions minimized the required amount of polydopamine and provided coatings that maintained a reasonable transparency. Even after seven spray coating steps, the average light transmittance throughout the visible range exceeded 80% (Figure 4c). To corroborate this relatively high transmission, given the absorptive properties of PDA, we estimated the film thickness from cross-sectional SEM images, which indicate layer thicknesses

Figure 4. Investigation of coating processes. (a) Schematic illustration of the LISs fabrication with various methods based on an unreacted dopamine solution. (b) CAH of glass slides coated with both reacted and unreacted dopamine solution via spray coating for seven times with 100 mM silicone oil or dip coating of unreacted solution for 96 h at RT or of reacted dispersion for 180 s. (c) UV-vis transmittance measurements of the glass slides coated with various spray cycles.

Figure 5. Substrate-independent functionalization process. a) CAH of various materials coated via spray- or dip coating of either reacted or unreacted one-step mixtures. b–d) Stain-free removal of a water droplet of a PDA-based LIS coating on copper (b), PMMA (c), and PTFE (d) substrates, deposited by 7 spray coating cycles of the unreacted dispersions.

in the range of tens of nanometers, with a slightly increased film thickness for the spray coated samples compared to the dip-coated ones (Figure S7a,b, Supporting Information). Noteworthy, this estimated film thickness is in the range of typical PDA coatings on colloidal particles, which can be easily assessed via the change in hydrodynamic diameter.^[77]

In preliminary experiments, we assessed the mechanical stability of the fabricated LIS coatings to impacts by touching, cutting, and cleaning with a cotton cloth (Figure S8a–d, Supporting Information). The coatings retained their repellency characteristics after touching and cutting, underlining the self-healing capabilities imparted by the liquid lubricant. After the cloth rubbing, the surface exhibited signs of damage along the rubbing direction and lost its liquid repellency, presumably by a combination of material failure and removal of lubricant. While pure PDA coatings can typically exhibit a modulus in the range,^[79] it seems that the incorporation of the MAP-PDMS additives weakens the mechanical properties. We note, however, that several approaches exist to increase the mechanical properties, which may similarly strengthen our one-step coatings as well. These approaches include the incorporation of nanoparticles to increase mechanical robustness,^[80] the addition of metal ions to resist to compressive strains,^[81] the annealing at elevated temperature to enforce chemical crosslinking,^[79] or the addition of molecules with multiple amino groups, which act as further crosslinking points.^[82]

Having optimized the one-step coating process, we capitalize on the capacity of the mussel-inspired PDA chemistry to bind to a broad range of surface materials. In Figure 5, we demonstrate that our process allows the deposition of an efficient liquid-repellent coating independent of the underlying substrate by coating a range of different substrates, including soda-lime glass, aluminium (Al), copper (Cu), steel, polymethylmethacrylate (PMMA), polypropylene (PP), and polytetrafluoroethylene (PTFE). We coated all materials by the different coating methods investigated for glass substrates in Figure 4 and used contact angle hysteresis measurements to assess the formation of a LIS coating. Repellent coatings with a contact angle hysteresis below 10° were formed on the different substrate materials by both dip and spray coating with reacted or unreacted solutions (Figure 5a). Figure 5b–d shows time-lapse images taken from Movies S3–S5 in the Supporting Information of the stain-free removal of a dyed water droplet on copper, PMMA and PTFE modified by spray-coated of an unreacted solution (7 spray cycles). The high transparency

and limited staining of the PDA coating can be seen in the images.

The versatility of the mussel-inspired chemistry combined with the possibility to effectively cover large areas and complex sample geometries by spray- or dip coating in the one-step coating process affords applicability in technologically relevant examples and every-day life. We demonstrate the versatility of our coating methods by four instructive examples. Figure 6a,b (see also Movies S6 and S7, Supporting Information) compares a reference and a coated scalpel and shows the reduction of ketchup adherence. Figure 6c compares the adhesion of impinging rain droplets, simulated by adding water via a spray bottle to coated and uncoated polycarbonate (PC) windows. While rain droplets remained stuck on the reference, a self-cleaning effect was observed on the coated sample (see also Movies S-8 and S9, Supporting Information). The ability to coat polymer materials that do not exhibit typical surface functionalities onto which a coating can anchor underlines the versatile binding capacities of PDA, which may find applications in self-cleaning surfaces in building infrastructure, electric landlines, or automobiles.

Figure 6d–f shows examples of complex substrate geometries that can be coated via the dip coating process. A wooden honey spoon (Figure 6d; and, Movie S10, Supporting Information) and cotton textiles (Figure 6e,f; and Movies S11 and S12, Supporting Information) can both be subjected to the one-step reaction mixture and rendered repellent. Due to the high surface area and complex shape of the samples, the dip coating process involving co-reaction with the surface for 96 h produced the best repellency characteristics. In this case, the brown coloration of the PDA coating is more pronounced compared to the spray coating procedures. It is especially visible on the coated cotton textiles, because of the increased surface area compared to a flat substrate.

3. Conclusion

In conclusion, we adapted a double bioinspiration concept to create substrate-independent liquid-repellent coatings. The coating combines the universal adhesion of mussel-inspired polydopamine chemistry with the efficient liquid repellency of lubricant-infused surfaces inspired by the pitcher plant. We devised a one-step process that simultaneously provides substrate-independent adhesion, surface functionalization with

Figure 6. Applications of substrate-independent one-step LISs fabrication method via mussel inspired PDA coating. a,b) Repellency tests with ketchup on (a) pristine scalpel and on (b) a scalpel coated with seven spray cycles of reacted PDA dispersion. (c) Water droplet adhesion in a simulated rain test on reference and coated PC windows. (d) Sequential photos of repellency towards honey of a coated wooden honey spoon. e,f) Difference in water repellency on coated and non-coated cotton samples. The brownish visual appearance of the PDA coating is more pronounced on the fabric sample due to its larger surface area.

PDMS polymer chains and lubrication with silicone oil. The reaction mixture can be conveniently applied by dip or spray coating and allows material-independent functionalization in a simple, convenient, and large-area process of substrates with complex geometries. In its current form, the methodology relies on the use of organic solvents, which may cause dissolution of some polymeric substrates, and induces a brownish appearance to the surface, which may limit its applicability in optical devices. Aside from these limitations, the ability to coat a broad range of materials in a simple and scalable one-step approach may broaden the general applicability of lubricant-infused surface coatings, for example toward wood, textiles, or polymeric materials that do not exhibit typical surface anchor groups.

4. Experimental Section

Materials: The glass substrates (microscope soda-lime glass slides, $76 \times 13 \times 1$ mm) were obtained from Thermo Fischer. Copper, aluminum, steel, stainless, PP, PMMA, PTFE slides were cut from bulk materials, purchased via the university workshop. The PC slides were kindly provided by Uvex safety group GmbH & Co. KG. Dopamine HCl ($\geq 98\%$, Sigma-Aldrich), triethylamine (99%, Sigma-Aldrich), TRIS ($\geq 99.9\%$, Carl Roth), 2,6-lutidine (98%, Sigma-Aldrich), piperidine ($\geq 99\%$, for synthesis, Carl Roth), monoaminopropyl-terminated

polydimethylsiloxane (MAP-PDMS, MCR-A11, $>95\%$, Gelest Inc.), silicone oil 10 cSt (PDMS 10 cSt, Sigma-Aldrich), HCl solution (1 N, Carl Roth), THF (99.9%, Carl Roth), and methanol ($\geq 99.5\%$, Carl Roth) were used without further purification. Water was used as double-filtered and deionized water ($18.2 \text{ M}\Omega \text{ cm}$, double reverse osmosis by Purelab Flex 2, ELGA Veolia).

Substrate Preparation: The glass and metal substrates were cleaned by ultrasonication at 60 W for 10 min first in ethanol (99.5% denaturated, Carl Roth) and then in acetone ($\geq 99.5\%$, Carl Roth) and subsequently dried in air at room temperature. Prior modification, they were activated in an oxygen plasma oven for 5 min at 100 W at 0.2 mbar oxygen (99.999%, Air Liquide) gas pressure. The polymer substrates were ultrasonicated 10 min in ethanol and dried in air and did not undergo oxygen plasma treatment.

PDA Coating: First, the dopamine aqueous solutions were prepared by dissolving dopamine (2 g L^{-1}) and TRIS ($10 \times 10^{-3} \text{ M}$) in water to pH 8.5. The substrates were placed in a glass vial with 40 mL of the dopamine solution and left to react 22 h at room temperature while stirring at 900 rpm. Afterward the samples were rinsed with water and dried in air at room temperature. The PDA deposition in organic solvents took place in methanol, where dopamine HCl and the organic bases ($20 \times 10^{-3} \text{ M}$), triethylamine, piperidine, or 2,6-lutidine, were dissolved. Afterward the substrates were washed in the same solvent as the solution for three times and dried in air at room temperature.

PDA Functionalization: The PDA coated substrates were placed in solution of THF with $20 \times 10^{-3} \text{ M}$ MAP-PDMS and 10 mol equivalent of TEA for 10 days at room temperature.

Preparation of Functionalized PDA Solutions/Dispersions: A mixture of dopamine HCl (10.5×10^{-3} M), TEA (20×10^{-3} M), MAP-PDMS (20×10^{-3} M), and silicone oil at various concentrations were allowed to react at room temperature for 96 h. The resulting dispersions were applied for the “reacted PDA” coatings. The unreacted solution was prepared in the same manner and applied within 1 h after the preparation. Both reacted and unreacted PDA mixtures were applied either by dip or by spray coating as described below.

Dip Coating: This procedure describes the dip coating both in unreacted solution and reacted dispersion. The dip coating in an unreacted solution was carried out in following way. The codeposition of PDA, MAP-PDMS, and inert silicone oil on a substrate took place in a closed glass bottle with a mixture of 1:1 v/v of methanol and THF with dopamine HCl (10.5×10^{-3} M), TEA (20×10^{-3} M), MAP-PDMS (20×10^{-3} M) and silicone oil at various concentrations, for 96 h at room temperature. Eventually the substrates were taken out and allowed to dry in air at room temperature. For the dip coating in a reacted dispersions (see above), the following protocol was used. The cleaned substrates were dipped in a 120 mL of a prereacted dispersion with 100×10^{-3} M silicone oil in a glass staining box for 180 s at room temperature. The substrates were then let to dry in air at room temperature.

Spray Coating: The above-mentioned dispersions or solutions were transferred to a spray bottle with atomizer. The substrates were sprayed at a 45° inclination angle at a distance of 20 cm various times and the solvent was allowed to evaporate at room temperature in air for at least 30 s between the spray cycles. Large surfaces, e.g., PC plates, were coated with a thin layer chromatography sprayer for 10 s at 2 bar nitrogen gas pressure at 30 cm distance from the vertical sample.

Characterization of Surface Wetting: The wetting behavior was determined with a contact angle measurement device (Dataphysics OCA) and the software (SCA202 V 3.50.1) provided by the manufacturer. Water droplets of 4 μ L (Milli-Q grade) were dispensed from a glass syringe equipped with a 0.5 mm outer diameter needle. For each measurement, at least 8 droplets were measured and average to obtain the reported data. The CAH measurements were carried out with a tilting stage and 8 μ L Milli-Q water droplets.

The software SCA202 was not able to recognize the water droplets at tilting angles above 30° . In this case, every 25th or 8th frame in the videos were extracted with the scene filter in the vlc software and evaluated with ImageJ 1.52p after converting them in 32 bit images. A plugin in ImageJ, DropSnake from Stalder et al.,^[74] was applied to determine the contact angle. The SA were determined with the angle tool within the software ImageJ 1.52p.

Characterization of Surfaces: The surface was characterized with SEM (Zeiss AG; Gemini 500) with an accelerating voltage of 1 kV, a 15 μ m aperture and the InLens detector. The cross-sectional SEM micrographs were taken on an 85° sample holder. AFM were carried on a JPK Instruments in tapping mode in air with a cantilever type HQ:NSC18/Al BS (MikroMasch) with a nominal force constant of 28 N m⁻¹ and a resonance frequency of 75 kHz.

Elemental Analysis of the Surface: XPS analysis was performed on a Quantera II instrument (Physical Electronic) with monochromatic Al K-alpha X-ray radiation and ≤ 7.5 μ m spatial resolution. The measurements were operated with 15 kV. Survey spectra from 0 to 1100 eV binding energy were obtained at 280 eV pass energy. High-resolution spectra were carried out at 140 eV pass energy.

Mechanical Testing: One sample of each process category was subjected to different mechanical stresses, including by pressing a finger on the surface, applying three razor cuts and rubbing with a lint-free cloth. After each test, the water repellency and slipperiness were investigated by adding a 8 μ L water droplet at the sample inclined at $\approx 10^\circ$. At the end of all tests the samples surfaces were investigated by optical microscope (Ergolux, Ernst Leitz Wetzlar, model 020-448.026) at a 16x magnification and the images were taken with a CMOS camera (Thorlabs, type DCC3260C).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

liquid infused surfaces, liquid repellency, mussel-inspired chemistry, polydopamine, slippery surfaces, spray coating

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