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Superhydrophobic Coatings

Bioinspired Self-Healing Superhydrophobic Coatings**

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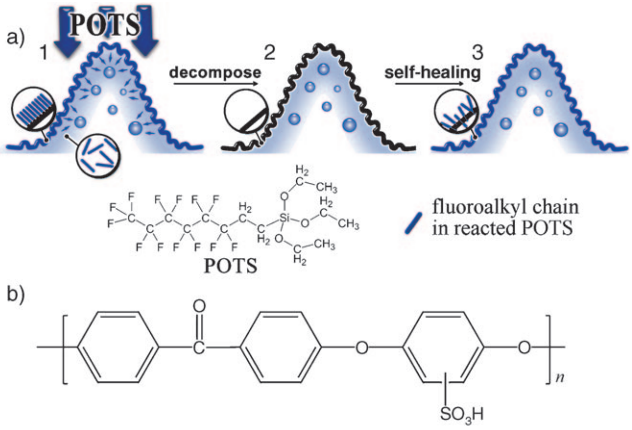
The lotus and many other living things exhibit the unusual wetting characteristic of superhydrophobicity after millions of years of evolution.[1] The study of lotus leaves reveals that nature accomplishes this fascinating function by combining micro- and nanoscaled hierarchical structures with low-surface-energy materials.[2] To date, superhydrophobic coatings promise a wide range of applications from self-cleaning surfaces to corrosion-resistant, antiadhesive, and drag-reducing coatings.[3] However, the poor durability of artificial superhydrophobic coatings seriously hinders their practical applications.[4] When exposed to an outdoor environment, low-surface-energy materials on the surface of the superhydrophobic coatings decompose under sunlight or are scratched away by sand in the wind or by animals, thus leading to permanent destruction of the superhydrophobicity. Generally, low-surface-energy materials have to be redeposited to recover the superhydrophobicity of artificial superhydrophobic coatings, which is inconvenient or expensive to accomplish.

Plants maintain their superhydrophobicity by regenerating the epicuticular wax layer after they are damaged, which is well known as a self-healing function.[5] Endowing artificial superhydrophobic coatings with a self-healing ability is believed to provide an efficient and long-desired way to solve these problems. Although several types of self-healing coatings have been fabricated,[6] the bestowal of a natural common self-healing function to lifeless artificial superhydrophobic coatings is still confronted with tremendous challenges. Inspired by the self-healing superhydrophobicity of living plants, herein we report for the first time an artificial way to fabricate self-healing superhydrophobic coatings. This study represents a key step towards fabricating artificial superhydrophobic coatings for practical applications.

Our strategy to design self-healing superhydrophobic coatings is shown in Scheme 1a. The key step is the fabrication of porous polymer coatings that are rigidly flexible and have micro- and nanoscaled hierarchical structures. After chemical vapor deposition (CVD) of a fluoroalkylsilane, these coatings become superhydrophobic because of the formation of a covalently attached fluoroalkylsilane layer.[2f] Importantly, these superhydrophobic coatings can preserve a large number of reacted fluoroalkylsilane moieties as healing agents. Once the primary top fluoroalkylsilane layer is decomposed or scratches are made on the superhydrophobic coating, the preserved healing agents can migrate to the coating surface under a slightly humid environment to heal the superhydrophobicity of the coatings like a living plant. The rigidly flexible superhydrophobic coatings, which have a well-balanced rigidity and flexibility, can make the coatings scratch-resistant and concomitantly facilitate the migration of healing agents.



Scheme 1. a) Working principle of self-healing superhydrophobic coatings: 1) the porous polymer coating with micro- and nanoscaled hierarchical structures can preserve an abundance of healing agent units of reacted fluoroalkylsilane; 2) the top fluoroalkylsilane layer is decomposed and the coating loses its superhydrophobicity; 3) the preserved healing agents can migrate to the coating surface and heal the superhydrophobicity. b) Chemical structure of sulfonated poly(ether ether ketone) (SPEEK).

Layer-by-layer (LbL) assembly is a substrate-independent method for the fabrication of various kinds of coatings with well-tailored chemical compositions and architectures.[7] The polymeric porous coatings with micro- and nanoscaled hierarchical structures are prepared by LbL assembly of polyelectrolyte complexes of poly(allylamine hydrochloride) (PAH) and sulfonated poly(ether ether ketone) (SPEEK, sulfonation degree ≈82%, Scheme 1b) with poly(acrylic acid) (PAA). The preformed PAH–SPEEK complexes with a molar excess of PAH are positively charged and have an average diameter of approximately 527 nm (see the Supporting Information). The formation of multilayered (PAH–SPEEK/PAA)$_n$ coatings (where n is the number of deposition cycles) is based on the electrostatic interaction between oppositely charged PAH–SPEEK complexes and PAA.

The scanning electron microscopy (SEM) images in Figure 1a and b indicate that the (PAH–SPEEK/PAA)$_{60.5}$ coating (a half cycle means PAH–SPEEK complexes are the

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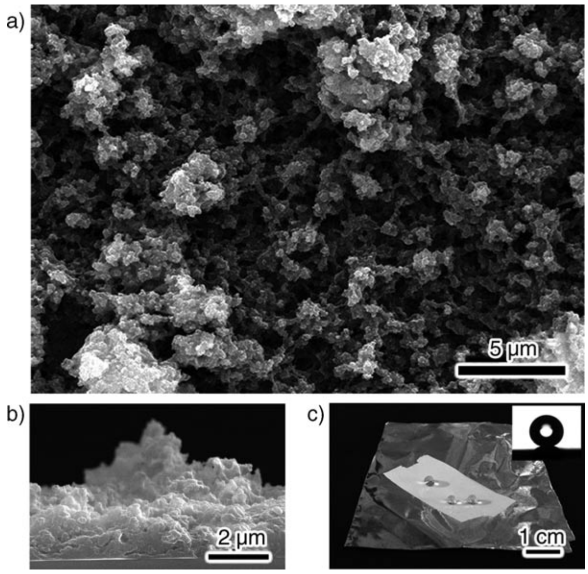

Figure 1. a) Top-view and b) cross-sectional SEM images of a (PAH–SPEEK/PAA)$_{60.5}$ coating on a silicon wafer. c) Photograph of a (PAA/PAH–SPEEK)$_{60}$ freestanding superhydrophobic coating transferred onto an aluminum foil. Inset: static contact angle of a superhydrophobic (PAA/PAH–SPEEK)$_{60}$ coating deposited on a silicon wafer.

outermost layer) deposited on a silicon wafer is highly porous and rough, with micro- and nanoscaled hierarchical structures owing to the loosely stacked spherelike PAH–SPEEK complexes. The thickness of the (PAH–SPEEK/PAA)$_{60.5}$ coating determined from its cross-sectional SEM image is (2.7 ± 0.4) µm. Then the coating was thermally cross-linked to enhance its mechanical robustness by forming amide bonds between the carboxylate and amine groups.[8] SEM investigation confirms that the hierarchical structures in (PAH–SPEEK/PAA)$_{60.5}$ coatings are well retained after thermal cross-linking. Upon CVD of 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (POTS) at 120 °C for 3 h, superhydrophobic coatings were finally obtained. POTS molecules are covalently attached to the polyelectrolyte coating as POTS reacts with free carboxylic acid, amine groups, and neighboring POTS in the coating.[2f]

The superhydrophobic (PAH–SPEEK/PAA)$_{60.5}$ coatings can be conveniently deposited on a large variety of substrates, including silicon wafers, nonflat substrates of aluminum heat sink, silicone, and glass tubes (see the Supporting Information), because of the flexibility of the LbL assembly method for coating fabrication.[9] The superhydrophobic (PAH–SPEEK/PAA)$_{60.5}$ coatings have a water contact angle of 157° (by cycle fitting) and a sliding angle as low as 1° (inset in Figure 1 c), which means that water droplets roll off easily from such coatings. Freestanding superhydrophobic (PAA/PAH–SPEEK)$_{60}$ coatings of large area can be released from the underlying substrate and transferred to other kinds of substrates that are inconvenient for conducting LbL assembly, or unstable to thermal cross-linking or the dipping solution, to render them superhydrophobic (Figure 1 c).[10]

The self-healing ability of the superhydrophobic (PAH–SPEEK/PAA)$_{60.5}$ coating was investigated by treating the coating with O_2 plasma to simulate the decomposition of the low-surface-energy POTS layer on the coating surface. After 5 min of O_2 plasma treatment, the coating became superhydrophilic like a (PAH–SPEEK/PAA)$_{60.5}$ coating without POTS deposition (Figure 2 a, bottom). The covalently attached POTS layer on the coating surface was etched away by the O_2 plasma. O_2 plasma treatment also produce oxygen-containing hydrophilic groups on the coating surface.[11] The highly rough and porous coating structure combined with the hydrophilic nature of polyelectrolytes and oxygen-containing groups explains the superhydrophilicity of the plasma-treated PAH–SPEEK/PAA coating. After being transferred to an ambient environment with a relative humidity (RH) of 40 % for 4 h, the O_2 plasma-treated (PAH–SPEEK/PAA)$_{60.5}$ coating restores its superhydrophobicity, with a contact angle of 157° and a sliding angle of less than 2° (Figure 2 a, top). The recovery of the superhydrophobicity implies that the O_2 plasma-treated (PAH–SPEEK/PAA)$_{60.5}$ coating is covered again with fluoroalkyl chains.

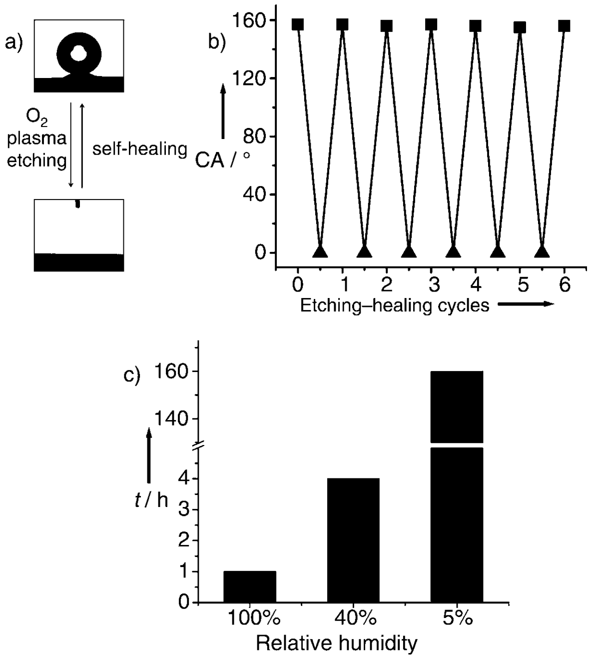

Figure 2. a) Reversible transition between superhydrophobic (top) and superhydrophilic (bottom) states of the coating upon O_2 plasma etching and self-healing. b) Contact angle (CA) of O_2 plasma-treated coating (▲) and the coating after self-healing (■). c) Length of time required for O_2 plasma-treated coatings to restore their original superhydrophobicity under different environmental humidities.

As shown in Figure 2 b, the etching–healing process can be repeated many times without decreasing the superhydrophobicity of the self-healed (PAH–SPEEK/PAA)$_{60.5}$ coating. SEM images confirm that the coatings after several etching–healing cycles still have the micro- and nanoscaled hierarchical structures that are essential for superhydrophobicity (see the Supporting Information). We found that the self-healing of the superhydrophobic (PAA/PAH–SPEEK)$_{60}$ coatings is humidity-dependent, with a more accelerated self-healing process under a more humid environment and vice versa (Figure 2c). Therefore, water participates in the self-healing process of the superhydrophobic PAH–SPEEK/PAA coatings. The self-healing function can be achieved in superhydrophobic PAH–SPEEK/PAA coatings when the coating deposition cycles exceed 30.5. The freestanding superhydrophobic $(PAA/PAH–SPEEK)_{60}$ coating in Figure 1c is also proved capable of self-healing.

The ability of porous superhydrophobic $(PAH–SPEEK/PAA)_{60.5}$ coatings to preserve and facilitate the migration of reacted POTS (denoted rPOTS), which are prerequisites for the self-healing function, was investigated by analyzing the distribution of fluoroalkyl chains in the coatings. Trace 1 in Figure 3a displays the X-ray photoelectron spectrum of the as-prepared superhydrophobic $(PAH–SPEEK/PAA)_{60.5}$ coating. The fluorine signal associated with POTS is detected at 688 eV, which confirms that the surface of the coating is covered with covalently attached POTS molecules. Then the coating was etched by an Ar^+ plasma (3 kV, 3 μA) for 2, 7, and 17 min and the in situ X-ray photoelectron spectra were immediately recorded (traces 2–4 in Figure 3a). The cross-sectional SEM image indicates that about 1 μm of the PAH–SPEEK/PAA coating was removed after 17 min of Ar^+ plasma etching. As shown in traces 2–4 in Figure 3a, the fluorine signals decrease with increasing etching time, thus indicating that the rPOTS has a gradient distribution in the $(PAH–SPEEK/PAA)_{60.5}$ coatings with its concentration gradually decreasing from the top surface to the interior. The fluorine signal is still observable for the $(PAH–SPEEK/PAA)_{60.5}$ coating even after 17 min of Ar^+ plasma etching, which confirms that the porous PAH–SPEEK/PAA coatings can act as a reservoir to accommodate an abundance of rPOTS molecules. The high porosity of the $(PAH–SPEEK/PAA)_{60.5}$ coating allows deep diffusion of POTS molecules into the interior during the CVD of POTS. As shown in trace 5 in Figure 3a, a self-healed $(PAH–SPEEK/PAA)_{60.5}$ coating that was first etched by O_2 plasma for 5 min and then subjected to a humid environment has a high content of surface fluoroalkyl chains, which confirms the migration of rPOTS to the coating surface.

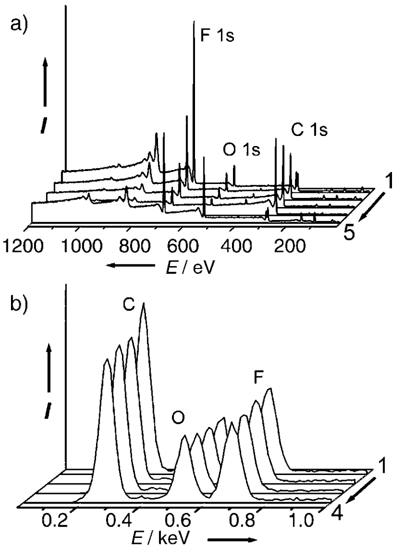

Figure 3. a) X-ray photoelectron spectra of an as-prepared superhydrophobic coating (1), the same coating after Ar^+ plasma etching for 2 (2), 7 (3), and 17 min (4), and an O_2 plasma-etched coating after self-healing (5). b) EDX spectra of the as-prepared superhydrophobic coating (1) and the same coating after two (2), four (3), and six cycles (4) of O_2 plasma etching and self-healing.

We propose the self-healing process of the superhydrophobic coating as follows. After decomposition of the surface rPOTS layer, the superhydrophobic PAH–SPEEK/PAA coating becomes superhydrophilic and can absorb water in a humid environment. The covalently attached hydrophobic POTS molecules underneath the damaged surface of the PAH–SPEEK/PAA coating migrate to the outer surface through rearrangement of polyelectrolyte chains to minimize the free energy of the interface between the coating and the surrounding air. Meanwhile, the oxygen-containing hydrophilic groups produced by O_2 plasma treatment become buried inside the hydrophilic polyelectrolyte coating.[11] The migrated fluoroalkyl chains, like the wax secreted by plants, heal the impaired superhydrophobicity of the PAH–SPEEK/PAA coating. The adsorbed water softens the coating[12] and drives the migration of fluoroalkyl chains, which explains the fact that self-healing of the superhydrophobic PAH–SPEEK/PAA occurs in a humid environment. The self-healing process of our superhydrophobic coatings is quite similar to the surface rearrangement of O_2 plasma-treated polystyrene.[11]

Because energy-dispersive X-ray analysis (EDX) has a deeper depth detection than X-ray photoelectron spectroscopy, the amount of rPOTS in the $(PAH–SPEEK/PAA)_{60.5}$ coating after repeated O_2 plasma etching and self-healing was examined by EDX measurements. As shown in Figure 3b, the EDX spectrum of the as-prepared $(PAH–SPEEK/PAA)_{60.5}$ superhydrophobic coating shows a F/O/C atomic ratio of 1:1:3.8, thus indicating that the porous $(PAH–SPEEK/PAA)_{60.5}$ coating can preserve a large amount of rPOTS during the CVD process. The area of the F peaks after two, four, and six cycles of O_2 plasma etching and self-healing decreases slightly compared with that for the as-prepared superhydrophobic coating, thus demonstrating that the rPOTS molecules consumed in each self-healing process occupy only a small fraction of the totally preserved rPOTS in the coating. Therefore, the longevity of the self-healing function of the superhydrophobic coatings is guaranteed.

In practical applications, superhydrophobic coatings are unavoidably rubbed or scratched by sand in the wind or by animals, which would lead to destruction of the hierarchical structures. Therefore, mechanical stability is also essential to the durability of the self-healing function of the superhydrophobic coatings. The scratch resistance of the superhydrophobic $(PAH–SPEEK/PAA)_{60.5}$ coatings was evaluated by a homemade scratch tester (see the Supporting Information), which comprises a piece of 1500-mesh sandpaper and weights of different mass. The sandpaper had a contact area of $1 \times 1\ cm^2$ with the underlying superhydrophobic coating, and was dragged with a speed of $1\ cm\,s^{-1}$. After being scratched by the sandpaper under a 10 kPa pressure, no scratch was observed on the $(PAH–SPEEK/PAA)_{60.5}$ coating and the superhydrophobicity of the coating showed no decrease. Upon scratching under a 20 kPa pressure, several shallow scratches caused by stress concentration appeared on the surface of the coating (Figure 4 a,b). The area of the scratches was less than 10 % of the total area of the coating. However, the surface of the scratched areas was still rough.

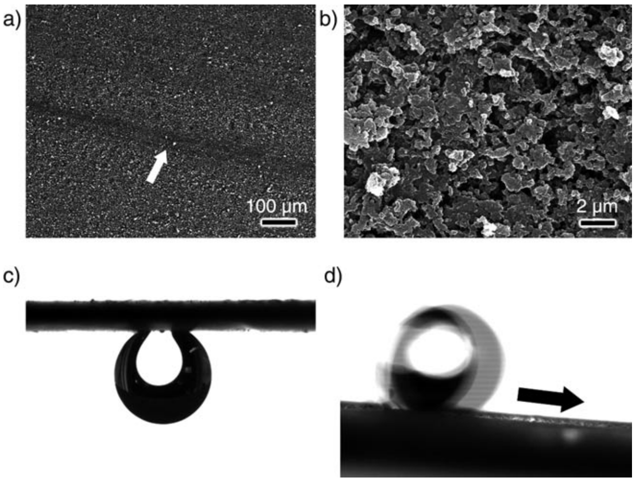

Figure 4. a) Top-view SEM image of the scratched coating. b) Enlarged SEM image of the scratches in (a) (marked with an arrow). c,d) Wetting characterization of the scratched coating before (c) and after self-healing (d).

When measured immediately, the scratched (PAH–SPEEK/PAA)$_{60.5}$ coating is superhydrophobic (154°) but highly adhesive as the water droplet is pinned on its surface even when the coating is upside down (Figure 4 c). The exposed hydrophilic polyelectrolyte complexes in the scratches increase the adhesion of the coating toward water. After the scratched coating was subjected to an environment of 100 % RH, it readily became superhydrophobic with a water contact angle of 156° and a sliding angle of about 5° (Figure 4 d). The superhydrophobicity can be self-healed even when scratches are made on the superhydrophobic (PAH–SPEEK/PAA)$_{60.5}$ coatings. The combination of rigid SPEEK with flexible PAH and PAA produces rigidly flexible PAH–SPEEK/PAA coatings, which endows the resultant coatings with satisfactory scratch resistance because the hierarchical structures on the PAH–SPEEK/PAA coatings can deform reversibly to avoid fracture caused by scratching. Meanwhile, the rigidly flexible coating becomes flexible enough for convenient migration of healing agents of rPOTS in a humid environment. It is also worth mentioning that the rPOTS molecules preserved in the coating produce silica backbones, which are capable of enhancing the resistance of the superhydrophobic coatings to O_2 plasma etching.

In summary, we show for the first time that self-healing superhydrophobic coatings can be fabricated by preserving healing agents consisting of reacted fluoroalkylsilane in the coatings, which are porous and rigidly flexible. While rigid superhydrophobic coatings are neither scratch-resistant because of the easy fracture of the rigid nanostructures under scratching nor capable of self-healing because of the tight confinement of the healing agents in the coating, the rigidly flexible the PAH–SPEEK/PAA coatings are essential to realize the self-healing function. The healing of the superhydrophobicity of the coatings, which requires the migration of the preserved reacted fluoroalkylsilane to the coating surface, can be easily accomplished in a humid ambient environment. The self-healing of our superhydrophobic coatings can be repeated many times without decreasing the superhydrophobicity. It is anticipated that the introduction of a self-healing function into robust superhydrophobic coatings will open a new avenue to extending the lifespan of superhydrophobic coatings for practical applications.

Experimental Section

Details of the materials, modification of substrates, CVD, and characterization of the PAH–SPEEK/PAA coatings can be found in the Supporting Information.

Fabrication of self-healing superhydrophobic coatings: An aqueous dispersion of PAH–SPEEK complex, which had a PAH to SPEEK feed monomer molar ratio of 10:1, was prepared by rapidly pouring PAH solution (5 mg mL^{-1}) into vigorously stirred SPEEK solution (0.5 mg mL^{-1}) followed by adjusting the pH of the dispersion to 5.0 with 1 M NaOH. The LbL deposition of PAH–SPEEK/PAA coatings was conducted automatically by a programmable dipping machine (Dipping Robot DR-3, Riegler & Kirstein GmbH) at room temperature. Silicon wafers were covalently linked with sulfonate groups to enhance the adhesion of the superhydrophobic coatings to the substrate. Other substrates, including those for the fabrication of freestanding superhydrophobic coatings, were predeposited with a positive layer of poly(diallyldimethylammonium chloride) (PDDA). The sulfonate-modified substrates were first immersed in an aqueous dispersion of PAH–SPEEK complex for 20 min followed by rinsing in three water baths for 1 min each. Next, the substrate was immersed in an aqueous PAA solution (1 mg mL^{-1}, pH 3.5) for 20 min, also followed by rinsing in three water baths for 1 min each. In this way, one bilayer of PAH–SPEEK/PAA coating was fabricated. The deposition of PAH–SPEEK and PAA layers was repeated until the desired layer number was reached. No drying step was used in the deposition procedure unless it was in the last layer. The fabrication of PAH–SPEEK/PAA coatings on PDDA-modified substrates started with the deposition of a PAA layer. Thermal cross-linking of the PAH–SPEEK/PAA coatings was conducted by heating the film at 180 °C for 2 h. Superhydrophobic coatings were obtained after CVD of POTS on thermally cross-linked PAH–SPEEK/PAA coatings. To obtain freestanding superhydrophobic coatings, (PAA/PAH–SPEEK)$_{60}$ coatings were released from PDDA-modified silicon wafers by immersing the coatings in an aqueous solution of pH 2.0 for 30 min (see the Supporting Information).[10]

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