Improving the Mechanical Durability of Superhydrophobic Coating by Deposition on to a Mesh Structure

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Superhydrophobic surfaces (SHSs) require a combination of a rough nano- or microscale structured surface topography and a low surface energy. However, its superhydrophobicity is easily lost, even under relatively mild mechanical abrasion, when the surface is mechanically weak. Here, we develop a method that significantly increases the mechanical durability of a superhydrophobic surface, by introducing a mesh layer beneath the superhydrophobic layer. The hardness, abrasion distance, flexibility and water-jet impact resistance all increase for the commercially available Ultra-ever Dry superhydrophobic coating. This is attributed to the increased mechanical durability offered by the mesh, whose construction not only increases the porosity of the SHS coating but acts as a third, larger structure, so that the superhydrophobic layer is now composed of a three-level hierarchical structure: the mesh, micropillars and nanoparticles.
Graphical abstract
1. INTRODUCTION

In recent years, a growing number of researchers have been studying how to fabricate superhydrophobic surfaces (SHSs), which display high static contact angles (SCA) and low sliding angles (SA) for a water drop\(^1\). SHSs have wide application in daily life, in situations that require self-cleaning\(^2\), anti-freezing\(^3\), non-sticking of snow\(^4\), anti-corrosion\(^5\), anti-biofouling\(^6\), etc. In general, the superhydrophobicity of a SHS is dependent on both the chemical composition and the topography of the surface\(^7\). Many fabrication processes have been reported, including a hydrothermal method\(^8\), electrodeposition\(^9\), etching processes\(^10\), spray coating\(^11\), atomic layer deposition\(^12\) and sol–gel processing\(^13\).

However, applications are often limited by the poor mechanical stabilities of SHSs because their nanoscale structures, with high aspect ratios, are intrinsically mechanically fragile and can be destroyed by rather low mechanical stresses\(^14,15\). Various methods have been proposed to improve the mechanical durabilities of SHSs. While, for example, Liu et al. used composite ceramic coating to improve mechanical durability\(^16\), some soft materials are also good choices for anti-abrasion SHSs\(^17\).

Hierarchal roughnesses are widely used to improve the hydrophobicity and durability of SHS\(^14\). For example, Groten et al.\(^10\) manufactured three types of photolithographically created structural model surfaces (microscale structures, nanoscale structures and composite structures) that were ion-couple plasma-etched to produce SHSs with improved mechanical durability. Based on their results, they hypothesized that the composite structures had increased mechanical stability.

Ou et al.\(^15\) reported similar composite structures on copper substrates, fabricated by chemical etching. Then, treatment of the etched surface with 1H,1H,2H,2H-perfluorodecanethiol produced
a superhydrophobic surface. However, it had poor wear resistance, due to the loss of low surface energy molecules and a change in surface morphology. Huovinen et al.\textsuperscript{18} introduced additional, larger microscale features, and found improved mechanical wear properties.

Using a low surface energy material, such as PTFE or PVDF, which will protect the SHS from abrasion\textsuperscript{19,20,21,22}, our group introduced nano- and microscale porous structures in PTFE superhydrophobic coatings, improving their anti-abrasion properties\textsuperscript{23}.

In this paper, we present a simple method for enhancing the mechanical durability of the commercially available Ultra-ever Dry superhydrophobic coating product. Its mechanical durability, including hardness, and water-jet impact and abrasion resistances, are greatly improved by introducing a larger scale nylon mesh as a substrate for the superhydrophobic coating. We believe that the cause of the durability enhancement is directly attributable to the integrated 3D network introduced by the mesh structure.

2. EXPERIMENTAL SECTION

Figure 1. Schematic of preparation of the superhydrophobic coating on nylon mesh

2.1. Materials
Ultra-Ever Dry coatings 4001 and 4002 were purchased from Ultra Tech International, Inc. Low carbon steel substrates (30 x 25x 0.28mm), were obtained from Wuxi Guangyuan Auspicious Metal Materials Co., Ltd. (China). The nylon mesh, available in different mesh grades, was purchased from Shanghai Xingan Woven Fabric Co., Ltd.(China). The double-side tape was purchased from 3M Co., Ltd. (China).

2.2. Preparation of the SHS coating

The meshes were rinsed sequentially with deionized water and ethanol, and then dried at room temperature. The SHSs were fabricated in two steps, presented schematically in Figure 1. First, the nylon mesh and substrate were joined by double-sided tape, forming a sandwich. The superhydrophobic coating was sprayed on to the sandwich and then dried at room temperature. The spraying pressure of the spray gun was 0.8MPa, and the amount of solution sprayed was 0.3mL/cm², at a spraying distance of 15 cm; all these processes were carried according to the manufacturer’s instructions.

2.3. Characterizations

The surface structures were examined by field emission scanning electron microscopy (FESEM, Nova Nano-SEM, FEI, USA). The static contact angle (SCA) and sliding angle (SA) were measured with a Krüss DSA20 apparatus at ambient temperature. The volume of the individual water droplets were 7μL. The average SCA and SA values were obtained by measuring at least five different positions per sample. The stability, including wear/water-impact/hardness resistance, of the as-fabricated sample was also evaluated, and the conditions for testing, listed in Figure 3, are those previously recommended²⁴.

3. RESULTS AND DISCUSSION

3.1. Surface structures
The FESEM images of a typical nylon mesh (grade 400) (Figure 2a and 2b) demonstrate that the mesh fibers are smooth; their diameters are \( \sim 50 \pm 5 \mu m \), with the distance between fibers being \( \sim 25 \) to \( \sim 100 \mu m \). FESEM images of the superhydrophobic Ultra-Ever Dry coating (Figure 2c and 2d) and the coating on a mesh structure (Figure 2e and 2f) reveal that pillars form on the original surfaces. For the SHS coating, surface morphology can be composed by microstructure pillars and nanoparticles\(^2^4\), the pillar diameters range from \( \sim 20 \) to \( \sim 40 \mu m \), and the distance between the pillars is approximately \( \sim 25 \) to \( \sim 50 \mu m \), which is consistent with a previous study\(^2^4\). For the coating on the mesh structure, the pillar diameters are similar, while the distance between the pillars is \( \sim 40 \) to \( \sim 80 \mu m \), and they appear taller than for the coating without mesh. All the pillars, for samples with and without mesh, are covered with nanoparticles (Figure 2). The pore structures of the coatings on the mesh are much taller, as seen in the SEM photo micrographs in Figure 2c, 2d, 2e and 2f.

Figure 2. FESEM images of (a) and (b) nylon mesh, (c) and (d) Ultra-Ever Dry coating, and (e) and (f) Ultra-Ever Dry coating on nylon mesh.
3.2. Mechanical durability

Mechanical durability or robustness is one of the most important aspects necessary for the industrial application of SH coating. It is typically evaluated by sandpaper abrasion test\textsuperscript{14,25,26,27}. The abrasion resistance of our films was evaluated by the sandpaper abrasion test (Figure 3a). The water droplet dependences of both the static contact angle (SCA) and slide angle (SA), as a function of abrasion cycle or abrasion distance, have been used to characterize the mechanical durability of a SHS. The variation in our SA values on the abrasion distance (1 cycle=2x15cm), using different mesh grades, can be found in Figures 3 and 4. The abrasion resistances of all the mesh-containing samples are greatly improved (Figure 3a, 3b) when using mesh. The change of SA of the SHS both with and without mesh, as a function of abrasion distance, can be divided into two parts: the slope first increases slowly over an abrasion distance of less than 500cm, before becoming more rapid, reaching \(\sim 90^\circ\), with the water droplet pinned to the surface. The tendency of the SA to increase with abrasion distance was slower with than without mesh, especially for the grade 400 mesh, which has the best abrasion resistance. It is interesting to note that the SA of the SHS without mesh can be rapidly pinned after \(\sim 600\)cm abrasion distance (\(\sim 20\) abrasion cycles). The wear-resistance, or anti-abrasion property, of the SHS on mesh depends on the mesh grade.
Figure 3. (a) Schematic of the abrasion test employed to evaluate the mechanical durability of superhydrophobic coatings, (b) sliding angle of SHS, as a function of abrasion distance, with a load of $\sim 200$ g, and (c) an enlargement of the first 1000 cm of abrasion distance in Figure 3b.

A typical change of SCA with slide distance can be found in Figure 4. One notes that the SCA slowly decreases with abrasion distance, from $\sim 152^\circ$ to $\sim 142^\circ$, while SA increases from $\sim 3^\circ$ to $\sim 90^\circ$. The scatter of the SCA data increases with abrasion distance, as seen in Figure 4. All these results indicate that the dependence of the SCA on abrasion distance is relatively small, although the SA variation on the abrasion distance is great, suggesting more nanostructures were lost from the SHS during the abrasion process (the outermost nanostructures are associated with the SA$^2$). This is consistent with the surface morphology change seen by SEM, and discussed below. The similarity of SA values both with and without mesh suggests both SHSs have similar abrasion mechanisms.
Figure 4. Typical SA and SCA as a function of sliding distance on the SH coating containing a grade 400 mesh.

Figure 5 shows photomicrographs of the coatings following abrasion testing. The outer layers of the coatings, both with and without mesh structures, are seen to have been abraded. However, there are many more pores in the sample with the mesh, compared to that without the mesh. The meshes remain coated, although the nanostructures on the outer surface appear to have been removed by the sandpaper.

Figure 5. A comparison of (a,b,e,f) SEM photomicrographs of SH coatings before, and (c,d,g,h) after the abrasion test. (a)-(d) are of a SH coating without mesh and (e)-(h) are with mesh.
3.3. Water-jet impact testing

Figure 6 shows the mechanical durabilities of our SHSs on water-jet impact testing. Table 1 lists the hardness values of the coatings. The results show that the SA can be improved by using mesh structures; both 300 and 400 grades are the best, on water-impact jet testing. Using 300 and 400 grade meshes, it takes 40min of water-jet impact testing to pin water droplets, while this time is 30min without mesh structures. SCA values decrease from > 150° to ~ 135° for the mesh structures although the value drops to <130° after 20min, in the absence of mesh. These results indicate that mechanical stability is greatly improved for soft impact (water-jet) on using mesh structures.

Figure 6. (a) A water-jet impact setup and (b) SA and SCA as a function of water-jet impact time for the SH coating on different meshes.

The hardness of the coating was evaluated by pencil scratching. As showing in Table 1, the hardness increases on using mesh, and it reaches a maximum for grade 400, consistent in with our abrasion and water-jet impact testing. Figure 7 shows SEM photomicrographs of the SH coating before (a, b, e, f) and after (c, d, g, h) water-jet impact testing. It is seen that the nanoparticles on the outer surface have been worn away, with or without mesh. The difference
between the two SH coatings is then limited to the pores seen in the photomicrographs. This suggests that the durability improvement of the mesh-containing SH coating is due to the presence of larger pores for the mesh-containing coating.

![SEM photomicrographs](image)

Figure 7. SEM photomicrographs of the SH coating (a,b,e,f) before, and (c,d,g,h) after water-jet impact testing. Here, (a)-(f) are of a SH coating without mesh, and (e)-(h) are of a coating with mesh.

The SA dependence on abrasion distance, as seen in Figures 3b and 3c, suggests that there is a difference for different mesh grades. The best abrasion resistance was found for 400 grade mesh, having an abrasion resistance distance (the distance over which water droplet remains pinned) of almost 5000cm, compared to 600cm without the mesh. The change of SA slope with abrasion distance, as shown Figure 4, from 0.0299 for the SHS without mesh to 0.013 for the SHS with mesh, is more than halved. The reduced slope indicates the removal or wear of surface nanoparticles is retarded. The same tendency for the SA as a function of abrasion distance, both with and without mesh, is seen in Figure 4. This suggest that both have same wear mechanism, and can be attributed to two abrasion processes, the first being the loss of nanoparticles from the upper surface, and the second, the wear of the micropillars. The nylon mesh can be considered a larger microstructure, with the micropillars smaller microstructures; the larger microstructures enhance mechanical stability, as suggested in reference18. This can be understand as (1) the increase of SHS roughness on using mesh structures, because the mesh structure is larger than
that of the original microstructure, and (2) the increased pore size and number of pores of the SHS coating, which assists in protecting nanoparticles from loss during the abrasion process, since the nanoparticles are better protected in the pores.

Table 1. Hardness of the SH coating as a function of different grades of mesh

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<th>mesh grade</th>
<th>0</th>
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<th>300</th>
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Although the exact mechanism for the improved wear resistance of the SH coating, on using the mesh structures, is unclear, it may be that the larger microscale structure assists in protecting the micropillars as well as the fragile, fine-scale nanostructures. Because the mesh is integrated into the whole layer, its presence enhances both the hardness and the water-jet resistance of the coating. Because the mesh structure is inexpensive compared with previously reported processes\(^\text{18}\), it is easily commercialized and engineered.

4. CONCLUSIONS

The present work reveals a simple, low cost method that lends itself to the mass production of mechanically robust SHSs. The improved mechanical durability can be attributed the large microstructured mesh, and the increased porosity of the SHS coating that protects the smaller, weaker micro- and nanostructures. The method can be used with any superhydrophobic coatings.

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