Facile fabrication of self-repairing superhydrophobic coatings†

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A self-repairing superhydrophobic organic coating comprising poly(styrene), fluorinated poly(methylsiloxane), fluorinated alkyl silane modified silica nanoparticles and photocatalytic titania nanoparticles shows self-repairing ability after mechanical damage, photocatalytic self-cleaning performance, and thus long-term outdoor durability.

In the past decades, superhydrophobic surfaces have drawn tremendous attention because of their potential applications in self-cleaning, nonwetting, anticorrosion, antireflection, anti-fogging, anti-icing, etc. Unfortunately, the artificial superhydrophobic surfaces known to date easily lose non-wettability due to sunlight, physical rubbing and organic contamination, which seriously hampers their practical applications.1

Fabrication of superhydrophobic surfaces with self-repairing ability would be the best strategy to realize their long-term durability.2 Li et al. fabricated self-healing superhydrophobic coatings containing fluoroalkyl silane in their porous structure.9 Once the top layer was decomposed, the preserved fluoroalkyl silane migrated to the surface to heal the superhydrophobicity. Wang et al. prepared a superhydrophobic and superoleophobic surface via deposition of a mixture of fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) and hydroyzed FAS on fabrics.10 Due to the movement of the FD-POSS molecules to the surface under heating, the fabrics could maintain the superhydrophobicity even after 100 cycles of the plasma-and-heat treatment, suggesting the self-healing ability of the surface. Liu et al. reported a self-healing hydrophobic surface using polydopamine coated mesoporous silica as a reservoir material of octadecylamine that can release and accomplish self-healing.11 Clearly, all these superhydrophobically self-repairing ability were achieved by supplying the surface with hydrophobic substances that were stored beforehand in the interior of the surface.

Besides the above “migration of hydrophobic compound” strategy, a self-healing strategy based on the self-organization of colloidal particles at interfaces under annealing was also found for a mixture of perfluorinated wax/colloidal silica particles.12

Recently, “self-repairing” superhydrophobic surfaces were reported based on the porous coatings. Due to the self-similar structure of the bulk to the top surface, the surface could sustain its superhydrophobicity after the top layer was mechanically removed. For instance, Deng et al. developed a transparent robust superamphiphobic surface by ordered deposition of a layer of porous candle soot on a glass slide, coating the soot template with a silica shell, calcinating the hybrid carbon–silica network to remove the carbon core, and coating the silica shell with semifluorinated silane.13 The surface displayed a porous morphology and kept its superamphiphobicity when the top layer was removed by water impact or sand abrasion. Similarly, Manna et al. fabricated superhydrophobic porous polymer films via layer-by-layer assembly of branched poly(ethyleneimine) and poly(vinyl-4,4-dimethylazlac-tone).14 The film can not only sustain superhydrophobicity after physical erosion but also fully recover superhydrophobicity using a water-assisted approach after the film is severely crushed. Although these results are interesting, the fabrication processes are time-consuming and too complicated for most practical applications.

In the past years, we reported a facile and large-scale method to produce superhydrophobic coatings based on a hydrophobic poly(fluoro)siloxane binder and photocatalytic TiO2 nanoparticles (P25).15 The coatings displayed excellent resistance to organic contamination. However, it still could not recover its micro/nano-structure surface upon mechanical damage. In this communication, the coating compositions were changed to polystyrene (PS) and fluorinated SiO2 nanoparticles (FMS, Fig. S1, ESI†) although z2,0-bis(hydroxypropyl)-terminated poly(2,2,3,3,4,4,4-heptafluorobutylmethylsiloxane) (PMSF) and TiO2 nanoparticles were the same as those used in the previous method.15 Interestingly, the superhydrophobic surfaces formed with these constituents could be recovered under UV-irradiation not only when they were polluted with organics but also when they were mechanically damaged. This excellent self-repairing ability assured their prominent...
superhydrophobic durability in both accelerated weathering tests and outdoor service.

In the current superhydrophobic coatings, PS acted as the main polymer binder. PMSF was merely used as the reservoir of the hydrophobe and not as the binder anymore, its role being different from that it played previously.\(^{15}\) To store hydrophobic components as well as it can possibly, the PMSF/PS mass ratio was designed to have the maximum value, 0.42, above which the superhydrophobic coatings have a poor adhesion force with the substrates.

Being similar to those reported superhydrophobic coatings based on hydrophobic polymer binder and nanoparticles,\(^{15,16}\) the “lotus effect” superhydrophobic coatings can be readily obtained herein above a critical nanoparticle load. As shown in Fig. 1a, the critical FMS content required to obtain a superhydrophobic surface [water contact angle (WCA) > 150° and sliding angle (SA) < 10°] is 28 wt% at a fixed TiO\(_2\) nanoparticle content of 6 wt%. Namely, the critical total nanoparticle load is 34 wt%. The superhydrophobicity may have resulted from the hydrophobic ingredients, i.e. PMSF, FMS, and PS, of the coatings as well as from the micro/nano-rough surface composed of large irregular microscale aggregates (size: 2–10 \(\mu\)m) and nanoapophysis (size: 20–60 nm) (Fig. 1b). These superhydrophobic surfaces can be observed on different substrates such as paper, wood, glass, polypropylene, tin and aluminum (Fig. S3, ESI\(^{†}\)).

The FMS/TiO\(_2\)-based superhydrophobic coatings and the control experiment based methylated SiO\(_2\) nanoparticles (TS-530, a commercial product) and TiO\(_2\) nanoparticles (TS-530/TiO\(_2\)-based superhydrophobic coating), were subjected for the accelerated weathering tests. As shown in Fig. 1c, the FMS/TiO\(_2\)-based superhydrophobic coatings displayed a slight increase in WCA, and an almost constant SA value as low as 10° within 720 h of accelerated weathering, suggesting an excellent durability of the superhydrophobic performance. Contrarily, the control superhydrophobic coating lost its superhydrophobicity after accelerated weathering for 216 h and even became hydrophilic after 720 h of accelerated weathering test (Fig. S4, ESI\(^{†}\)). Because of the excellent stability of C–F bonds with a bonding energy of up to 485 kJ mol\(^{-1}\), the fluorinated groups at the surfaces of SiO\(_2\) nanoparticles are difficult to decompose under UV irradiation even in the presence of photocatalytic TiO\(_2\) nanoparticles.\(^{17}\) As a consequence, the FMS nanoparticles always keep their hydrophobicity and consecutively function as the hydrophobic nanobuilding blocks for the superhydrophobic coatings within the accelerated weathering tests. However, the methyl groups at the surfaces of TS-530 nanoparticles are easily decomposed under UV irradiation, especially in the presence of TiO\(_2\) nanoparticles, producing hydrophilic nanoparticles. In addition, the FMS/TiO\(_2\)-based superhydrophobic coating displayed a chalked surface after UV irradiation for 72 h due to the photodegradation of PS (Fig. S3, ESI\(^{†}\)), which may be responsible for the initial increment of WCA.

Fig. 1d presents the effect of the TiO\(_2\) nanoparticle content on the superhydrophobic durability of the coatings in accelerated weathering tests. The initial WCA increased with increasing TiO\(_2\) nanoparticle content, but, it was still below 150° at TiO\(_2\) nanoparticle contents lower than 4 wt%. The WCA gradually rose up after aging for all coatings due to photodegradation of PS. However, when the content of TiO\(_2\) nanoparticles increased to 8 wt%, the WCA of coatings started to decline after accelerated tests for 560 h and even below 150° after 720 h. A much quicker decrease of WCA was exhibited for the coating with 10 wt% of TiO\(_2\) nanoparticles, which lost its superhydrophobicity after only 432 h of acceleration tests. The reduction of WCA should be attributed to the photo-induced supra-amphiphilic TiO\(_2\) nanoparticles that were uncovered by enough hydrophobic polymer chains. So an appropriate amount of TiO\(_2\) nanoparticles (i.e., 6 wt%) is very critical. At this content, the coatings can not only display superhydrophobicity initially but also keep the superhydrophobicity for a long time under UV-irradiation. Moreover, these TiO\(_2\) nanoparticles can photocatalytically degrade PS to regenerate the rough surface structure (seen below), which is essential for superhydrophobicity, and provides the coatings with resistance to organic pollutants.

Mechanical wear is usually fatal to superhydrophobic surfaces, because it not only destroys the micro/nano-surface structure but also removes the hydrophobic substances from the top layers of surfaces.\(^{9}\) To evaluate the influence of mechanical wear and the self-repairing ability of the FMS/TiO\(_2\)-based superhydrophobic coating, the surface was polished using a piece of sandpaper under 10 or 20 kPa pressure (Fig. S6, ESI\(^{†}\)). The results showed that the surface still held its superhydrophobicity although a slight decrease of WCA was observed (155° → 150°) after 10 cycles of polishing under 10 kPa pressure, indicating a good mechanical durability of the superhydrophobic coating. Nevertheless, when the surface was polished under 20 kPa pressure, the WCA declined remarkably from 155 to 139° and the SA rose to 70° (Fig. S7, ESI\(^{†}\)). Very interestingly, this mechanically-damaged surface gradually recovered its “lotus effect” superhydrophobicity under UV irradiation,
as shown in Fig. 2a. This recovery of superhydrophobicity was vividly watched with our naked eye (Fig. 2b). Further repeated polishing did not deteriorate its self-repairing ability (Fig. S8, ESI†). The SEM image clearly showed that micro-protuberances disappeared and a relatively smooth surface appeared after polishing (Fig. 2c). After UV irradiation, the micro/nanosurface structure returned back again (Fig. 2d), which was also observed for the surface polished under 10 kPa (Fig. S9, ESI†). The SEM images of the polished surface after 10 cycles of abrasion under a 20 kPa pressure, and the repaired surface (192 h exposure in the accelerated weathering tester). (Composition: PMSF/PS/FMS/P25 = 17.1/40.9/36.0/6.0 wt/wt.)

Furthermore, the atomic composition in Table 1 from XPS analysis (Fig. S11, ESI†) displayed that the polished surface had a comparable atomic surface composition to its original one. After UV irradiation, the C atomic concentration decreased sharply and the Si and O atomic concentrations increased considerably, suggesting a serious degradation of the polymer in the coatings. It was due to the degradation of the polymer matrix that FMS nanoparticles and TiO₂ nanoparticles in the bulk had the chance to be exposed at the top surface to form the new hierarchical structure. Both the renewed surface roughness and the hydrophobic composition can assure the regeneration of the superhydrophobic surface.

The susceptibility of superhydrophobic surfaces towards particle contamination is eliminated by the self-cleaning effect. However, not all dusts can always be washed away with water. It has been shown that oily dusts can easily adhere to superhydrophobic coating in practical uses. Herein, we employed oleic acid as a model to examine the resistance to oily contaminants for the FMS/TiO₂-based superhydrophobic coating. FMS-based superhydrophobic coating as the control was also examined for the comparison. As shown in Fig. S12a (ESI†), the WCAs on both coatings decreased from 155 to 62° when oleic acid was cast on the surfaces of coatings. After accelerated weathering for 84 h, the FMS/TiO₂-based superhydrophobic coating recovered from the hydrophilic to the superhydrophobic state. In contrast, the FMS-based superhydrophobic coating did not show any changes and was still in the hydrophilic state (Fig. S12b–f, ESI†). Furthermore, even after seven cycles of oleic acid casting and accelerated weathering, the FMS/TiO₂-based superhydrophobic coating still recovered its superhydrophobic state (Fig. 3a). The results indicate that the TiO₂ nanoparticles in the coating can photocatalytically decompose the oleic acid and therefore endow the coatings with the resistance to oily contaminants.

The superhydrophobic durability of the FMS/TiO₂-based superhydrophobic coating and the control samples was further compared by outdoor exposure. All the superhydrophobic coatings displayed a slight increase in WCA at an early stage (Fig. S13, ESI†). Then the WCAs of both the FMS-based and TS-530/TiO₂-based superhydrophobic coatings decreased gradually and reached 124° and 135° (Fig. 3b and c), respectively, after 2160 hours of outdoor exposure. However, the FMS/TiO₂-based superhydrophobic coating still maintained superhydrophobicity (Fig. 3d) and its surface was...

### Table 1: Surface chemical composition of FMS/TiO₂-based superhydrophobic coating determined using XPS analysis

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface concentration (atom %)</th>
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<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Original surface</td>
<td>60.9</td>
</tr>
<tr>
<td>Polished surface</td>
<td>59.1</td>
</tr>
<tr>
<td>UV-irradiated</td>
<td>21.3</td>
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Fig. 3 (a) Changes of WCA for FMS/TiO₂-based superhydrophobic coatings as a function of the number of the repeated cycles of oleic acid adhesion and accelerated weathering (FMS-based coating composition: PMSF/PS/FMS/P25 = 17.1/40.9/36.0/6.0 wt/wt; FMS/TiO₂-based coating composition: PMSF/PS/FMS/P25 = 17.1/40.9/36.0/6.0 wt/wt). (a–d) photographs of water droplets (contact angles: 124°, 135° and 155°) on the FMS-based (b, c) and FMS/TiO₂-based (d) superhydrophobic surfaces after 2160 hours of outdoor exposure; (e, f) optical images of FMS/TiO₂-based (e) and FMS-based (f) superhydrophobic coatings after 2160 hours of outdoor exposure (FMS/TiO₂-based coating composition: PMSF/PS/FMS/P25 = 20.4/48.6/25.0/6.0 wt/wt).
cleaner than the FMS-based superhydrophobic surface after 2160 hours of outdoor exposure (Fig. 3e). The decreasing superhydrophobic durability may be owing to the decomposition of the hydrophobic components at the surface of the TS-530 nanoparticles for the TS-530/TiO2-based coating and to the contamination of small pollutant particles (such as “PM2.5” dust)\(^9\) or organic contaminants for the FMS-based superhydrophobic coating (Fig. 3f). It elucidates that the FMS/TiO2-based superhydrophobic coating has excellent long-term superhydrophobicity.

The self-repairing mechanism of the FMS/TiO2-based superhydrophobic coating is schematically depicted in Scheme 1. It is well known that the self-healing ability of naturally superhydrophobic plant leaves is typically based on the consecutive excretion of hydrophobic substances to surfaces and reestablishment of topographic structures as a result of biological growth processes.\(^7,^9\) Similarly to this process, in the FMS/TiO2-based superhydrophobic coating, the durable and hydrophobic ingredients, FMS nanoparticles and PMSF, work as the hydrophobic substances. When the damaged surface was irradiated using sunlight or UV, PS was decomposed first from the top layer due to the photolysis of TiO2 nanoparticles, increasing the pigment/binder ratio and finally forming a chalked surface. As a result, the FMS superhydrophobic surface formed again through the synergistic effect of the ingredients in the coatings.

Chalking, on the other hand, could shorten the service life of the coatings. If the chalking is limited to the top surface layer by blocking the penetration of UV light, the service life of the superhydrophobic coatings will be extended. Controlling the service life of superhydrophobic coatings is underway. Nevertheless, the chalked surface brings an advantage. Namely, small pollutant particles (such as “PM2.5” dust) piled on the surface will be removed with the chalked surface periodically under natural forces such as wind, rain and so on, which thoroughly renews the surface and is extremely beneficial for the long-term superhydrophobicity.

In summary, we have successfully fabricated a self-repairing superhydrophobic coating through a simple fabrication method using PS, PMSF, FMS nanoparticles and photocatalytic TiO2 nanoparticles as the components. The as-obtained superhydrophobic coatings can be readily sprayed on various substrates and exhibit good mechanical strength, excellent durability under UV irradiation and resistance to oily contaminants. More importantly, the surface topographic structure can be quickly regenerated after being damaged and thus this superhydrophobic feature can be recovered based on the synergistic effect of the coating components both in UV-accelerated weathering tests and under sunlight. Consequently, this superhydrophobic coating displays long-term superhydrophobicity and can be used on a large-scale for big outdoor objects, such as bridges, buildings, power towers, communication towers, and so on.

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**Notes and references**