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shuliang dong, Zhenlong Wang, Yukui Wang, Xuelin Bai, Yong Qing
Richard Fu, Bin Guo, Chaoliang Tan, Jia Zhang, and PingAn Hu

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Roll-to-Roll Manufacturing of Robust Superhydrophobic Coating on Metallic Engineering Materials

Shuliang Dong,[†] Zhenlong Wang,^{,†,‡} Yukui Wang,[†] Xuelin Bai,[†] Yong Qing Fu,[§] Bin*

Guo,^{,†} Chaoliang Tan,[#] Jia Zhang,^{*,†,‡} PingAn Hu[†]*

[†]Key Laboratory of Microsystems and Microstructure Manufacturing, Ministry of Education, Harbin Institute of Technology, No. 2 Yikuang Street, Harbin, 150080, China.

[‡]State Key Laboratory of Robotics and System, Harbin Institute of Technology, No. 2 Yikuang Street, Harbin, 150080, China.

[§]Faculty of Engineering & Environment, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK.

[#]Electrical Engineering & Computer Sciences, University of California at Berkeley, Berkeley, California 94720, United States

KEYWORDS: roll-to-roll manufacturing, robust superhydrophobic surface, EDM, metallic engineering materials, carbon nanoparticles

ABSTRACT: Creating a robust superhydrophobic surface on the conventional engineering materials at mass production is of great importance for self-cleaning, anti-icing, non-wetting surface and low flow resistance in industrial applications. Herein, we report a roll-to-roll

1 strategy to create durable and robust superhydrophobic surfaces with designed micro-/nano-
2 scale hierarchical structures on many conventional engineering materials by combining
3 electrical discharge machining, coating of carbon nanoparticles, and followed by oil
4 penetration and drying. The treated surface shows good superhydrophobic properties with
5 static water contact angle of $170\pm 2^\circ$ and slide angle of $3\pm 1^\circ$. The treated surface also exhibits
6 good resilience and maintains the performance after tested in various harsh conditions
7 including water flushing for several days, sand abrasion, scratching with sandpapers and
8 corrosive solution. Significantly, the superhydrophobic surfaces also shows a high efficiency
9 of self-cleaning properties even after oil-contamination during applications.

10 INTRODUCTION

11 Wettability of a solid surface is critical for both fundamental research and industrial
12 applications. A surface with a water static contact angle (CA) larger than 150° and a sliding
13 angle (SA) smaller than 10° is generally considered as a superhydrophobic surface,^{1,2} which
14 has advantages of non-wetting, self-cleaning and low flow resistance. The lotus surfaces,³
15 legs of water striders⁴ and butterfly wings⁵ are natural examples of superhydrophobicity.
16 Mimicking their surface morphologies using micro-/nano- structures leads to the
17 development of various artificial superhydrophobic surfaces, some of which are being applied
18 in industrial and biological processes.^{2,6} As well known, the water repellent ability of a
19 specific surface is strongly affected by its chemical composition, surface geometric structures
20 (or surface roughness) and superhydrophobicity. Therefore, chemical modifications and
21 development of micro-/nano-scale hierarchical structures are essential to achieve a low
22 surface energy and superhydrophobicity.²⁻⁷ Low surface energy materials were solely
23 employed to modify the rough surface to achieve the superhydrophobicity.^{1,2,6,7} However,
24 the weak wear resistance resulted in loss of the water repellency soon.⁸ As an alternative,
25 many different surface morphologies have been created to achieve more stable

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3 1 superhydrophobicity.^{2, 6, 8-10} Nevertheless, most of these are limited to polymers and colloidal
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5 2 materials.^{11, 12} These types of soft matter surfaces are unlikely to be widely applied in industry
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7 3 owing to their non-scalable techniques, poor mechanical resistance, and performance
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9 4 degradation with time.¹³ Recently, advanced techniques such as laser beam or chemical
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11 5 etching, oxidation, and surface coatings have widely been used, but they often suffer from the
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13 6 using of expensive equipments and/or complicated processes.¹⁴⁻¹⁹ Creating durable and robust
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15 7 superhydrophobic surface for industrial applications, one of the key concerns is how to
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17 8 successfully transfer lab-scale synthesis methods to large-scale and continuous
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19 9 manufacturing processes (such as roll-to-roll), especially for these widely used conventional
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21 10 engineering materials (such as steel, aluminum, copper, metallic composites).

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24 11 Electrical discharge machining (EDM) is widely used for fast and scalable machining
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26 12 process of metallic engineering materials. The electric discharge (i.e., spark) occurs between
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28 13 the tool electrode and work-piece, transferring the electric energy into a local heating (Figure
29
30 14 S1). As a result, an amount of material could be melted and vaporized, leaving large amounts
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32 15 of random distribution of cavities (often called craters) on the work-piece (Figure S1). As the
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34 16 work-piece is moved along the axis (i.e., X axis in Figure 1), the surface will be milled
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36 17 continuously, generating a continuous distribution of craters on the surface. The microscale
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38 18 craters generated on the surface of work-pieces are normally regarded as defects which
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40 19 degrade the machining accuracy,²⁰⁻²⁴ but they could be beneficial as a suitable substrate for a
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42 20 superhydrophobic coating. Recently, Chu *et al* achieved the fabrication of hydrophobic
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44 21 surfaces on the stainless steel^{20, 21} and aluminum alloy²² by designing special microscale
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46 22 grooves and then machined using wire EDM. Nevertheless, the machined surfaces exhibited
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48 23 non-uniform wettability with anisotropic properties in the parallel and perpendicular groove
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50 24 directions.²⁰⁻²² King *et al* realized a superhydrophobic surface on the steel by fabrication of
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52 25 micro-mushroom re-entrant structures using EDM.²³ Although the complex designs and
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54 26 machining were adopted, these attempts show a non-ideal performance in
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3 1 superhydrophobicity.²⁰⁻²³ Meanwhile, they have limited abilities for the large-scale
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5 2 manufacturing with robust surfaces especially on the curved surfaces.

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7 3 Here, we present a new roll-to-roll strategy to manufacture large-scale, durable and robust
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9 4 superhydrophobic surfaces on many conventional engineering materials. This is realized by
10
11 5 combining EDM, coating of carbon nanoparticles, and most importantly, oil penetration and
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13 6 drying. The superhydrophobic properties were evidenced by the static water contact angle of
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15 7 $170\pm 2^\circ$ and slide angle of $3\pm 1^\circ$ (Advancing/Receding angle $172\pm 1^\circ/169\pm 2^\circ$). The developed
16
17 8 superhydrophobic coating surface shows good resilience and maintains its performance after
18
19 9 tested in various harsh conditions including water flushing for several days, sand abrasion,
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21 10 scratching with sandpapers and corrosive solution. Our coatings can be used in many areas
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23 11 which are required for self-cleaning applications even after contaminated with oils.
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29 13 **RESULTS AND DISCUSSION**

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31 14 Figure 1 schematically illustrates our strategy for roll-to-roll manufacturing of the
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33 15 superhydrophobic coating on conventional engineering materials. It includes three steps: (I)
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35 16 The work-piece is firstly milled by EDM process to create microscale structures on its
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37 17 surface; (II) The surface is then coated with a layer of carbon nanoparticles by the burning
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39 18 flame of butane to form a superhydrophobic layer; (III) Droplets of penetrating oil is dropped
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41 19 onto the carbon coated surface and then heat-treated, thus transforming the fragile
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43 20 superhydrophobic surface into a durable and robust one.

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46 21 As mentioned above, EDM process will generate a continuous random distribution of
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48 22 microscale craters on the surface (Figure 1, Figure 2a and Movie S1), which could be used as
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50 23 a platform for superhydrophobic coating. The air was entrapped inside the craters underneath
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52 24 the water droplets, leading to an increase CAs from $66\pm 2^\circ$ to $95\pm 2^\circ$ (Figure S2a, b), thus
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54 25 realizing hydrophobicity and water repellency. Thereafter, the superhydrophobic layer was
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56 26 realized by putting the EDM-milled surface facing the outer burning flame of the butane with

1 a distance of 3–5 cm, and then a layer of carbon nanoparticles (i.e. soots) was deposited on
2 the milled surface as illustrated in Figure 1, Figure 2e and Movie S1. It can be seen that the
3 color of the sample surface was changed from luminous yellow (e.g. EDM milled copper
4 surface) to dark black (see Movie S1).^{25, 26} After the flame deposition, the CA values were
5 found to increase from $95\pm 2^\circ$ to $168\pm 2^\circ$ (Figure S2b, c), indicating the formation of a
6 superhydrophobic coating on the surface of work-piece. However, these carbon nanoparticles
7 have been proved very fragile since the interactions among carbon nanoparticles are only
8 physical ones and relatively weak.^{25, 26} When the water drop rolled off on the surface, it
9 carried away some of the soot (Movie S2) and the drop underwent a wetting transition from
10 $168\pm 2^\circ$ to $136\pm 5^\circ$. Obviously, it was impossible for the surfaces to withstand the harsh
11 conditions such as flushing of water and provide a long-term and high performance of water-
12 repellency. In order to improve the stability of the surface, the penetrating oils such as
13 kerosene were sprayed onto the coated carbon layer, and then heat-treated at 310°C for 3–5
14 minutes. The durability of the superhydrophobic coating was found to be improved
15 significantly and the CA can be further increased to $170\pm 2^\circ$ (Figure S2d). The values of
16 advancing and receding contact angle are summarized in Table S1.

17 As mentioned above, the superhydrophobic surface could be achieved by both modifying
18 surface structures and decreasing the surface energy. We systematically investigated the
19 morphology of each step to evaluate the hierarchical structures of coating. Figure 2b shows a
20 typical scanning electron microscope (SEM) image of EDM milled copper surface with
21 randomly distributed craters. An enlarged SEM image (Figure 2c) shows a smooth surface
22 within craters and a few nanoscale clusters deposited at the bottom of the craters (Figure 2d).
23 The average lateral diameter and depth of craters are in the range of 10–20 μm and 1.3–2.5
24 μm , respectively, at an EDM discharge current of 1.75 A, leading to an average roughness of
25 1.36 μm (value of R_a , see Figures S3 and S4). The structural size of craters can be facilely
26 controlled by varying the discharge current at a given voltage (Figures S3 and S4). Therefore,

1 the surface roughness can be controlled to achieve the optimal superhydrophobic condition
2 (Figure S5).

3 The burning flame of butane provides a layer of carbon soots to the sample surfaces
4 with, which in principle does not change morphology of EDM milled surfaces at microscale
5 (Figure 2f), but will partially fill the inner spaces of craters with numerous carbon
6 nanoparticles (Figure 2g,h). Herein, a strong synergistic effect of hierarchical structures from
7 microscale craters and nanoscale carbon soots leads to an improved superhydrophobicity with
8 CA values of $168\pm 2^\circ$ and SA values of $4\pm 1^\circ$ (Advancing/Receding angle $170\pm 1^\circ/166\pm 2^\circ$),
9 respectively (Figure S2c). The penetration and drying processes of penetrating oil (kerosene
10 used in this study shown in Figure 2i) create more nanoscale convex structures on carbon
11 soots (Figure 2k, l) during the shrinking and drying of kerosene without noticeably
12 influencing the microscale craters (Figure 2k, l). The water-repellency has also been
13 improved and the obtained average CA values are $170\pm 2^\circ$ and SA values of $3\pm 1^\circ$
14 (Advancing/Receding angle $172\pm 1^\circ/169\pm 2^\circ$) (Figure S2d, Figure S5, and Movie S3). The
15 randomly distributed carbon nanoparticles are clustered together under the driving force of the
16 capillary force, which is generated during the evaporation and drying stage of the kerosene.

17 To identify the functionality of the craters, a smooth surface of C17200 was machined by
18 using the conventional turning and milling, respectively. Both of surfaces show a smaller
19 roughness (Ra 0.8) compared with the EDM milled surface (Ra 1.36, Figure S6). After the
20 same flame deposition and kerosene penetration and drying process, the CAs and SAs on the
21 turning surfaces are only $150\pm 2^\circ$ and $7\pm 3^\circ$ (Figure S6d inset), while they are $147\pm 2^\circ$ and
22 $10\pm 4^\circ$ on the milling surface (Figure S6g inset), respectively. Obviously, both of smooth
23 surfaces exhibit a worse superhydrophobicity. Therefore, the rough surface with a microscale
24 structures is better in this case as the platform for superhydrophobic coating.

25 In order to verify the chemistry changes on the sample surfaces, we have investigated the
26 crystalline structures and chemical states on the sample surfaces after each key process. X-ray

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3 1 diffraction (XRD) pattern (Figure 3a) shows that there are two broad and weak peaks around
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5 2 2 θ =24.3° and 43.2° corresponding to the (002) and (100) planes of typical turbostratic
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7 3 graphite, indicating that the disordered carbon structures were formed during the EDM
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9 4 milling (Figure 3a black curve). These structures were reported to appear in the EDM process
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11 5 by using the kerosene as electrolyte.²⁷ After the flame deposition of soot and penetration and
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13 6 drying of kerosene, the two diffraction peaks became sharpened with increased intensity
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15 7 revealing the formation of graphite crystals (Figure 3a blue and red curve). The newly
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17 8 observed diffraction peak at 17.9° could be assigned to C60 formed during drying of kerosene
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19 9 in air, which is consistent with those reported in literatures.²⁸⁻³⁰ No other new diffraction
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21 10 peaks were observed, indicating that there was no new chemical compound formed during the
22
23 11 later process. Furthermore, transmission electron microscope (TEM) image of flame
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25 12 deposited soot shows agglomerated particles which are spherical with diameters in the range
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27 13 of 20–50 nm (Figure S7a). High resolution TEM image displays the solid spherical
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29 14 morphologies with turbostratic structure in atomic lattice (Figure S7b), which is consistent
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31 15 with the XRD results shown in Figure 3a. After kerosene penetration and drying, the
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33 16 interplanar spacing is the same as before (Figure S7c, d). It is about 0.365 nm for both
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35 17 samples (Figure S7b, d), which is similar to the XRD results in Figure 3a. Raman spectra
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37 18 (Figure 3b) shows only two clear peaks centered at ~1340 cm⁻¹ (D peak) and ~1580 cm⁻¹ (G
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39 19 peak) in all the steps, which are assigned to turbostratic graphite characters of coating.²⁹ No
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41 20 apparent peak shift indicates that there are no changes in the vibration modes and chemical
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43 21 bonds or coating stress. High-resolution XPS C1s spectra (Figure 3c) reveal typical carbon
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45 22 structures hybridized with planar hexagonal graphitic rings of sp² (normalized at 284.5 eV)
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47 23 and tetrahedral structure of sp³ (285.6±0.3 eV).³¹ The other peaks at 288.8±1.1 eV (Figure 3c
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49 24 blue curve) and 286.4 eV (Figure 3c red curve) are assigned to C=O and C–O, respectively,
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51 25 which are mainly from oxidation of carbon during flame based soot deposition and kerosene
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53 26 drying process, as well as surface adsorption. It is noteworthy to point out that the absence of
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1 carbon–copper bond indicates that only physical adsorption of carbon happens on the surface.
2 All the spectra in Figure 3 reveal that only a layer of carbon coating on the treated surface
3 without other apparent carbon based chemical bonds detected. Therefore, the impressive
4 superhydrophobicity and water repellency can be solely attributed to the formation of micro–
5 /nano– structures.

6 To highlight advantages of our method, we have compared the CA values of our
7 achievements with the related results reported in the literatures (Figure S8).^{20-23, 25, 26, 32-34} The
8 CA values of carbon coatings on smooth surfaces (i.e., silicon wafer and glass slide) were
9 found to be in the range of 145–160°, whereas they were found to be 154–162° on the EDM
10 milled surface without further treatment. Obviously, the synergistic effect of micro craters and
11 carbon nanoparticles in our method promotes the water–repellency ability to its maximum,
12 showing the merits of our strategy.

13 Since the EDM is a powerful technology to control the morphology of milled surface, the
14 superhydrophobic features can be facilely modified (Figures S3-S5). For instance, applying a
15 higher discharge current in the EDM process provides much higher energy in one pulse,
16 leading to much more materials to be removed in the unit time. Thus, larger sizes of craters
17 with higher roughness can be achieved on the samples discharged (Figures S3 and S4). In
18 addition, since the EDM method has a capacity of machining all types of metallic materials,
19 we have successfully obtained superhydrophobic coatings on various conventional
20 engineering materials as shown in Figure 1 bottom left. Therefore, based on the integration of
21 industry–scale processes of EDM technology, flame deposition and penetration and drying of
22 oil, we have developed a facile and scalable roll–to–roll compatible approach to create
23 superhydrophobic coating on conventional engineering materials.

24 The poor surface robustness is the main issue limiting the widespread industrial
25 applications of most currently developed superhydrophobic coatings, since the commonly
26 used chemical modification and nanoscale structures are frequently mechanically weak and

1 readily abraded/damaged.³⁵ Our newly designed superhydrophobic surface shows good
2 resilience and maintains its performance after various harsh tests including several days of
3 water flushing, sand abrasion and sandpapers scratching (Figure S9). For example,
4 impingement the coating surfaces using water droplets with a diameter of 2.6 ± 0.3 mm and a
5 velocity of 1.4 m s⁻¹ (the velocity is equal to those in a vernal rain) did not cause apparent
6 damage of the water-repellency ability for at least 7 days, whereas the superhydrophobic
7 surface lasted at least 3 days with a good performance when the impingement velocity was
8 increased to 2 m s⁻¹ (Figure S9a and Movie S4). This shows a significantly improved
9 durability compared with those reported in the literature using the carbon nanoparticles coated
10 with SiO₂ substrates³⁶ or sprayed TiO₂ nanoparticles³⁷ as well as carbon soot coated on
11 smooth plate.^{32, 33, 38, 39}

12 Sand impinging was also used to test the mechanical durability of our developed
13 superhydrophobic surfaces, using the sand particles with an average diameter of 300–500 μm
14 and an impinging velocity of 2.5–3.0 m s⁻¹ corresponding to an impinging energy of
15 $1.4\sim 6.9\times 10^{-7}$ J (Figure S9b). This similar impinging condition was used in ref. 26 which was
16 reported to heavily damage the superhydrophobic surface.²⁶ Nevertheless, our newly
17 developed coating still rendered a good water-repellency properties and the superhydrophobic
18 coating still showed a high CA of 160° after 40 g sands impinging at the same position
19 (Figure S9c). Another 10–20 g sands were needed to damage the superhydrophobicity of the
20 beneath coating at the same position, which led to the significant decreases of the CA below
21 150°.

22 We also performed sandpaper abrasion tests with coated surface faced-down to sandpaper
23 (Grit No. 1000) under a normal weight of 50 g (i.e., estimated normal pressure of 1.357 kPa)
24 and then moved the coated surfaces on the sandpaper with a reciprocating speed of 18–25 mm
25 s⁻¹ (Figure S9d). The CA values were measured after each 100 mm long abrasion distance and
26 the results are summarized in Figure 4a. The CA values were kept in the range of 150°–172°

1 with a 1200 mm long abrasion, indicating a robust superhydrophobic coating without
2 significant damages under the tested mechanical abrasion. Meanwhile, the SA values were
3 measured to be below $\sim 10^\circ$ within 300 mm abrasion distance, but the values were found to
4 increase with the increase of the abrasion distance (Figure 4a). Obviously, there are two
5 stages of hydrophobic modes within the 1200 mm sandpaper abrasion distance, which would
6 be discussed in future. Furthermore, a scotch tap test was proceed to evaluate the adhesion
7 performance of the as-prepared superhydrophobic coatings.^{40, 41} Figure S10 shows a gradually
8 decrease of CA value from 172° to 155° within six peeling attempts on the oil penetration and
9 drying coatings, while it rapidly decreases at the second peeling attempt on the flame
10 deposition soot. As a result, as-prepared superhydrophobic coating has a relative strong
11 adherence between the substrate and coating.

12 To reveal the corrosive properties of as-prepared superhydrophobic coatings, they were
13 investigated by the potentiodynamic polarization curves (Tafel) and electrochemical
14 impedance spectroscopy (EIS) in the 3.5 wt% NaCl solution at room temperature. Figure 4b
15 shows the Tafel curves of the C17200 surface at each state during the superhydrophobic
16 coating. The values of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were
17 obtained by Tafel extrapolation from the potentiodynamic polarization curves.^{42, 43} The details
18 of Tafel polarisation curves are summarized in Table S2. Therefore, the inhibition efficiency
19 (η_{IE}) corresponding to the corrosion resistance property can be calculated by,^{44, 45}

$$20 \quad \eta_{IE} = \frac{i_0 - i_{corr}}{i_0} \times 100\% \quad (1)$$

21 Where i_0 and i_{corr} are the current density collected from the original C17200 surface and as-
22 prepared superhydrophobic surface, respectively. The E_{corr} of the surface after penetration and
23 drying process can reach 28 mV, which is quite more positive than the original surface (-81
24 mV), EDM milled surface (-83 mV) and Flame deposition soot surface(-27 mV). The i_{corr} of
25 the surface lows to 6.31×10^{-8} A cm^{-2} which is decreased by more than 4 order magnificent

1 compared to that of the original surface ($3.47 \times 10^{-4} \text{ A cm}^{-2}$). Meanwhile, as-prepared
2 superhydrophobic surface shows the largest η , about 10 times compared to EDM milled
3 surface, indicating an achievement of good anticorrosion protection with coating.

4 Furthermore, EIS tests were carried out to evaluate the electrochemical corrosion behaviors
5 and anticorrosion of as-prepared superhydrophobic coatings. Figure 4c and d shows the
6 Nyquist plots and Bode plots of the C17200 sample at each process. The diameter of the
7 impedance semicircle represents the polarization resistance of the work electrode (i.e.,
8 C17200 sample at each stage). Significantly, it increases sharply approaching to a hundred of
9 $\text{k}\Omega \cdot \text{cm}^2$ after oil penetration and drying process (Figure 4c), which is about 400 times
10 compared to the original and after EDM milled material. Figure 4d shows the Bode plots
11 (impedance modulus $|Z|$ as a function of frequency) of the four samples in 3.5 wt % NaCl
12 solution. As-prepared superhydrophobic surface has the highest impedance value around 150
13 $\text{k}\Omega \cdot \text{cm}^2$, which is 2 orders of magnitude larger than that of original surface or EDM milled,
14 and 1 orders of magnitude larger than that of flame deposition soot in the low frequency
15 region. According to EIS tests, as-prepared superhydrophobic coating provides excellent
16 corrosion protection for bare C17200 substrate.

17 To reveal the potential application in the highly saline environment,⁴⁶ we have compared
18 the long-term stability of superhydrophobic surface before and after penetration and drying
19 process in the 3.5 wt% NaCl solution. After penetration and drying process, the
20 superhydrophobic coating exhibits a promising stability up to 39 hours, while it merely lasts
21 ~ 3 hours without further process (Figure S11a). The loose carbon soots and low adhesion to
22 substrate after the flame deposition was easily damaged by the corrosive solution, resulting in
23 decreasing ability of water repellency. Further oil penetration and drying process will dense
24 the carbon soots and improve the adhesion to the substrate, leading to an enhancement of
25 stability up to 39 hours. Figure S11b shows a digital picture of two piece of C17200 samples
26 immersing in corrosive solution. The bright surface after 3 hours corrosion suggests the air

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3 1 can be still trapped on the substrate and form the air film between the as-prepared
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5 2 superhydrophobic surface and solution.⁴¹ The EDM milled surface only with flame deposition
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7 3 became dark green after 39 hours corrosion (Figure S11c), indicating a heavy peeling off
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9 4 carbon soot from the substrate, while the oil-treated surface was keeping bright color.

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12 5 The coated surface shows good self-cleaning properties from the bouncing-water and
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14 6 continuous flushing droplets. Herein, cupric chloride hydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) powder as the
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16 7 artificial dirt was deliberately spread onto the coated surface (Figure 5a), and then collected
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18 8 and carried away by the rolling off droplet and left a cleaning line along its flow trajectory
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20 9 (Figure 5b). The final color of the rolling droplet becomes light green, indicating the effective
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22 10 removal of dirt. This change can be explained by the droplet's picking up the dirt during its
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24 11 rolling on the surface (Figure 5e). Usually, the superhydrophobic coatings are very fragile to
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26 12 oil contamination, losing their self-cleaning properties.⁴⁷ However, our superhydrophobic
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28 13 surface has already been pretreated with oil during preparation (Figure 1, step III), and further
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30 14 oil contaminants during service would not degrade its self-cleaning ability. Figure 5c,d show
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32 15 the rolling off of water droplets on the oil contaminated coatings, and the dirt was removed
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34 16 along the trajectory although the droplet was not a perfect sphere due to wettability of oil
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36 17 contaminants (Figure 5d). The principle can be explained using Figure 5f, which is similar to
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38 18 those for the slippery liquid infused porous surfaces.^{48, 49}

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42 19 The mechanism of enhanced water repellency can be explained by the thermodynamic
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44 20 formula.⁵⁰ Figure S12a and b show a typical SEM image of the EDM milled C17200 surface
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46 21 after the flame deposition and oil penetration and drying process, respectively. Many
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48 22 protrusions were formed between the adjacent craters after EDM milled. Figure S12c shows a
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50 23 model of cross section of the protrusions shown in Figure S12a, in which the outline of
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52 24 protrusion is smaller than a semicircle ($\alpha < \pi/2$). According to Ref. 50, the water droplets tends
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54 25 to be a homogeneous wetting as $\alpha < \pi/2$. Therefore, the contact angle can be expressed as:

$$\cos \theta = \begin{cases} r \cos \theta_p & r \cos \theta_p \geq -1 \\ -1 & \text{otherwise} \end{cases}$$

(2)

where r and θ_p represents the roughness ratio and represents the contact angle of carbon particles deposited on a plane, respectively. After oil penetration and drying process, the thickness of carbon soot reduced to $\sim 1/4$ of its original thickness (Figure 6d, e), leading to the outline of protrusion bigger than a semicircle ($\alpha > \pi/2$) shown in Figure S12d. In this condition, the contact angle can be expressed as

$$\cos \theta = (\pi - \theta_p) \cos \theta_p + \sin \theta_p - 1 \quad (3)$$

Since the θ_p was in the range of $145\text{--}160^\circ$,^{25,26,32-34} the CAs were calculated to be in the $157.9\text{--}170.4^\circ$ by Eq (3). In our experiments, the CAs of as-prepared superhydrophobic coatings were $170 \pm 2^\circ$, which are consistent with the theoretical values ($157.9\text{--}170.4^\circ$).

The enhancement of durability of superhydrophobic coating could be explained by improved adhesion among carbon nanoparticles and improved adhesion to the substrate by the clustering of carbon nanoparticles during the penetration and drying processes. Figure 6a-c illustrate the mechanism induced by the morphology change of carbon nanoparticles. The porous structure (Figure 6a, d, g) and intrinsic oil wetting properties of deposited carbon soots make the kerosene fully penetrating into the carbon layer (Figure 6a). At the drying stage, carbon nanoparticles are subjected to capillary forces at the liquid-gas-solid interfaces (Figure 6b). The capillary pressure (Δp) between two sphere particles on the liquid-solid interface is given by Laplace's formula:⁵¹

$$\Delta p = \gamma \left(\frac{1}{R_1} - \frac{1}{R_2} \right) \quad (4)$$

where R_1 and R_2 are the principal radii of the external curvature of the bridge surface, and γ is the surface tension between the kerosene-air interface.

1 For a cylindrical capillary of radius R and liquid on a substrate with a wetting angle θ , the
2 pressure, Δp , can be rewritten by:

$$\Delta p = \frac{2\gamma \cos \theta}{R} \quad (5)$$

3
4 As the wetting liquid (e.g. kerosene) occupies a position with the highest capillary
5 potential, it carries the carbon nanoparticles to coalescence together spontaneously thereby
6 forming capillary pores (Figure 6b). During the drying process, the moving kerosene tends to
7 occupy those positions who can ensure the minimum energy of whole system. Therefore, a lot
8 of meniscuses are formed among the carbon nanoparticles, pulling or pushing apart the
9 neighbouring particles (Figure 6b). The magnitude of capillary forces depends on the size of
10 meniscus (R) and different amplitudes of stresses are generated which cause the cluster of
11 particles as shown in Figure 6f. Obviously, there is a continuous increase of capillary pressure
12 during the evaporation of kerosene (Figure 6f), which makes the soot layer become denser
13 (Figure 6c, h). The clustered of carbon nanoparticles will significantly reduce the thickness of
14 carbon soot (e.g. from 17 μm to 4 μm , Figure 6d, e), densify the soot layer, and improve its
15 adhesion to the substrate (Movie S5). Enlarged cross-section SEM images of carbon
16 nanoparticles in Figure 6d, e show the dense film after dried. As a result, the elastic modulus
17 of the carbon layer was increased from 0.387 GPa to 0.916 GPa measured from
18 nanoindentation before and after kerosene penetration and drying process (Figure 6i). In
19 addition, the protrusion between the adjacent craters will protect the carbon nanoparticles
20 within them from carrying out by the drop water or mechanical abrasion (Figure S13). The
21 carbon nanoparticles in the protrusion areas (Figure S13, marked with red circles, area A)
22 were removed by the scratching or impinging, while they kept the same within the craters
23 (Figure S13 marked with yellow circles, area B). Thus, the superhydrophobicity did not
24 change dramatically as the abrasion going on. The densification of carbon nanoparticles and
25 increased elastic modulus will enhance the resistance of external mechanical damage such as

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3 1 water flushing, sand abrasion and scratching thereby enhancing the stability of
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5 2 superhydrophobic coatings.^{52, 53}

3 **CONCLUSION**

4 We presented a roll-to-roll manufacturing strategy for durable and robust superhydrophobic
5 surfaces on conventional engineering materials by combining EDM, carbon nanoparticle
6 deposition and oil penetration and drying process. The controlled microscale craters on EDM
7 surface provide an ideal platform for deposition of carbon nanoparticles to form a hierarchical
8 micro-/nano- structures, which showed quite good water-repellency and superhydrophobicity
9 with an CA up to $170\pm 2^\circ$ and SA values of $3\pm 1^\circ$ (Advancing/Receding angle $172\pm 1^\circ/169\pm 2^\circ$).

10 The oil penetration and drying process densified the carbon layer and increases the strength
11 by ~ 3 times, thereby providing the good durability under the harsh water flushing, mechanical
12 abrasion and corrosion testing. Furthermore, the superhydrophobic coatings also showed a
13 high efficiency of self-cleaning properties even after oil-contamination during applications.

14 **EXPERIMENTAL SECTION**

15 ***Roll-to-roll superhydrophobic coating of engineering materials.*** In the experiments,
16 foils/plates of various engineering materials (typical thickness of 50 μm), including beryllium
17 copper alloy (C17200), titanium alloy (Ti-6Al-4V), stainless steel (06Cr19Ni10), aluminum
18 alloy (Al2024), Ni-based superalloy (GH4169), were purchased from DongGuan Jia Sheng
19 Copper Co., Ltd, China, and then ultrasonically cleaned in ethanol and deionized water before
20 used in the EDM machining. A bulk of copper (99.9% purity) with length of 10 mm and
21 width of 25 mm was used as the tool electrode. The foil was programmed to move by a feed
22 roller and generated a machined track at a speed of 0.24–0.5 mm s^{-1} (Figure 1 and Movie S1).
23 The typical materials removal rate was about 18–31 $\text{mm}^3 \text{min}^{-1}$. During the process, an EDM
24 milling was firstly carried out with a commercial EDM machine,⁵⁴ and the tool electrode
25 (cathode) and a work-piece (anode) were immersed in the kerosene (dielectric work solution,
26 EDM-3, Mobil, SUA). After ultrasonically cleaning, the milled surface was faced vertically

1 to the flame of butane with a distance of 3–5 mm from outside flame. With a butane
2 consuming rate of 1.5 sccm (standard–state cubic centimeter per minute), a black carbon layer
3 has been deposited onto the milled metal surfaces. Finally, the penetrating oil such as
4 kerosene was dropped onto the carbon layer at a rate of about 1–5 $\mu\text{L s}^{-1}$ and then heated to
5 310 °C in air for 3–5 min to evaporate the kerosene (Figure 1 and Movie S1).

6 **Characterization.** The surface treated foils were cut into pieces with dimensions of 12×25
7 mm² for the characterization. The morphology of the specimens was analyzed using a
8 scanning electron microscope (SEM, Supra 55 Sapphire, Carl Zeiss, Germany) at an
9 acceleration voltage of 10 kV and a transmission electron microscopy (TEM, JEM–2100F,
10 JEOL, Japan) at an acceleration voltage of 200 kV. The 3D morphology and corresponding
11 profile curves were characterized using a laser confocal microscope (OLS3000, Olympus,
12 Japan). XRD patterns of the samples were analyzed using X–ray diffractometer (XRD,
13 Empyrean, Panalytical, Netherlands) with Cu K α 1 $\lambda=0.154$ nm. Chemical states of elements
14 were analyzed using X–ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo
15 Fisher Scientific, USA). Raman spectroscopy (LabRAM XploRA, incident power of ~1 mW,
16 pumping wavelength of 532 nm) was used to obtain the lattice vibration and chemical
17 bonding information. Elastic moduli of as–coated and oil treated carbon layers on substrate
18 were measured using nanoindentation (Nano–indenter G200, Agilent, USA). The indentation
19 force–displacement curves were analyzed by a method outlined by Domke to calculate each
20 elastic modulus.⁵⁵ Water static contact angle (CA), and sliding angle (SA) were measured
21 using an optical contact angle meter system (JC2000C1, Shanghai Zhongchen Digital Technic
22 Apparatus Co., Ltd. China) in air at room temperature. A droplet of 5 μL water was used in
23 each test and five different readings at different areas on the surface of specimens were
24 measured to obtain an average value. The static contact angle was calculated using the
25 Young–Laplace method.^{56, 57} In this paper, CA and SA refer to water static contact angle and
26 water sliding angle in the paper respectively, unless specifically noted.

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3 1 ***Mechanical and corrosion durability tests of superhydrophobic coatings.*** The durability of
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5 2 the as-prepared superhydrophobic surface resistance to impinging of water drops was tested
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7 3 with the water drops fall down to the coating from 100 mm (velocity of 1.4 m s^{-1}) and 210
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9 4 mm (velocity of 2 m s^{-1}) height. The substrate was fixed with a titling angle of 45° to ground
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11 5 (Figure S9a). The diameter of the water drops was about $2.6 \pm 0.3 \text{ mm}$. The time interval
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13 6 between two water drops was about 0.5–0.8 s. In addition, sandpaper abrasion and sand
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15 7 impinging tests were employed to evaluate the mechanical durability. The coated surface was
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17 8 faced down to sandpaper (Grit No. 1000) with a normal weight of 50 g (i.e., estimated normal
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19 9 pressure of 1.357 kPa) and moved at a reciprocating speed of $18\text{--}25 \text{ mm s}^{-1}$ (Figure S9d). The
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21 10 CA values were measured after each 100 mm long abrasion. The sand impinging test was
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23 11 performed using the sand grains with diameter of 300–500 μm and an impinging velocity of
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25 12 $2.5\text{--}3.0 \text{ m s}^{-1}$ corresponding to an impinging energy of $1.4\text{--}6.9 \times 10^{-7} \text{ J}$. The substrate was
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27 13 fixed with a tilting angle of 45° to ground (Figure S9b). According to the ASTM D3359-02
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29 14 standard, the Scotch tape test was carried out to evaluate the adhesion performance of as-
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31 15 prepared superhydrophobic coating. In detail, a piece of tape was firstly pressed against the
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33 16 as-prepared superhydrophobic coating. And then, the contact angle was measured after each
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35 17 peeling attempt. Each of the reported CA represents the average of five measurements at
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37 18 different positions. Electrochemical corrosion behavior was examined by potentiodynamic
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39 19 polarization curves (Tafel) and electrochemical impedance spectroscopy (EIS) in 3.5 wt%
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41 20 NaCl solution at room temperature on the electrochemical workstation (CHI660D, CH
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43 21 Instruments Inc.). The experiments were performed in a three-electrode cell with a graphite
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45 22 electrode as the counter electrode, as-prepared sample as the working electrode, and
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47 23 silver/silver chloride (Ag/AgCl, 3 M KCl) electrode as the reference electrode. Polarisation
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49 24 curves were recorded at a scanning rate of $1 \text{ mV} \cdot \text{s}^{-1}$. EIS experiments were carried out at
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51 25 frequencies ranging from 10^5 to 10^{-2} Hz at open circuit potential with the amplitude of the
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53 26 perturbation voltage of 10 mV. The as-prepared superhydrophobic surface was immersed in
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3 1 3.5 wt% NaCl solution for a long time to reveal the potential application in the highly saline
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5 2 environment. Each test was repeated more than three times to verify the repeatability of the
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7 3 results.
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3 1 **ASSOCIATED CONTENT**

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6 2 **Supporting Information**

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9 3 Supporting information contains: EDM scheme, characteristics, additional graphs, tables and
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11 4 images (Figures S1–S13)

12
13
14 5 Tables (Table S1 and S2)

15
16 6 Video S1-S5 (AVI)

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19 7 **AUTHOR INFORMATION**

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21
22 8 **Corresponding Author**

23
24 9 *wangzl@hit.edu.cn. *guobin@hit.edu.cn. *zhangjia@hit.edu.cn

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26
27 10 **Author Contributions**

28
29 11 J. Z and Z. L. W supervised the project with designing the experiment and analyzing the
30
31 12 results. S. L. D carried out the experiments, characterization, testing. and wrote the draft. X.
32
33 13 L. B and Y. K. W performed some tests. Y. Q. F, P. A. H , B. G and C.T. provided
34
35 14 modifications on the draft. All the authors discussed the results and commented on the
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37 15 manuscript.

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41 16 **Notes**

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Figure Captions

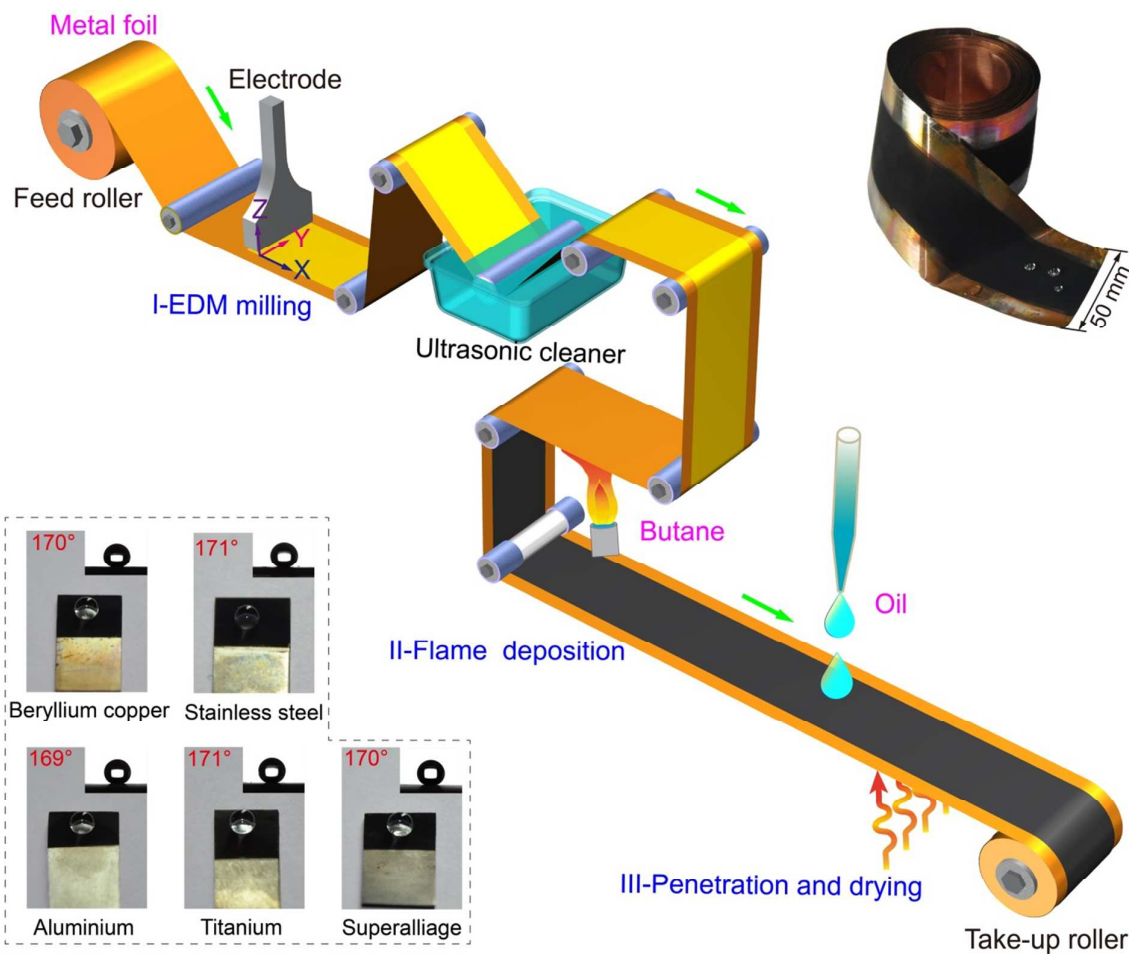


Figure 1. Schematic illustration of roll-to-roll strategy for manufacturing superhydrophobic coating on conventional engineering materials. Step I: Work-piece is milled by EDM process and craters are generated simultaneously. Step II: Milled surface is coated with a layer of soot by the flame of butane. Step III: kerosene penetration and drying the coatings. Inset in bottom left shows superhydrophobic coating on five types of engineering materials with CAs. Inset in top right shows a coils of superhydrophobic coated copper foil (i.e., C17200 beryllium copper alloy).

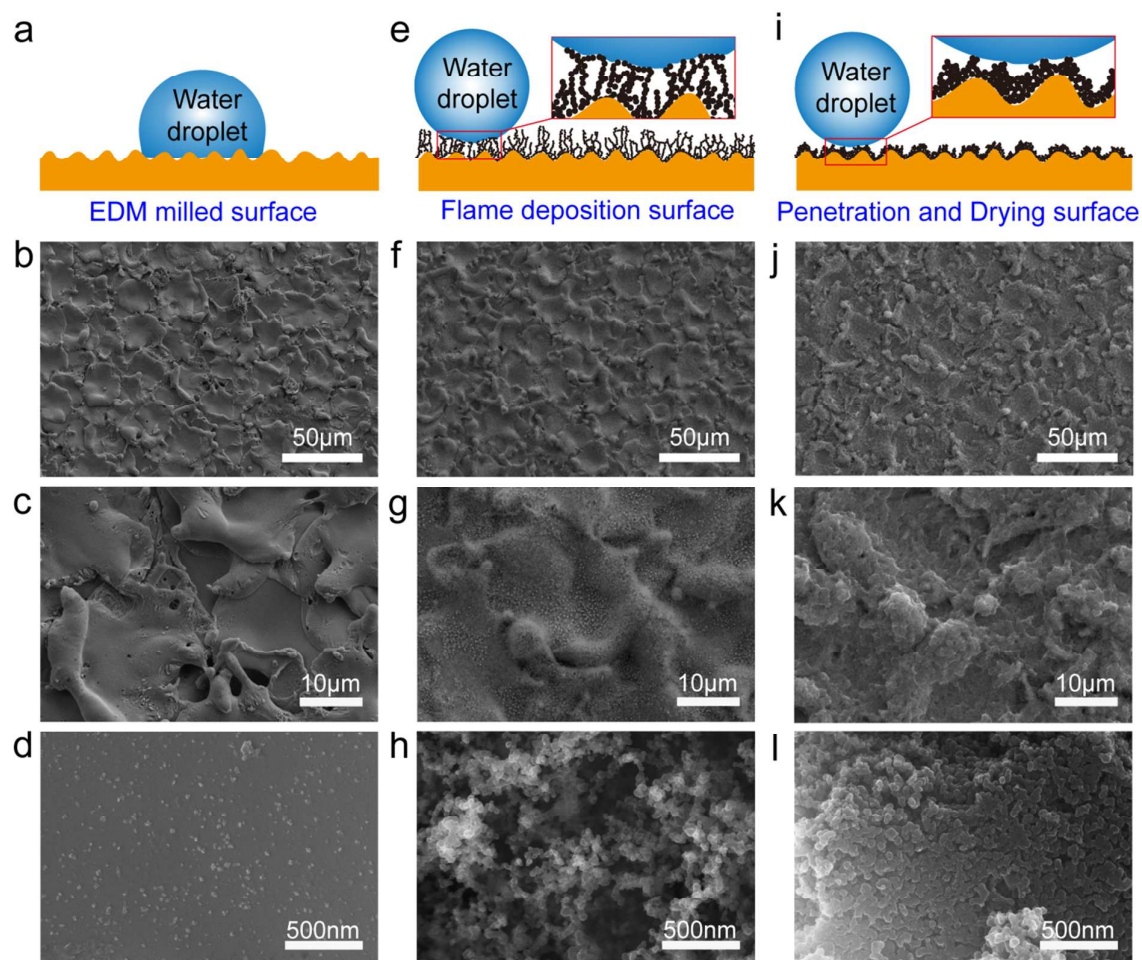


Figure 2. Morphologies evolution of the coating on C17200. (a), (e) and (i) Scheme of morphology of the surface of work-piece during superhydrophobic coating. SEM images of surface morphologies at different magnifications of after EDM milling (b)-(d), flame deposition (f)-(h) and penetration and drying (j)-(l) process.

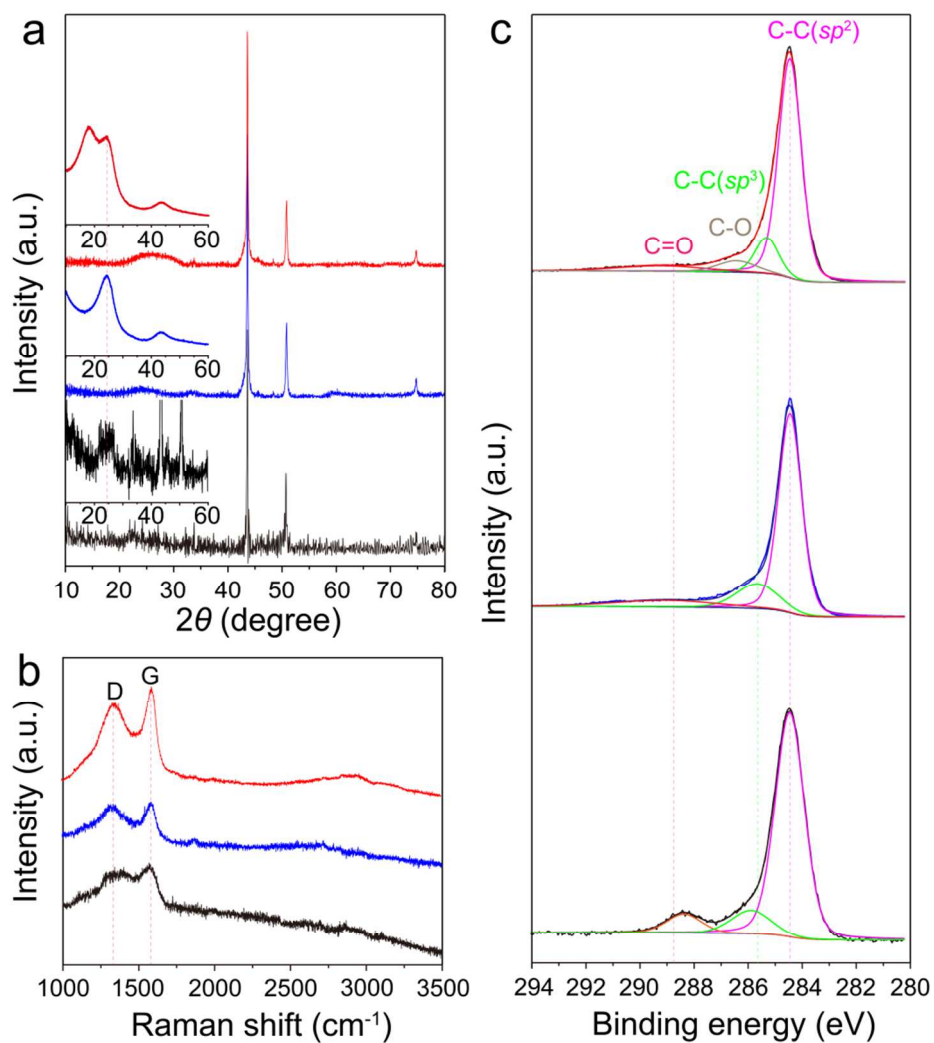


Figure 3. Characterization of chemical structure of superhydrophobic coatings. (a) XRD pattern, (b) Raman spectra and (c) High-resolution XPS scanning of C1s spectra of species after EDM milling (black curve), flame deposition (blue curve) and kerosene penetration drying (red curve), respectively.

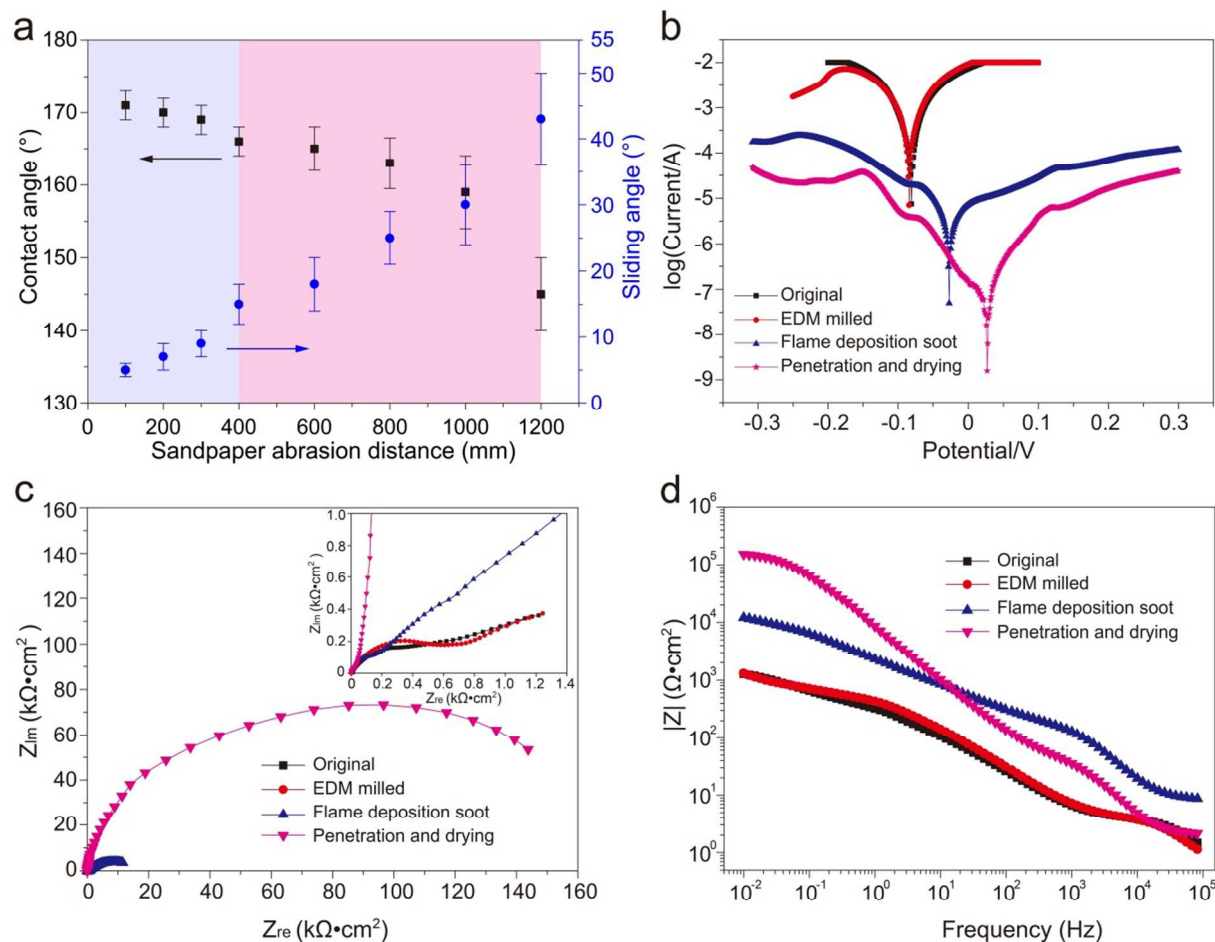


Figure 4. Durability of the superhydrophobic coatings. (a) Plot of mechanical abrasion distance and water contact and sliding angle. (b) Potentiodynamic polarization curves, (c) Nyquist plots and (d) Bode plots of the original beryllium copper alloy (C17200) surface, EDM milled surface, flame deposition soot and oil penetration and drying surface in the neutral solution (3.5 wt% NaCl) for 30 min. The insets figure in (c) is the enlarged scope of Nyquist plots in the high frequency range.

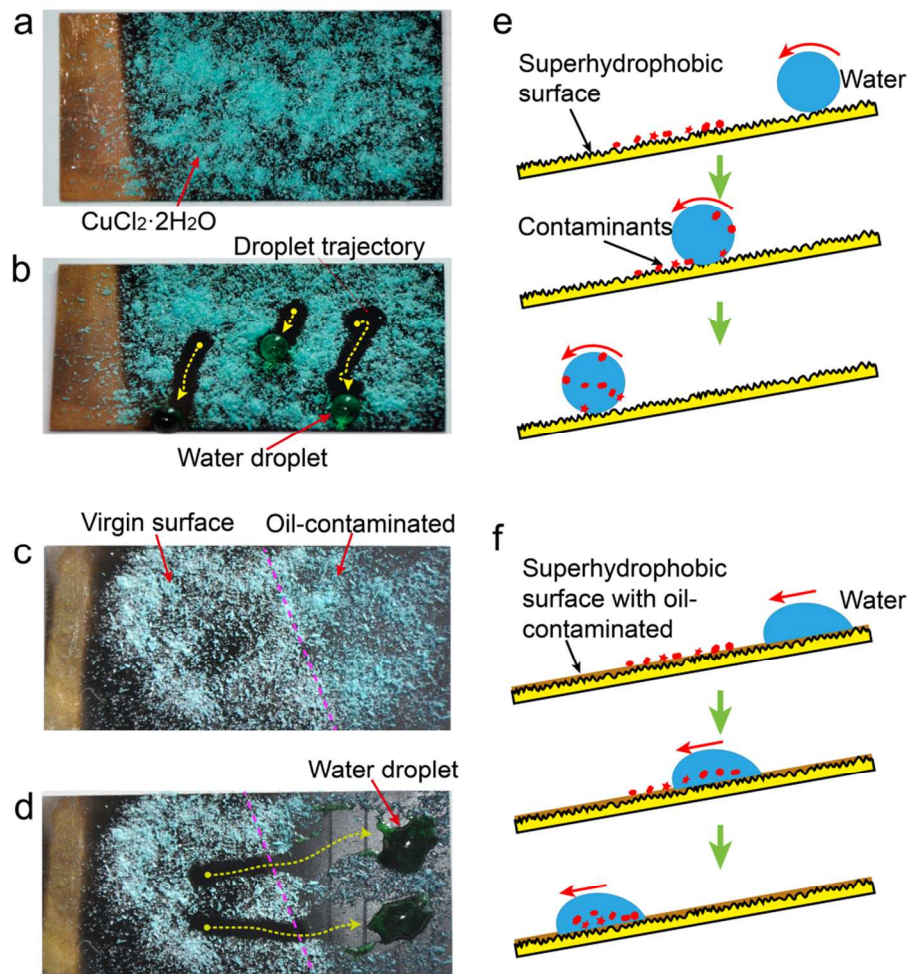


Figure 5. Self-cleaning performance of superhydrophobic coating on C17200. (a) Artificial dirt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) spread on coating surface. (b) Water droplets roll off on coating surface with dirt. (c) Artificial dirt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) spread on coating surface pre-contaminated by oil. (d) Water droplets roll off on coating surface after oil contaminated. (e), (f) Mechanism of self-cleaning process of as-developed superhydrophobic coating and after oil contaminated, respectively.

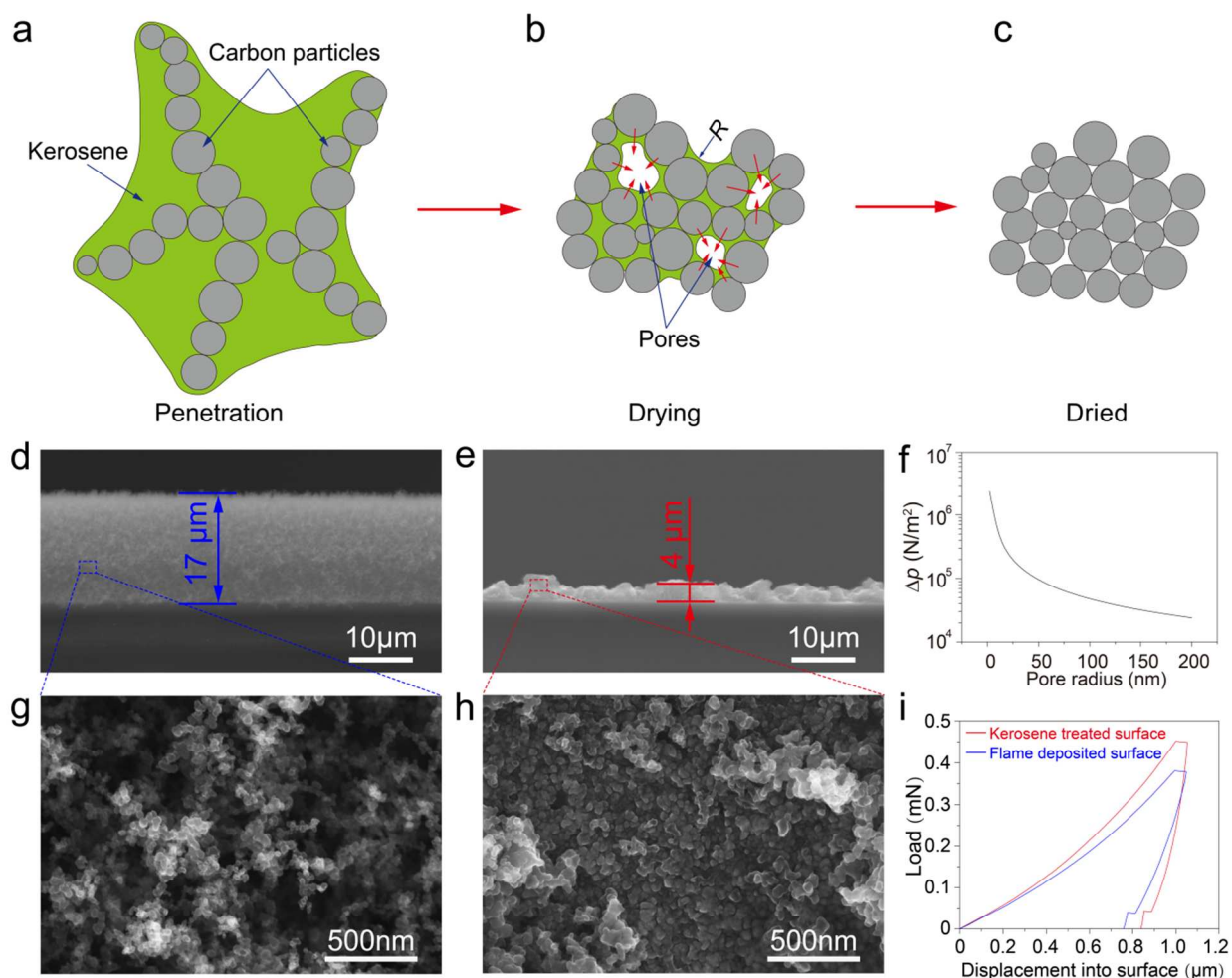
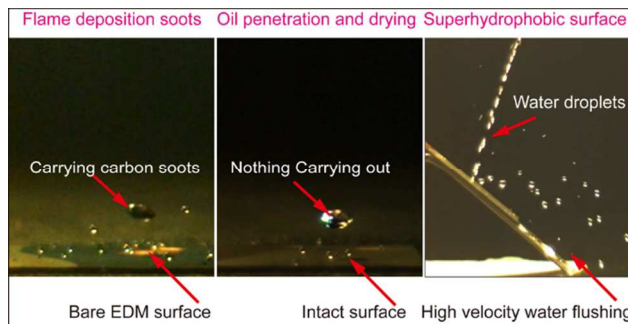


Figure 6. Enhancement of durability of superhydrophobic coatings after kerosene penetration and drying process. (a)-(c) Schematic illustration of penetration and drying process of flame deposited carbon nanoparticles film with kerosene. (d), (e) Cross-section SEM images of flame deposition carbon soot and after kerosene penetration and drying. (f) Capillary pressure (Δp) as a function of pore radius. (g), (h) Enlarged SEM images of (d) and (e) show morphology of carbon soot. (i) Load-displacement curve as the flame deposition film and after kerosene penetration and drying taken from nanoindentation.

Roll-to-Roll Manufacturing of Robust Superhydrophobic Coating on Metallic Engineering Materials

TOC



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