

Supplementary Materials

A superrobust superhydrophobic PSU composite coating with self-cleaning, wear-and corrosion-resistance

Huaiyuan Wang*, Xiguang Zhang, Zhanjian Liu, Yixing Zhu, Shiqi Wu, Yanji Zhu

S1. Modification of MMT Nanoparticles

The MMT nanoparticles modified with PDMS were prepared as follows. First, 5 ml PDMS were added into the 40 ml liquid mixtures of ethyl alcohol, H₂O and KH-550 (18:1:1) and stirred for 30 min at 45°C. To the resulting solution, 1 g MMT were slowly added to be uniformly dispersed in 10 min and airtight stirred for 12 h at 45°C. The prepared particles were separated by filter and washing with ethyl alcohol, therefore, dried at 80°C.

S2. FT-IR and XPS

Fig. S1 presents the FT-IR spectra of pure MMT (a) and the MMT modified with polydimethylsioxane (PDMS) (b). The 1103.46 cm⁻¹ and 471 cm⁻¹ peaks are ascribed to symmetric stretching and bending vibration absorptions of Si-O-Si, respectively. In the spectrum of Fig. 1(b), the band at 2965.18 cm⁻¹ corresponds to the asymmetric C-H stretching, which confirmed the presence of PDMS on MMT particles surface.

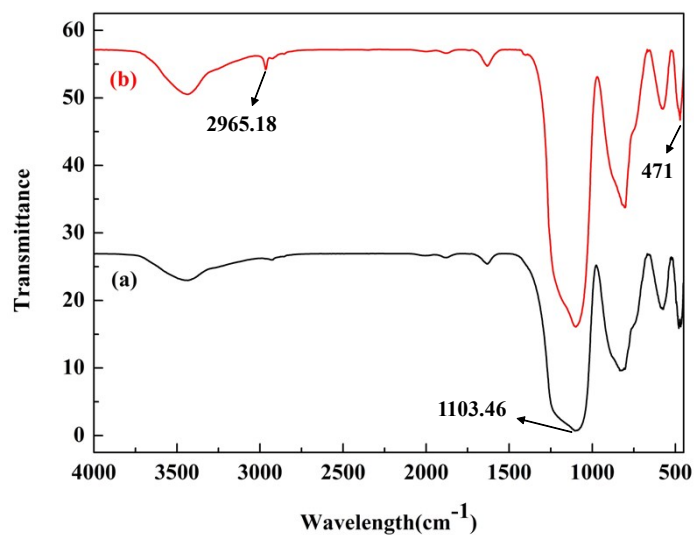


Fig. S1. FT-IR of the prepared pure MMT coating (a) and the MMT modified with PDMS (b)

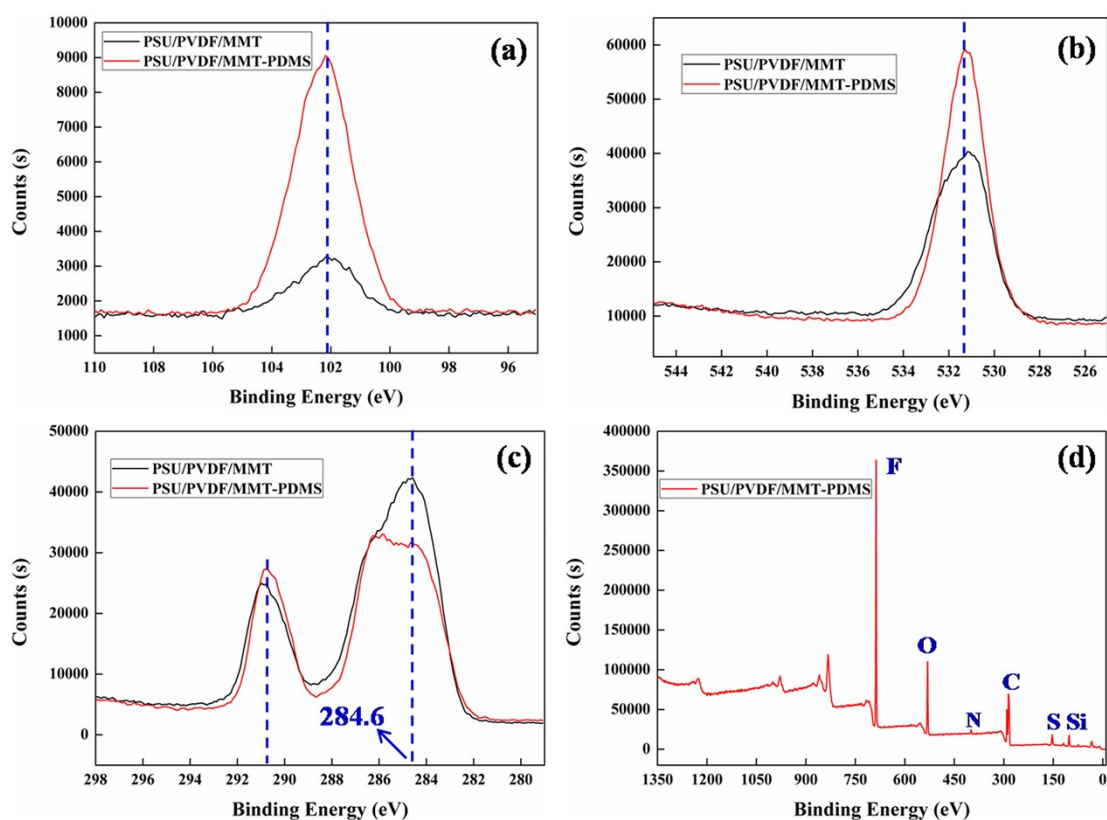


Fig. S2. XPS spectroscopy of Si2p (a), O1s (b) and C1s (c) of the prepared coatings and the XPS full spectroscopy of the superhydrophobic coating (d).

What's more, we have added XPS tests to confirm the reaction between MMT and PDMS. As shown in Fig. S2 (a, b), the elements of silicon and oxygen have been enhanced obviously with the addition of PDMS. Moreover, the C-C bonds (284.6 eV) declined significantly (Fig. S2(c)). It can be mainly attributed to that PDMS replaced the $-C_2H_5$ of KH-550. Thus, the XPS result was further confirmed the presence of the reaction. Furthermore, we can distinctly get the information of the surface chemical composition. As shown in Fig. S2 (d), plenty of F, C, O and a small amount of N, S, Si were emerged on the surface of the fabricated coating. In addition, the auger peaks of F and O were appeared at 833.0 eV and 979.7 eV, respectively.

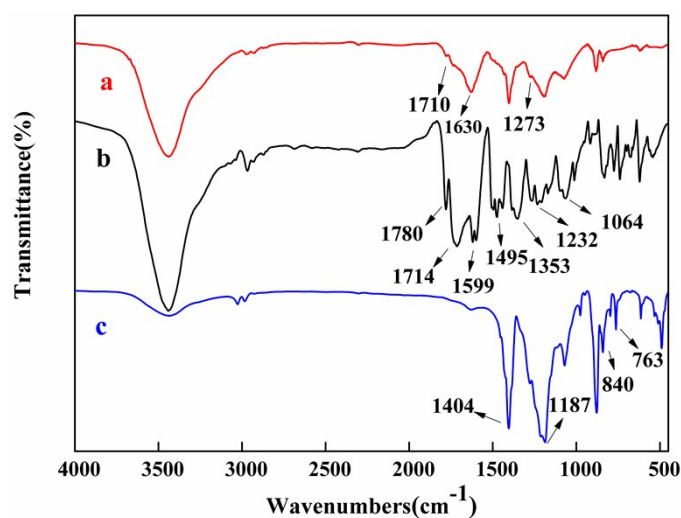


Fig. S3. FT-IR of the prepared PSU/PVDF/MMT-PDMS coating (a), the pure PSU (b) and the pure PVDF (c)

Fig. S3 presents the FT-IR spectra of pure PVDF, pure PSU and the prepared coating. In the spectrum of PSU (Fig. S3b), the bands at 1064

cm^{-1} and 1353 cm^{-1} are ascribed to the symmetrical and the asymmetrical stretching vibration absorptions of $\text{O}=\text{S}=\text{O}$, respectively. The band at 1232 cm^{-1} corresponds the asymmetric C-O-C stretching of aryl ether group. The bands at 1495 cm^{-1} and 1599 cm^{-1} are attributed to the vibration absorptions of benzene ring. Meanwhile, the bands at 1714 cm^{-1} and 1780 cm^{-1} are due to the stretching vibration absorptions of $-\text{COOH}$ group which modified in PSU.

From the spectrum of pure PVDF (Fig. S3c), the absorption peaks at 1187 cm^{-1} and 1404 cm^{-1} are corresponds to the stretching vibration of $-\text{CF}_2$ and the deformation vibration of $-\text{CH}_2$, respectively. The visible-absorption bands at 763 cm^{-1} , 840 cm^{-1} , 976 cm^{-1} are associated with the α -phase crystals of the PVDF.

Compared with the PSU and the PVDF, the spectrum of the prepared coating shows some different absorption bands (Fig. S3a). The new peak at 1630 cm^{-1} is correspond to the stretching vibration of $\text{C}=\text{C}$, which can contribute to the cross-link effect of PVDF, generated from the dehydrofluorination of PVDF. The formation of $\text{C}=\text{C}$ can also enhance the adhesion of the prepared coatings. Furthermore, the PSU reaction with the $-\text{NH}_2$ on the surface of MMT-PDMS generate the disappearance of $-\text{COOH}$ (1714 cm^{-1} and 1780 cm^{-1}). In Fig. S3a, the new bands at 1273 cm^{-1} and 1710 cm^{-1} are ascribed to the $-\text{C}=\text{O}$ and $-\text{C}-\text{N}-$ vibration absorptions, respectively.

S3. The adhesive ability of the coating

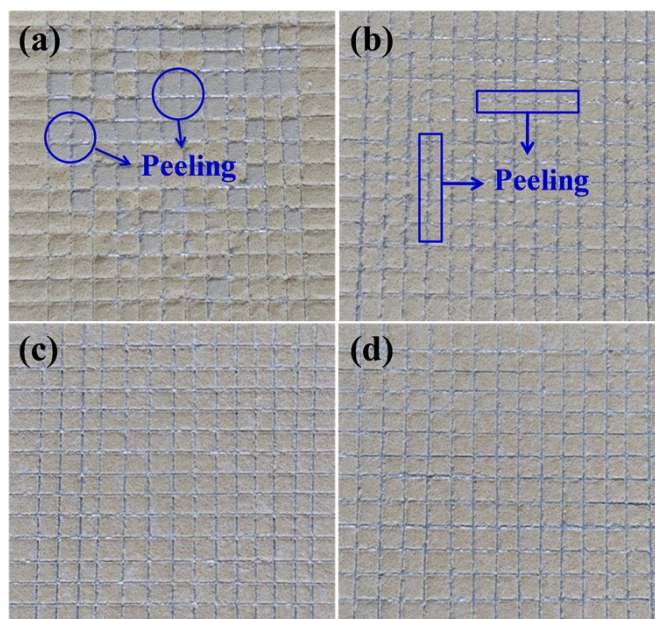


Fig. S4. The adhesive ability of the PSU/PVDF/MMT-PDMS superhydrophobic coatings (a: 9:1, 6 wt.% MMT-PDMS, b: 8:2, 9 wt.% MMT-PDMS, c: 7:3, 12 wt.% MMT-PDMS, d: 6:4, 12 wt.% MMT-PDMS)

The adhesive ability of the prepared coating was tested according to the GB/T9286, which divided the adhesive ability into 5 grades. The adhesive ability experiment was carried out by using a razor to scribe the resultant aluminum plate into 2 mm×2 mm gridding to expose the substrate, and then the adhesive tapes were used to press and pull to remove the scored surface from the substrate after 5 min. As shown in Fig. S4a, the superhydrophobic PSU/PVDF/MMT-PDMS (9:1, 6 wt.% MMT-PDMS) coating has large amounts of peeling (more than 65%) at the cross incision of the scratches, which can be classified into Grade 5. While the test results of the PSU/PVDF/MMT-PDMS (8:2, 9 wt.% MMT-PDMS) superhydrophobic coating increased to Grade 2 according

to the impacted area desquamated between 5% and 15% in the cross incision (Fig. S4b). The PSU/PVDF/MMT-PDMS (7:3, 12 wt.% MMT-PDMS) and PSU/PVDF/MMT-PDMS (6:4, 12 wt.% MMT-PDMS) superhydrophobic coatings both demonstrated excellent adhesion strength, which can be classified into Grade 1 due to the exfoliation of the cross incision less than 5% (Fig. S4c, S4d). For the curing process, dehydrofluorination of the PVDF macromolecule led to the formation of C-C or C=C functional groups, which resulted in cross-link effect and enhanced adhesion between the substrate and the PSU/PVDF/MMT-PDMS coating. Therefore, adding proper content PVDF in the PSU/PVDF/MMT-PDMS composite coating can improve the adhesion of the coating to the substrate.

S4. DSC

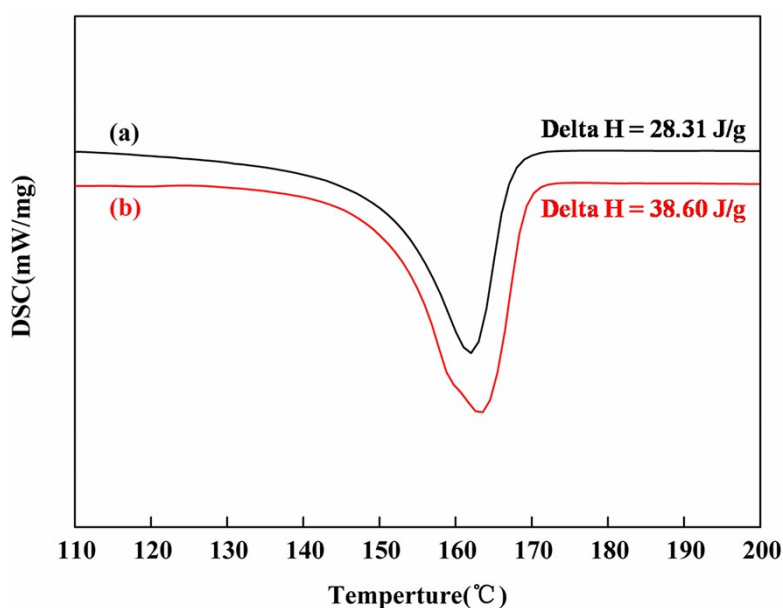


Fig.S5 DSC thermograms of the pure PVDF coating (a) and the PVDF/MMT-PDMS (12 wt.%) coating (b)

S5. Sand test

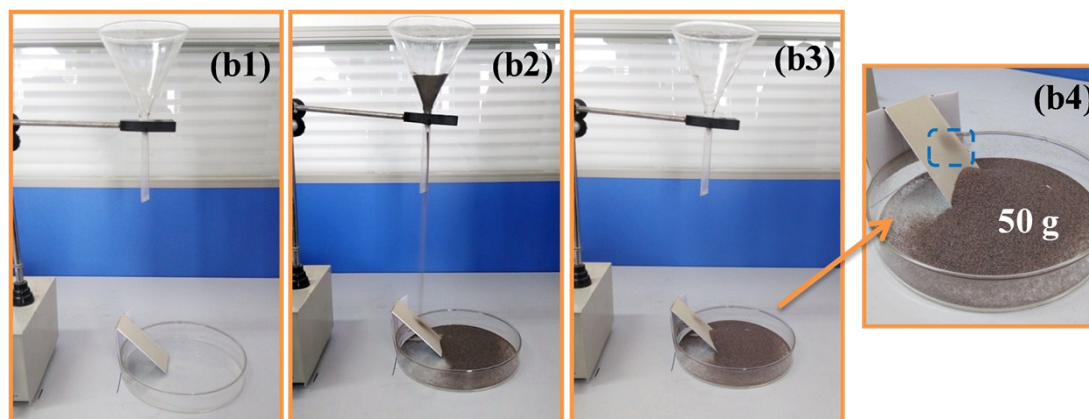


Fig. S6 Physical picture of the sand abrasion on the surface of prepared

superhydrophobic coating (a, b, c, d).

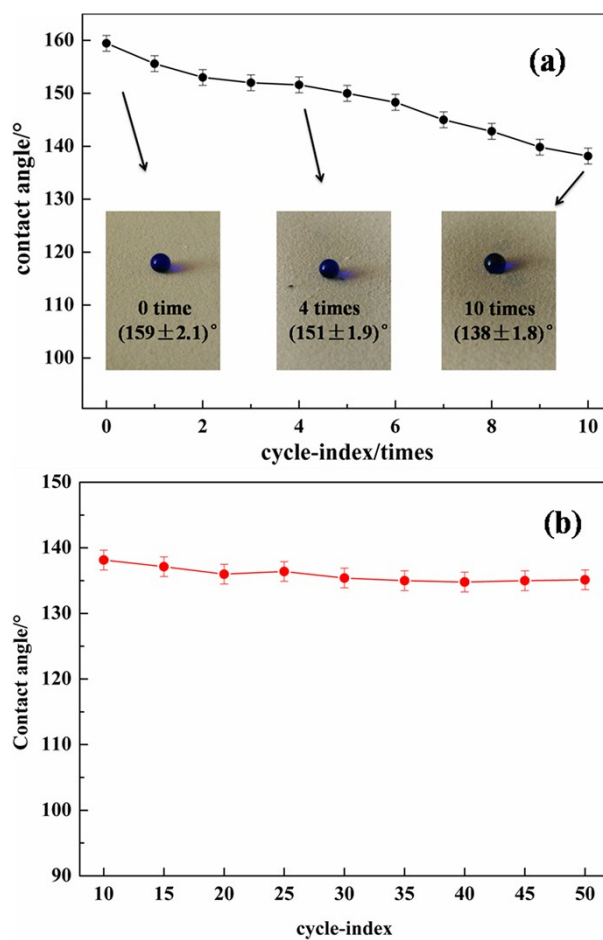


Fig. S7. Influence of the sand abrasion on the wettability of the PSU/PVDF/MMT-

PDMS coating (a): cycle-index from 0 to 10, (b): cycle-index from 10 to 50.

S6. Abrasion Test

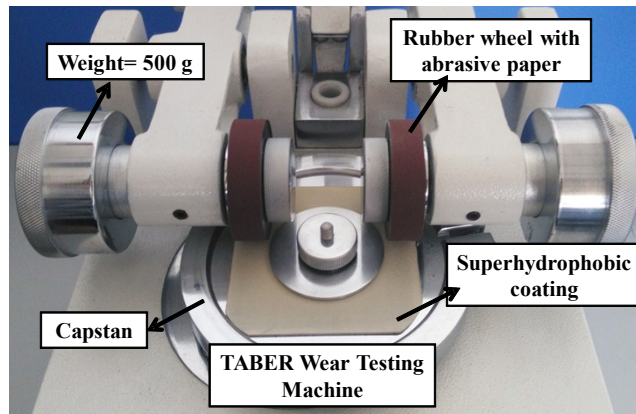


Fig. S8. The actual test pattern of the abrasion resistance

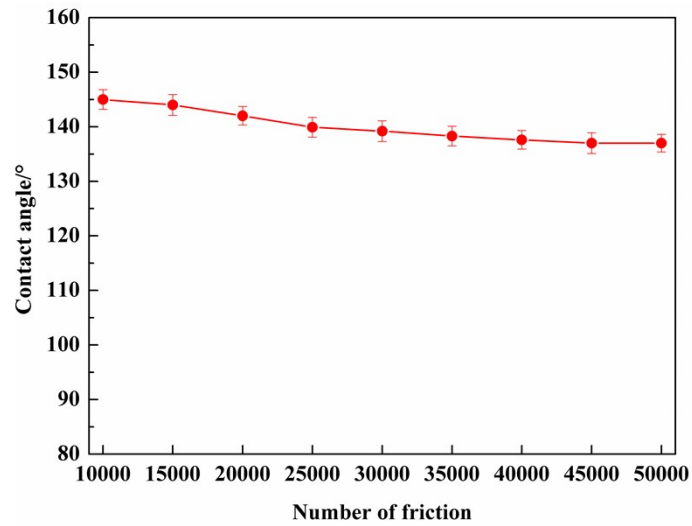


Fig. S9. Influence of the abrasion on the wettability of the PSU/PVDF/MMT-PDMS coating