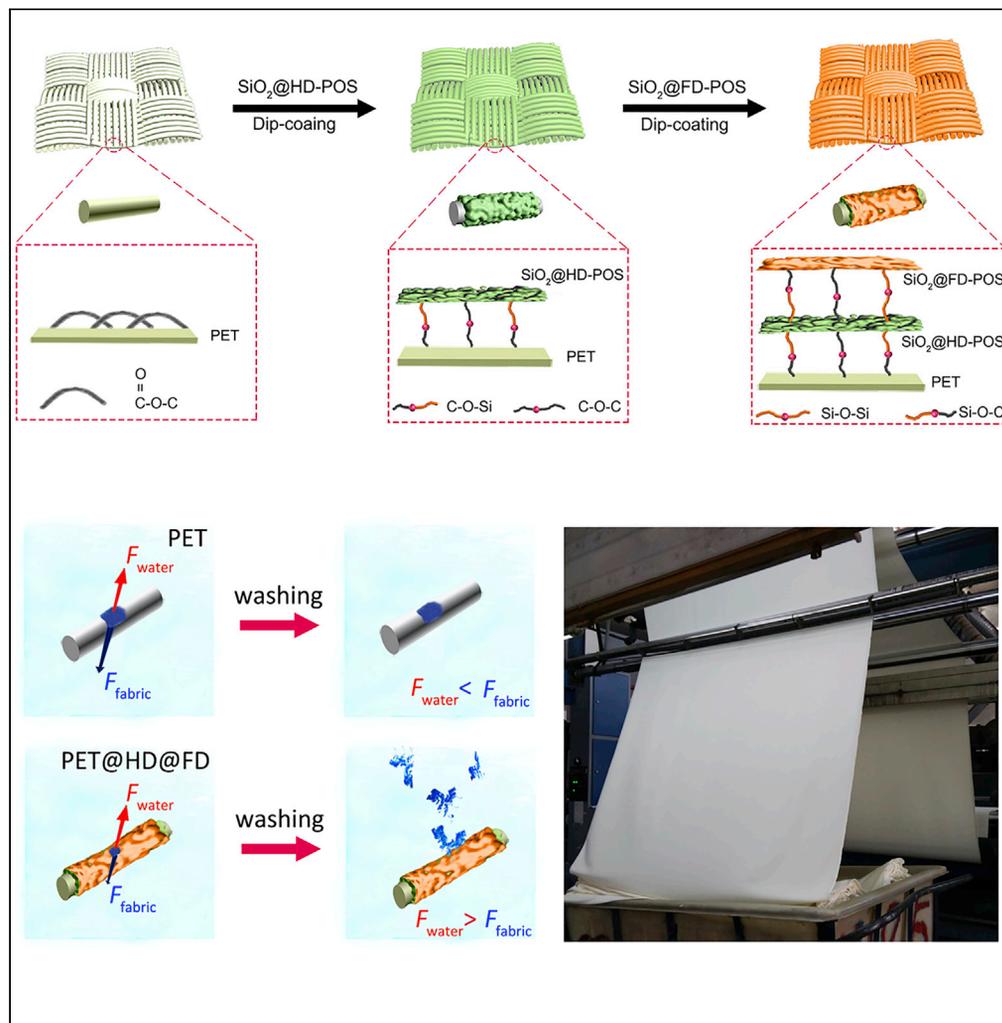


Article

Super pressure-resistant superhydrophobic fabrics with real self-cleaning performance



Ning Tian, Kai Chen, Hui Yu, Jinfei Wei, Junping Zhang

jpzhang@licp.cas.cn

Highlights
Superhydrophobic fabrics with real self-cleaning performance are prepared

The fabrics show high durability and pressure-resistance, low liquid adhesion force

The contaminated fabrics can be cleaned by home machine laundering without detergent

The fabrics can be scaled up using the conventional fabric finishing line

Tian et al., iScience 25, 104494
June 17, 2022 © 2022 The Author(s).
<https://doi.org/10.1016/j.isci.2022.104494>



Article

Super pressure-resistant superhydrophobic fabrics with real self-cleaning performance

Ning Tian,^{1,2} Kai Chen,^{1,2} Hui Yu,^{1,2} Jinfei Wei,¹ and Junping Zhang^{1,2,3,*}

SUMMARY

Detergents are extensively used for laundry, causing significant negative impacts on water bodies, plants and animals. Superhydrophobic fabrics are promising to reduce detergent consumption but suffer from low pressure resistance. Here, we report super pressure-resistant superhydrophobic fabrics prepared using polysiloxane modified SiO₂ nanoparticles with epoxy groups. The fabrics show real self-cleaning performance, essentially different from the conventional self-cleaning property of solid particles loosely placed on superhydrophobic surfaces. The contaminated fabrics by various stains can be completely cleaned by home machine laundering without using any detergent whereas the traditional superhydrophobic fabrics cannot. This is owing to excellent abrasion and washing durability, low liquid adhesion force, superior pressure-resistance and vapor-resistance of the fabrics, originating from the low surface energy and dense micro/nanostructure. Moreover, the superhydrophobic fabrics can be scaled up using the conventional fabric finishing line with low cost. The superhydrophobic fabrics will help significantly reduce the global detergent consumption.

INTRODUCTION

Detergents are extensively used in daily life and half of them are for laundry (Joshi-Navare et al., 2013). Over 60 million tons of detergents were consumed in 2016 and the consumption is rapidly increasing (Nur et al., 2016; Scheibel, 2004; Uzma et al., 2018; Warne and Schifko, 1999). However, surfactants and phosphates as the main components of detergents are harmful to surface water, aquatic organisms, wildlife and human beings, which has received much concern (Balcioglu, 2019; Goel and Kaur, 2012). Although great efforts have been made to optimize the formulation of detergents, their heavy use is still causing significant negative impacts on water bodies, plants and animals (Arthur et al., 2012; Giagnorio et al., 2017). Thus, novel materials for reducing the use of detergents for laundry are highly desired.

Superhydrophobic fabrics are promising to reduce or even avoid the use of detergents because of their self-cleaning property (Cheng et al., 2019; Lim et al., 2010; Liu et al., 2020, 2021). Many methods such as chemical vapor deposition, dip-coating and surface grafting have been developed to fabricate superhydrophobic fabrics (Deng et al., 2010; Li et al., 2016a; Xue et al., 2015; Zhang et al., 2019). Moreover, various novel superhydrophobic fabrics with the features of highly durable (abrasion and washing) (Tian et al., 2020; Wang et al., 2013; Zhou et al., 2017), self-healing (Dong et al., 2019; Lahiri et al., 2019; Wang et al., 2011; Zhou et al., 2013) and/or multifunctional (e.g., flame retardant, antibacterial, conductive, and hemostatic) (Chen et al., 2015; Li et al., 2016b, 2019b; Wu et al., 2016) have been reported. Besides, there are already some commercial emulsion products (e.g., TG-5003E from Dakin and Zelan R3 from DuPont) for preparing superhydrophobic fabrics using conventional fabric finishing lines.

However, the existing superhydrophobic fabrics still can be wetted and contaminated by small or high speed/pressure droplets despite their self-cleaning property to solid particles (Geyer et al., 2020). This is owing to their low repellency to small droplets and low liquid impalement resistance. Pressure (hydrostatic or dynamic) can trigger an irreversible transition of droplets from the Cassie-Baxter state to the Wenzel state by squeezing out the air at the solid-liquid interfaces (Verho et al., 2012). Consequently, small or high speed/pressure droplets can easily penetrate into the microstructure of superhydrophobic fabrics, and thus wet and contaminate them. In fact, this is one of the key issues hindering practical applications of superhydrophobic surfaces (Peng et al., 2018; Teisala et al., 2018; Wong et al., 2020). As a result, detergents are still necessary to wash off stains on superhydrophobic fabrics like common fabrics.

¹Center of Eco-material and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

²Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, PR China

³Lead contact

*Correspondence: jpzhang@licp.cas.cn
<https://doi.org/10.1016/j.isci.2022.104494>



Here, we report preparation of super pressure-resistant superhydrophobic fabrics with real self-cleaning performance by sequentially dip-coating and curing polyester (PET) fabrics in the emulsions of hexadecyl polysiloxane modified SiO₂ nanoparticles (SiO₂@HD-POS) and perfluorodecyl polysiloxane modified SiO₂ nanoparticles (SiO₂@FD-POS) with epoxy groups. The superhydrophobic PET@HD@FD fabrics feature low liquid adhesion force, superior pressure-resistance (hydrostatic and dynamic) and vapor-resistance, originating from the low surface energy and dense micro-/nanostructure compared with other superhydrophobic fabrics. Consequently, the contaminated PET@HD@FD fabrics by various stains can be completely cleaned in one cycle of home machine laundering without using any detergent, whereas the contaminated pristine PET fabric and other superhydrophobic PET fabrics cannot. So, the PET@HD@FD fabrics show real self-cleaning performance, which is essentially different from the conventional self-cleaning property to solid particles loosely placed on superhydrophobic surfaces.

RESULTS

Preparation of Superhydrophobic PET@HD@FD fabrics

First, the SiO₂@HD-POS emulsion with epoxy groups was prepared by HCl-catalyzed hydrolytic condensation of hexadecyltrimethoxysilane (HDTMS) and (3-glycidyloxy propyl)trimethoxysilane (GPTMS) with SiO₂ nanoparticles. Similarly, the SiO₂@FD-POS emulsion with epoxy groups was prepared using 1,1,2H,2H-perfluorodecyltriethoxysilane (PFDTES) and GPTMS. The superhydrophobic PET@HD@FD fabrics were prepared by sequentially dip-coating and curing PET fabrics in the SiO₂@HD-POS and SiO₂@FD-POS emulsions (Figure 1A). Once immersed in the acidic SiO₂@HD-POS emulsion, the -OH groups on the surface of the PET microfibers could adsorb SiO₂@HD-POS (Rahman Bhuiyan et al., 2018; Tian et al., 2020; Zhang et al., 2021). The bonding between PET and SiO₂@HD-POS was enhanced by curing at 140°C (Hong et al., 2016; Kehrlé et al., 2018). During subsequent immersion in the SiO₂@FD-POS emulsion, SiO₂@FD-POS was adsorbed on the PET@HD fabric by hydrogen bonding of the -OH groups between them (Liu et al., 2017; Tian et al., 2020). The bonding between SiO₂@HD-POS and SiO₂@FD-POS was strengthened by curing at 140°C because of condensation of the -OH groups between them (Figure S1). Superhydrophobic PET fabrics (Z-PET and P-PET) were also prepared using commercial reagents Zelan R3 (fluoro-free) and PF206 (fluorinated) for comparison.

The PET@HD@FD fabric in large size (1.8 × 1.2 m) can be readily prepared by the simple method (Figure 1B). The color parameters of the PET and PET@HD@FD fabrics are almost identical ($L^* = 81.3$, $a^* = -0.15$ and $b^* = -0.59$, Figure 1C). The PET fabric is composed of microfibers ~10 μm in diameter with smooth surface (Figures 1D and 1E). In contrast, the surfaces of the PET@HD and PET@FD fabrics are very rough (Figure S2). The PET microfibers are uniformly coated with aggregates of SiO₂@HD-POS or SiO₂@FD-POS nanoparticles, forming hierarchical micro-/nanostructures. Differently, the PET@HD@FD fabric shows a denser micro-/nanostructure (Figures 1F and 1G). The coating has negligible influence on the tensile strength and handle of the PET fabric (Table S1), but slightly reduces the air permeability from 307.7 mm s⁻¹ to 277.7 mm s⁻¹.

The C, O, Si and F elements are detected on the surface of the PET@HD@FD fabric by both energy dispersive spectrometers (EDS, Figure S3) and XPS (Figure 1H). The C 1s peak is composed of CF₃ (293.8 eV), CF₂ (292.4 eV), C-O/C-OH (286.5 eV), and C-C/C-H/C-Si (284.8 eV) peaks (Figure 1I). The Si 2p peak is composed of Si-C (102.0 eV), Si-O (103.3 eV) and Si-O-Si (103.9 eV) peaks (Figure S4) (Chen et al., 2020; Qing et al., 2020). The F content reaches 37.84 at%, indicating presence of abundant perfluorodecyl groups on the surface of the fabric (Li et al., 2019a).

Superhydrophobicity and durability

The PET fabric is superhydrophilic, whereas the Z-PET, P-PET, PET@HD, PET@FD and PET@HD@FD fabrics are superhydrophobic with water droplets spherical in shape on their surfaces and water jets can bounce off completely (Figure S5). However, the PET@HD, PET@FD and PET@HD@FD fabrics have a similar lower water shedding angle (WSA = 5.6–7.0°) than those prepared using commercial reagents (Figure 2A). In addition, the 9 μL water droplets hanging on a 0.53 mm diameter needle can be easily transferred to the superhydrophobic fabrics by contacting the fabrics except for the PET@FD and PET@HD@FD fabrics (Figures 2B and S6). This is because the adhesion force of water droplets with the PET@FD and PET@HD@FD fabric is much lower than the other superhydrophobic fabrics (Figure 2C). This is further confirmed by the impact/bounce process of water droplets with 1 cm release height on the fabrics. Shorter contact time in the first impact/bounce cycle and more bouncing times were recorded for the PET@HD@FD fabric (Figures 2D, S7, and Video S1).

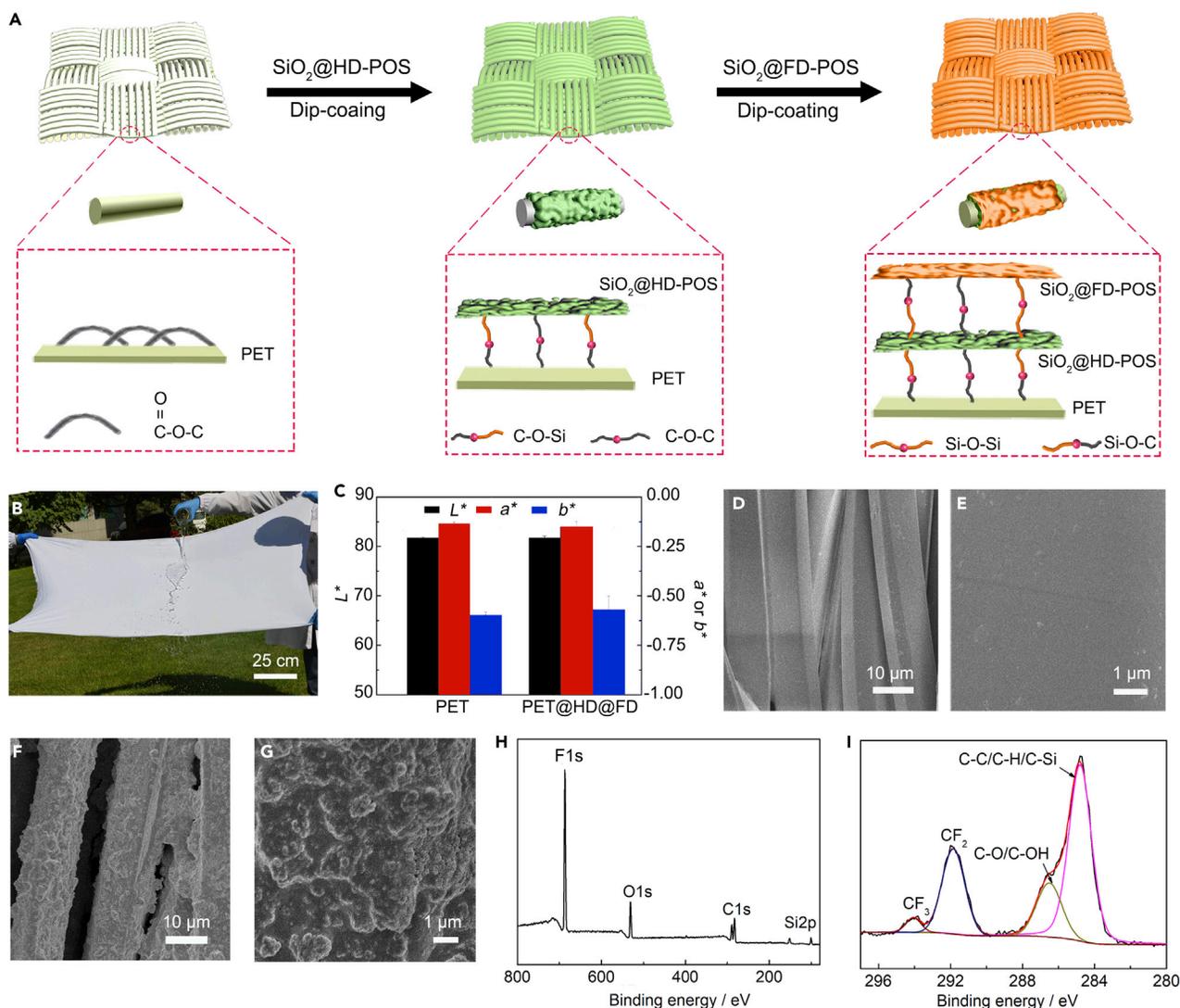


Figure 1. Preparation of superhydrophobic PET@HD@FD fabrics

(A) Schematic preparation of PET@HD@FD fabrics.
 (B) Photograph of the PET@HD@FD fabric in large size.
 (C) L^* , a^* , and b^* of the PET and PET@HD@FD fabrics (shown as means \pm SD, $n = 5$).
 (D–G) Scanning electron microscopic (SEM) images of the (D–E) PET and (F–G) PET@HD@FD fabrics.
 (H–I) (H) X-ray photoelectron spectrum (XPS) and (I) C 1s spectrum of the PET@HD@FD fabric.

The abrasion durability of the PET@HD@FD fabric was tested using the Martindale method (ASTM 4966) at 12 kPa (Zhou et al., 2017). The WSA increased gradually to $\sim 20^\circ$ after 20,000 cycles of abrasion (Figure S8A). The washing durability of the PET@HD@FD fabric was evaluated according to the AATCC 61–2006 2B test method. The WSA increased gradually to $\sim 30^\circ$ after 100 cycles washing (Figure S8B). Note that the weight of PET@HD@FD fabric decreased by $\sim 0.97\%$ and $\sim 1.47\%$, respectively, after 20,000 cycles of abrasion and 100 cycles washing (Figures S8C and S8D). The results demonstrate excellent abrasion and washing durability of the fabric. The gradual decline in superhydrophobicity is ascribed to the change in microstructures (Figures S8E–S8H).

Self-cleaning performance

All the superhydrophobic fabrics show conventional self-cleaning properties. Falling water droplets can easily remove sand particles ca. 200 μm in size on their surfaces (Figure S9). Nevertheless, the dry stains of blue-black ink micro-droplets formed by spraying on the superhydrophobic fabrics cannot be removed

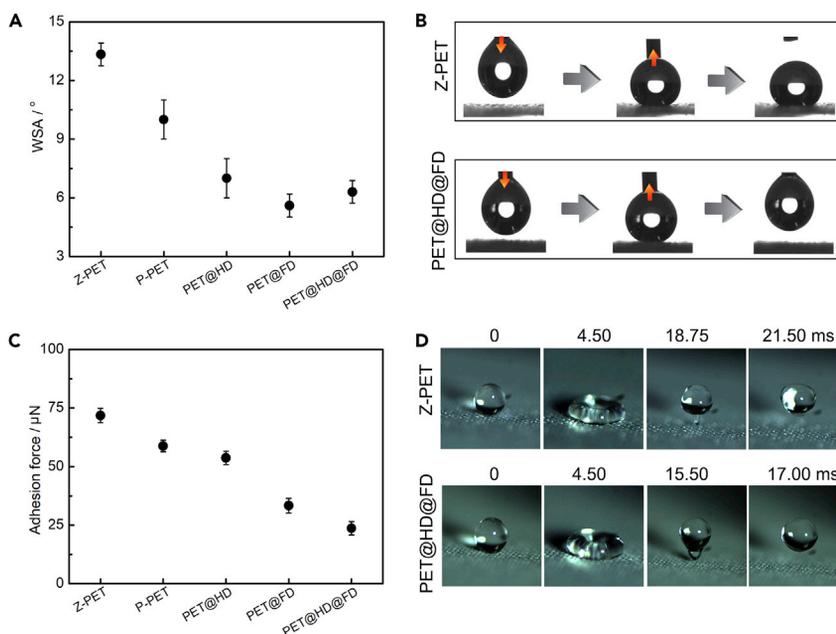


Figure 2. Superhydrophobicity of PET@HD@FD fabrics

(A) WSA of various fabrics (shown as means \pm SD, n = 5).

(B) Transferring of 9 μ L water droplets hanging on a 0.53 mm diameter needle by contacting with different fabrics.

(C) Adhesion forces of water droplets (9 μ L) with various fabrics (shown as means \pm SD, n = 5).

(D) Snapshots showing impact/bounce of 10 μ L water droplets with 1 cm release height on different fabrics.

by this way, although the fabrics are highly repellent to large ink droplets (10 μ L, Figures S10 and S11). This is because the ink micro-droplets (13–33 μ m in diameter) with high speed (~ 3.8 m s⁻¹) had penetrated into and adhered on the microfibers of the superhydrophobic fabrics (Figure S12) (Mueller and Kleinebudde, 2007).

Consequently, the real self-cleaning performance of various fabrics was evaluated by measuring their color parameters (L^* , a^* and b^*) after being contaminated by dry stains of blue-black ink micro-droplets and washed according to the AATCC 61–2006 2B test method but without any detergent. All the pristine fabrics have similar color parameters ($L^* \sim 83.2$, $b^* \sim 0.5$, Figures 3 and S13). The PET fabric was seriously contaminated by ink ($L^* 40.2$, $b^* -17.2$), whereas all the contaminated superhydrophobic fabrics had larger L^* and smaller b^* . This is because ink was absorbed uniformly by the superhydrophilic PET fabric, but contracted into small droplets on the superhydrophobic fabrics (Figure S14). Thus, superhydrophobicity is helpful to reduce contamination of fabrics by ink. After washing, the PET fabric was still seriously contaminated ($L^* 54.9$, $b^* -8.9$), whereas L^* and b^* of the superhydrophobic fabrics evidently recovered but to a different degree. Different from partial recovery of the other superhydrophobic fabrics, the PET@HD@FD fabric completely recovered its color parameters after washing, i.e., showing real self-cleaning performance. The self-cleaning performance of the PET@HD@FD fabric was further demonstrated by the ATR-FTIR and EDS analyses (Figure S15). The characteristic absorption peaks (e.g., -OH groups of tannin at 3302 cm⁻¹ and SO₄²⁻ at 611 cm⁻¹) and elements (e.g., Fe and S) of ink on the contaminated fabric completely disappeared after washing. Moreover, the ink stains can also be completely removed by handwashing, demonstrating excellent self-cleaning performance (Video S2 and Figure S16). In contrast, the contaminated PET fabric cannot be completely cleaned even by washing with detergent (Figure S17).

Besides the random ink stains, the patterned ink stains and stains formed by falling ink (1 mL) from 80 cm height on the 45° tilted PET@HD@FD fabric can also be completely washed away (Figures S18 and S19). The ink impact speed (~ 4 m s⁻¹) is faster than most dirt encountered in daily life (Wang et al., 2019). In addition, the stains formed by other fluids (e.g., pressed tomato sauce, sprayed coffee, sauce and brown sugar water) can also be completely removed via the same procedure without any detergent (Figures S20 and S21). In contrast, the stains on the other superhydrophobic fabrics can only be partially removed. Moreover,

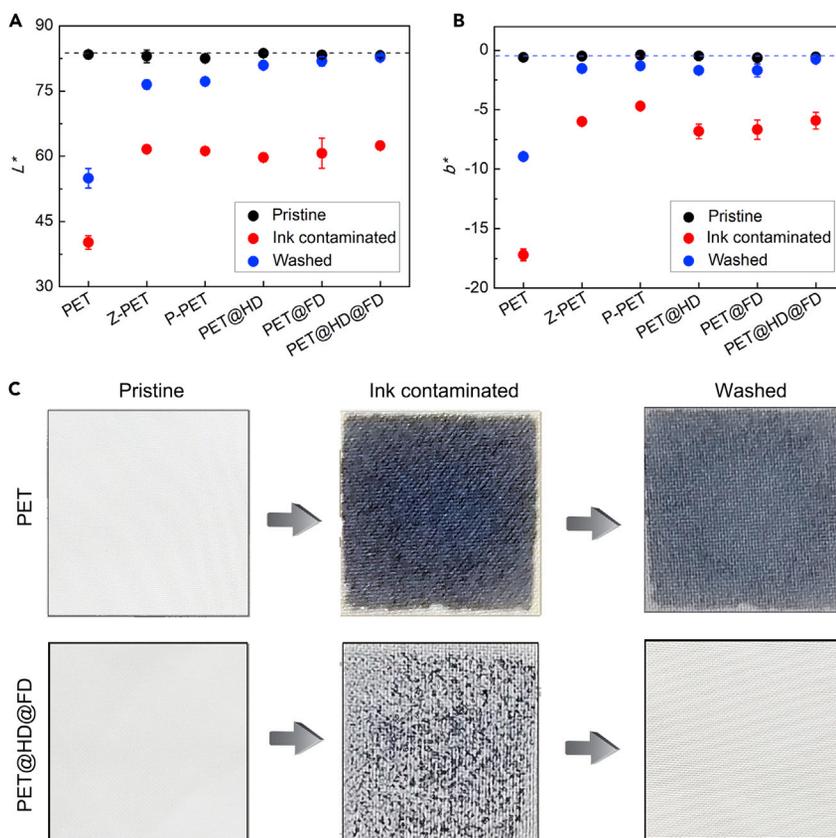


Figure 3. Self-cleaning performance of PET@HD@FD fabrics

(A–C) (A) L^* (shown as means \pm SD, $n = 5$), (B) b^* (shown as means \pm SD, $n = 5$) and (C) photographs of the pristine, ink contaminated and washed fabrics. The black dash line represents L^* and the blue dash line represents b^* of the pristine PET fabric.

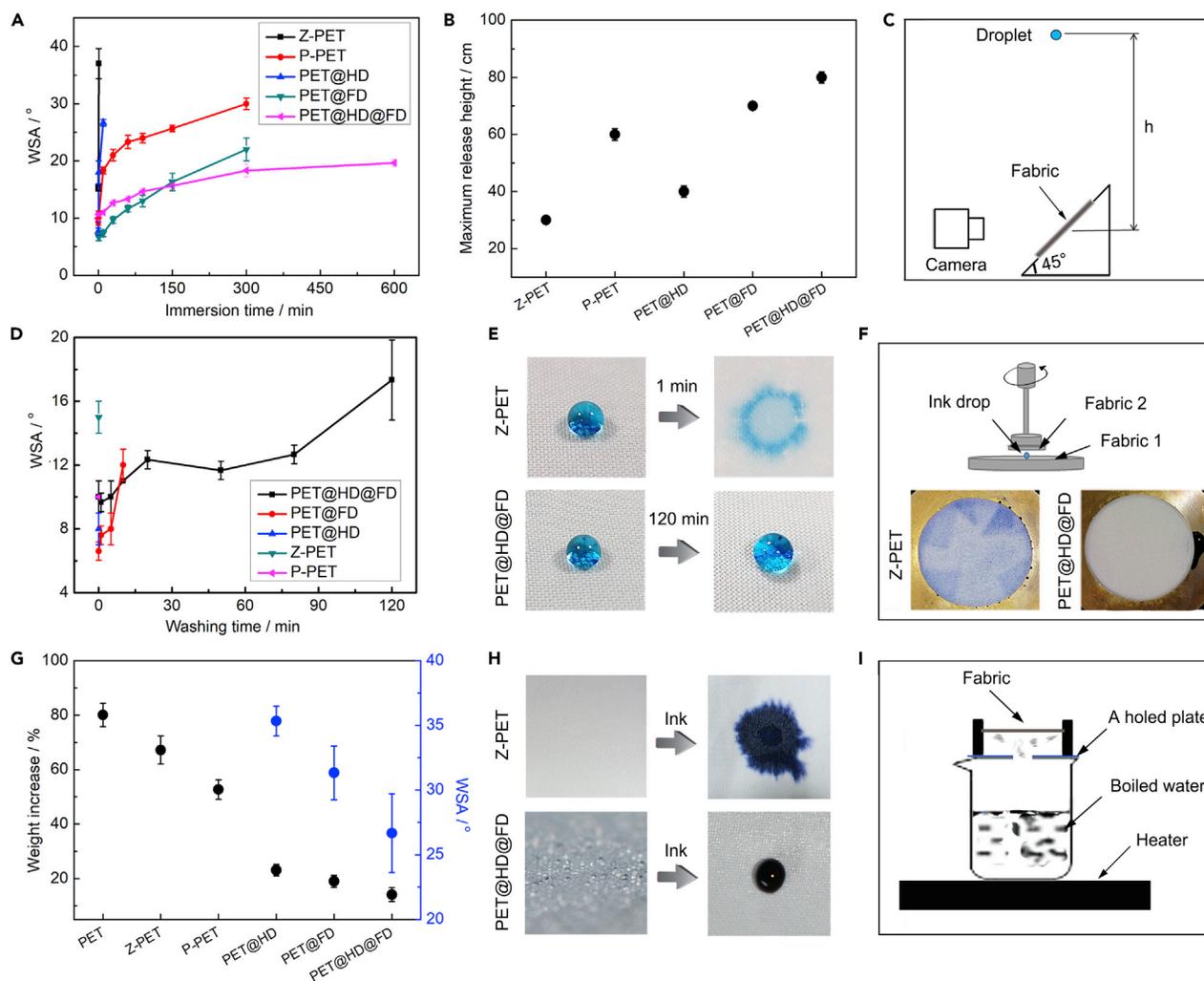
when the ink contaminated PET@HD@FD fabric was kept steadily in water (without detergent) for a short period of time, the stain fell off spontaneously and almost completely, but the others could not (Figures S22 and S23, Video S3).

Furthermore, the superhydrophobic coating can be applied onto various other fabrics including cashmere, silk, linen and aramid via the same procedure as the PET@HD@FD fabric. The fabrics became superhydrophobic despite the differences in the WSA (Figure S24). All the ink contaminated fabrics can recover their initial color parameters by washing without any detergent, showing good self-cleaning performance (Figure S25).

Pressure-resistance and vapor-resistance

The pressure-resistance of the superhydrophobic fabrics was evaluated by the hydrostatic pressure, water impalement, laundry shearing and squeezing & shearing tests. During the tests, the fabrics were wetted or remained dry. Even if it remained dry, the fabrics inevitably absorbed some moisture, which affected the three-phase contact line and thus caused an increase in the WSA. So, if the fabrics remained dry, the instant WSA was recorded immediately after the tests. Or else, the instant WSA will decrease quickly because of moisture evaporation (Figure S26A).

Once immersed in water at 1.0 m depth, the Z-PET and PET@HD fabrics showed significant increase in the instant WSA and were completely wetted after a short period of time (Figure 4A). For the P-PET and PET@FD fabrics, the instant WSA was below 30° after 300 min but were also wetted after 600 min. Differently, 600 min immersion only caused an increase in the instant WSA of the PET@HD@FD fabric to 19.6° and 18.6% weight increase (Figure S26B), indicating excellent hydrostatic pressure-resistance.



In the water impalement resistance test, the 45° tilted Z-PET fabric could withstand impact of a 10 μ L water droplet from 30 cm height and higher impact height caused pinning of water droplets on the fabric (Figures 4B, 4C, S27, and Video S4), i.e., transition from the Cassie-Baxter state to the Wenzel state. On the contrary, the PET@HD@FD fabric could withstand impact from at least 80 cm height, greatly higher than the other fabrics. Water droplets released from even higher will penetrate the PET@HD@FD fabric through the spaces among the microfibers, leaving the fabric completely dry.

In the laundry shearing test according to the AATCC 61–2006 2B test method but without any detergent, the Z-PET, P-PET and PET@HD fabrics were wetted in 1 min washing and the PET@FD fabric was wetted in 20 min washing (Figures 4D and 4E). In contrast, the PET@HD@FD fabric remained dry after 120 min washing, which only caused gradual increase in the instant WSA to \sim 18°. In the squeezing & shearing test of an ink droplet (20 μ L) between two pieces of the same fabrics under 9 kPa for 10 cycles, the

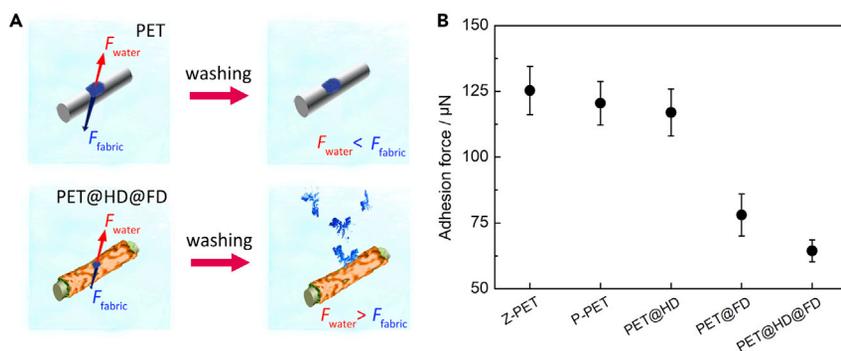


Figure 5. Mechanism of self-cleaning performance and high pressure-resistance

(A) Schematic illustration of forces loaded on the ink stain on different fabrics during washing.

(B) Adhesion force of ink droplets (9 μ L) with various fabrics (shown as means \pm SD, n = 5).

PET@HD@FD fabric kept clean whereas the other superhydrophobic fabrics were seriously contaminated (Figures 4F and S28).

After being exposed to $\sim 90^{\circ}\text{C}$ hot vapor for 5 min, the Z-PET and P-PET fabrics were completely wetted with evident weight increase ($>50\%$), whereas the other fabrics remained dry and superhydrophobic with small weight increase ($<25\%$) mainly because of condensation of water micro-droplets (Figures 4G–4I, S29, and S30). Ink (10 μ L) was dropped on the fabrics immediately after the test, which was absorbed quickly by the wet Z-PET and P-PET fabrics but remained spherical on the others. The increase in the WSA of the PET@HD, PET@FD and PET@HD@FD fabrics is owing to moisture uptake and condensation of micro-droplets in the test. The PET@HD@FD fabric has the lowest weight increase and WSA, demonstrating superior vapor-resistance. Note that all the fabrics will be wetted when the water vapor resistance test time is long enough.

Mechanism of self-cleaning performance and high pressure-resistance

The ink stain was adsorbed on the microfibers of the fabrics by van der Waals' and coulombic forces (F_{fabric}) (Compton and Hart, 1954). There are two forces loaded on the ink stain during washing (Figure 5A), F_{fabric} and the binding force between water and the stain via hydrogen bonding (F_{water}). F_{fabric} largely relies on surface properties of the microfibers and F_{water} is a constant under certain washing conditions. So, the stain can be washed away when $F_{water} > F_{fabric}$ but cannot when $F_{water} < F_{fabric}$. The fabrics showed different self-cleaning performance owing to the difference in F_{fabric} . The adhesion force between ink droplet and the PET@HD@FD fabric is the lowest (Figure 5B), which is consistent with its superior self-cleaning performance. The difference in F_{fabric} of various fabrics is ascribed to their different surface chemical composition (Figure S31 and Table S2). On the surface of the PET@HD@FD fabric there are abundant perfluorodecyl groups (37.84 at% F), which greatly reduce the surface energy. In contrast, the Z-PET fabric is fluoro-free and the P-PET fabric only has 2.02 at% F.

Besides the lowest F_{fabric} , the smallest contact area of ink stain with the PET@HD@FD fabric (Figure S14) because of its super pressure-resistance also contributes to the superior self-cleaning performance. The super pressure-resistance of the PET@HD@FD fabric originates from its low surface energy and dense micro-/nanostructure compared with other fabrics.

DISCUSSION

In summary, super pressure-resistant superhydrophobic fabrics are prepared. The superhydrophobic fabrics show excellent abrasion and washing durability, low liquid adhesion force, superior hydrostatic and dynamic pressure-resistance and high vapor-resistance, originating from the low surface energy and dense micro-/nanostructure. Unexpectedly, the contaminated fabrics can be completely cleaned by home machine laundering without using any detergent, showing real self-cleaning performance essentially different from the conventional self-cleaning behavior. Furthermore, large scale continuous production of the superhydrophobic fabrics is achieved using the conventional fabric finishing line with low cost (~ 3.9 CNY m^{-2} or ~ 0.6 USD m^{-2}) and high efficiency (~ 4 min) (Figures S32 and S33). In addition, the superhydrophobic coating can be applied onto various fabrics. We anticipate that the superhydrophobic fabrics will significantly reduce the global consumption of detergents.

Limitations of the study

Oily stains stuck on the superhydrophobic fabrics can hardly be removed by pure water through self-cleaning. On the other hand, material containing fluorine elements is harmful to the environment, and it would promote self-cleaning fabric application to prepare excellent self-cleaning fabric with environmentally friendly materials.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
 - Lead contact
 - Materials availability
 - Data and code availability
- EXPERIMENTAL MODEL AND SUBJECT DETAILS
- METHODS DETAILS
 - Preparation of Superhydrophobic PET@HD@FD fabrics
 - Preparation of superhydrophobic fabrics using commercial reagents
 - Measurement of WSA
 - Evaluation of abrasion and washing durability
 - Evaluation of self-cleaning performance
 - Evaluation of pressure-resistance
 - Evaluation of vapor-resistance
 - Characterization
- QUANTIFICATION AND STATISTICAL ANALYSIS

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2022.104494>.

ACKNOWLEDGMENTS

This study was supported by the National Natural Science Foundation of China (51873220).

AUTHOR CONTRIBUTIONS

N.T. and J.P.Z. conceived the concept. N.T. performed most of the experiments. K.C., H.Y., and J.F.W. performed a part of the tests. All authors have thoroughly discussed and analyzed the data. N.T. and J.P.Z. wrote the manuscript with contributions from all authors. J.P.Z. designed and supervised the work.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: March 21, 2022

Revised: May 4, 2022

Accepted: May 21, 2022

Published: June 17, 2022

REFERENCES

- Arthur, T., Harjani, J.R., Phan, L., Jessop, P.G., and Hodson, P.V. (2012). Effects-driven chemical design: the acute toxicity of CO₂-triggered switchable surfactants to rainbow trout can be predicted from octanol-water partition coefficients. *Green Chem.* *14*, 357–362. <https://doi.org/10.1039/c1gc15620a>.
- Balcioglu, E.B. (2019). Seasonal changes of LAS, phosphate, and chlorophyll-a concentrations in coastal surface water of the Prince Islands, Marmara Sea. *Mar. Pollut. Bull.* *138*, 230–234. <https://doi.org/10.1016/j.marpolbul.2018.11.027>.
- Chen, L., Park, S., Yoo, J., Hwang, H., Kim, H., Lee, J., Hong, J., and Woo, S. (2020). One-step fabrication of universal slippery lubricated surfaces. *Adv. Funct. Mater.* *7*, 2000305. <https://doi.org/10.1002/admi.202000305>.
- Chen, S., Li, X., Li, Y., and Sun, J. (2015). Intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric. *ACS Nano* *9*, 4070–4076. <https://doi.org/10.1021/acsnano.5b00121>.
- Cheng, Q.Y., Zhao, X.L., Weng, Y.X., Li, Y.D., and Zeng, J.B. (2019). Fully sustainable, nanoparticle-free, fluorine-free, and robust superhydrophobic cotton fabric fabricated via an eco-friendly method for efficient oil/water separation. *ACS Sustain. Chem. Eng.* *7*, 15696–15705. <https://doi.org/10.1021/acssuschemeng.9b03852>.

- Compton, J., and Hart, W. (1954). The theory of soil-fiber complex formation and stability. *Text. Res. J.* 24, 263–264. <https://doi.org/10.1177/004051755402400308>.
- Deng, B., Cai, R., Yu, Y., Jiang, H., Wang, C., Li, J., Li, L., Yu, M., Li, J., Xie, L., et al. (2010). Laundering durability of superhydrophobic cotton fabric. *Adv. Mater.* 22, 5473–5477. <https://doi.org/10.1002/adma.201002614>.
- Dong, X.L., Gao, S.W., Huang, J.Y., Li, S.H., Zhu, T.X., Cheng, Y., Zhao, Y., Chen, Z., and Lai, Y.K. (2019). A self-roughened and biodegradable superhydrophobic coating with UV shielding, solar-induced self-healing and versatile oil-water separation ability. *J. Mater. Chem. B*, 7, 2122–2128. <https://doi.org/10.1039/c8ta10869b>.
- Geyer, F., D'Acunzi, M., Sharifi-Aghili, A., Saal, A., Gao, N., Kaltbeitzel, A., Sloot, T.F., Berger, R., Butt, H.J., and Vollmer, D. (2020). When and how self-cleaning of superhydrophobic surfaces works. *Sci. Adv.* 6, eaaw9727. <https://doi.org/10.1126/sciadv.aaw9727>.
- Giagnorio, M., Amelio, A., Grüttner, H., and Tiraferri, A. (2017). Environmental impacts of detergents and benefits of their recovery in the laundering industry. *J. Cleaner Prod.* 154, 593–601. <https://doi.org/10.1016/j.jclepro.2017.04.012>.
- Goel, G., and Kaur, S. (2012). A study on chemical contamination of water due to household laundry detergents. *J. Hum. Ecol.* 38, 65–69. <https://doi.org/10.1080/09709274.2012.11906475>.
- Hong, S.H., Hong, S., Ryou, M.-H., Choi, J.W., Kang, S.M., and Lee, H. (2016). Sprayable ultrafast polydopamine surface modifications. *Adv. Mater. Interfaces* 3, 1500857. <https://doi.org/10.1002/admi.201500857>.
- Joshi-Navare, K., Khanvilkar, P., and Prabhune, A. (2013). Jatropha oil derived sophorolipids: production and characterization as laundry detergent additive. *Biochem. Res. Int.* 2013, 1–11. <https://doi.org/10.1155/2013/169797>.
- Kehrle, J., Purkait, T.K., Kaiser, S., Raftopoulos, K.N., Winnacker, M., Ludwig, T., Aghajamali, M., Hanzlik, M., Rodewald, K., Helbich, T., et al. (2018). Superhydrophobic silicon nanocrystal-silica aerogel hybrid materials: synthesis, properties, and sensing application. *Langmuir* 34, 4888–4896. <https://doi.org/10.1021/acs.langmuir.7b03746>.
- Lahiri, S.K., Zhang, P., Zhang, C., and Liu, L. (2019). Robust fluorine-free and self-healing superhydrophobic coatings by H3BO3 incorporation with SiO2-alkyl-silane@PDMS on cotton fabric. *ACS Appl. Mater. Interfaces* 11, 10262–10275. <https://doi.org/10.1021/acsami.8b20651>.
- Li, J., Kang, R., Tang, X., She, H., Yang, Y., and Zha, F. (2016a). Superhydrophobic meshes that can repel hot water and strong corrosive liquids used for efficient gravity-driven oil/water separation. *Nanoscale* 8, 7638–7645. <https://doi.org/10.1039/c6nr01298a>.
- Li, Z., Xu, Z., Liu, Y., Wang, R., and Gao, C. (2016b). Multifunctional non-woven fabrics of interfused graphene fibres. *Nat. Commun.* 7, 13684. <https://doi.org/10.1038/ncomms13684>.
- Li, Y., Hu, T., Li, B., Wei, J., and Zhang, J. (2019a). Totally waterborne and highly durable superamphiphobic coatings for anti-icing and anticorrosion. *Adv. Mater. Interfaces* 6, 1901255. <https://doi.org/10.1002/admi.201901255>.
- Li, Z., Milionis, A., Zheng, Y., Yee, M., Codispoti, L., Tan, F., Poulidakos, D., and Yap, C.H. (2019b). Superhydrophobic hemostatic nanofiber composites for fast clotting and minimal adhesion. *Nat. Commun.* 10, 5562. <https://doi.org/10.1038/s41467-019-13512-8>.
- Lim, H.S., Baek, J.H., Park, K., Shin, H.S., Kim, J., and Cho, J.H. (2010). Multifunctional hybrid fabrics with thermally stable superhydrophobicity. *Adv. Mater.* 22, 2138–2141. <https://doi.org/10.1002/adma.200903074>.
- Liu, J., Sun, Y., Zhou, X., Li, X., Kappl, M., Steffen, W., and Butt, H.J. (2021). One-step synthesis of a durable and liquid-repellent poly(dimethylsiloxane) coating. *Adv. Mater.* 33, e2100237. <https://doi.org/10.1002/adma.202100237>.
- Liu, J., Ye, L., Sun, Y., Hu, M., Chen, F., Wegner, S., Mailänder, V., Steffen, W., Kappl, M., and Butt, H.J. (2020). Elastic superhydrophobic and photocatalytic active films used as blood repellent dressing. *Adv. Mater.* 32, e1908008. <https://doi.org/10.1002/adma.201908008>.
- Liu, S., Zhou, H., Wang, H., Zhao, Y., Shao, H., Xu, Z., Feng, Z., Liu, D., and Lin, T. (2017). Argon plasma treatment of fluorine-free silane coatings: a facile, environment-friendly method to prepare durable, superhydrophobic fabrics. *Adv. Mater. Interfaces* 4, 1700027. <https://doi.org/10.1002/admi.201700027>.
- Mueller, R., and Kleinebudde, P. (2007). Comparison of a laboratory and a production coating spray gun with respect to scale-up. *AAPS PharmSciTech* 8, E21–E31. <https://doi.org/10.1208/pt0801003>.
- Nur-E-Alam, M., Islam, M.M., Islam, M.N., Rima, F.R., and Islam, M.N. (2016). Quality analysis, micellar behavior, and environmental impact of some laundry detergents available in Bangladesh. *Environ. Sci. Pollut. Res. Int.* 23, 5468–5476. <https://doi.org/10.1007/s11356-015-5724-8>.
- Peng, C., Chen, Z., and Tiwari, M.K. (2018). All-organic superhydrophobic coatings with mechanochemical robustness and liquid impalement resistance. *Nat. Mater.* 17, 355–360. <https://doi.org/10.1038/s41563-018-0044-2>.
- Qing, Y., Shi, S., Lv, C., and Zheng, Q. (2020). Microskeleton-nanofiller composite with mechanical super-robust superhydrophobicity against abrasion and impact. *Adv. Funct. Mater.* 30, 1910665. <https://doi.org/10.1002/adfm.201910665>.
- Rahman Bhuiyan, M.A., Ali, A., Islam, A., Hannan, M.A., Fijul Kabir, S.M., and Islam, M.N. (2018). Coloration of polyester fiber with natural dye henna (*Lawsonia inermis* L.) without using mordant: a new approach towards a cleaner production. *Fashion Text* 5, 2. <https://doi.org/10.1186/s40691-017-0121-1>.
- Scheibel, J.J. (2004). The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry. *J. Surfactants Deterg.* 7, 319–328. <https://doi.org/10.1007/s11743-004-0317-7>.
- Teisala, H., Geyer, F., Haapanen, J., Juuti, P., Mäkelä, J.M., Vollmer, D., and Butt, H.J. (2018). Ultrafast processing of hierarchical nanotexture for a transparent superamphiphobic coating with extremely low roll-off angle and high impalement pressure. *Adv. Mater.* 30, e1706529. <https://doi.org/10.1002/adma.201706529>.
- Tian, N., Wei, J., Li, Y., Li, B., and Zhang, J. (2020). Efficient scald-preventing enabled by robust polyester fabrics with hot water repellency and water impalement resistance. *J. Colloid Interface. Sci.* 566, 69–78. <https://doi.org/10.1016/j.jcis.2020.01.067>.
- Uzma, S., Khan, S., Murad, W., Taimur, N., and Azizullah, A. (2018). Phytotoxic effects of two commonly used laundry detergents on germination, growth, and biochemical characteristics of maize (*Zea mays* L.) seedlings. *Environ. Monit. Assess.* 190, 651. <https://doi.org/10.1007/s10661-018-7031-6>.
- Verho, T., Korhonen, J.T., Sainiemi, L., Jokinen, V., Bower, C., Franze, K., Franssila, S., Andrew, P., Ikkala, O., and Ras, R.H.A. (2012). Reversible switching between superhydrophobic states on a hierarchically structured surface. *Proc. Natl. Acad. Sci. U S A* 109, 10210–10213. <https://doi.org/10.1073/pnas.1204328109>.
- Wang, H., Xue, Y., Ding, J., Feng, L., Wang, X., and Lin, T. (2011). Durable, self-healing superhydrophobic and superoleophobic surfaces from fluorinated-decyl polyhedral oligomeric silsesquioxane and hydrolyzed fluorinated alkyl silane. *Angew. Chem. Int. Ed.* 123, 11635–11638. <https://doi.org/10.1002/ange.201105069>.
- Wang, H.D., Zhou, H., Gestos, A., Fang, J., and Lin, T. (2013). Robust, superamphiphobic fabric with multiple self-healing ability against both physical and chemical damages. *ACS Appl. Mater. Interfaces* 5, 10221–10226. <https://doi.org/10.1021/am4029679>.
- Wang, J., Wang, L., Sun, N., Tierney, R., Li, H., Corsetti, M., Williams, L., Wong, P.K., and Wong, T.-S. (2019). Viscoelastic solid-repellent coatings for extreme water saving and global sanitation. *Nat. Sustain.* 2, 1097–1105. <https://doi.org/10.1038/s41893-019-0421-0>.
- Wang, X., Mu, B., Xu, J., and Wang, A. (2021). Reversible thermochromic superhydrophobic BiVO4 hybrid pigments coatings with self-cleaning performance and environmental stability based on kaolinite. *ACS Appl. Mater. Interfaces* 13, 3228–3236. <https://doi.org/10.1021/acsami.0c20029>.
- Warne, M.S.J., and Schifko, A. (1999). Toxicity of laundry detergent components to a freshwater cladoceran and their contribution to detergent toxicity. *Ecotoxicol. Environ. Saf.* 44, 196–206. <https://doi.org/10.1006/eesa.1999.1824>.
- Wong, W.S.Y., Corrales, T.P., Naga, A., Baumli, P., Kaltbeitzel, A., Kappl, M., Papadopoulos, P., Vollmer, D., and Butt, H.J. (2020). Microdroplet contaminants: when and why superamphiphobic surfaces are not self-cleaning. *ACS Nano* 14, 3836–3846. <https://doi.org/10.1021/acsnano.9b08211>.

Wu, L., Zhang, J., Li, B., and Wang, A. (2013). Mimic nature, beyond nature: facile synthesis of durable superhydrophobic textiles using organosilanes. *J. Mater. Chem. B* 1, 4756. <https://doi.org/10.1039/c3tb20934b>.

Wu, M., Ma, B., Pan, T., Chen, S., and Sun, J. (2016). Silver-nanoparticle-colored cotton fabrics with tunable colors and durable antibacterial and self-healing superhydrophobic properties. *Adv. Funct. Mater.* 26, 569–576. <https://doi.org/10.1002/adfm.201504197>.

Xue, C.-H., Li, Y.-R., Hou, J.-L., Zhang, L., Ma, J.-Z., and Jia, S.-T. (2015). Self-roughened superhydrophobic coatings for continuous oil-water separation. *J. Mater. Chem.* 3, 10248–10253. <https://doi.org/10.1039/c5ta01014d>.

Zhang, J., and Seeger, S. (2011). Polyester materials with superwetting silicone

nanofilaments for oil/water separation and selective oil absorption. *Adv. Funct. Mater.* 21, 4699–4704. <https://doi.org/10.1002/adfm.201101090>.

Zhang, S., Liu, H., Tang, N., Ge, J., Yu, J., and Ding, B. (2019). Direct electronetting of high-performance membranes based on self-assembled 2D nanoarchitected networks. *Nat. Commun.* 10, 1458. <https://doi.org/10.1038/s41467-019-09444-y>.

Zhang, Y., Ying, L., Wang, Z., Wang, Y., Xu, Q., and Li, C. (2021). Unexpected hydrophobic to hydrophilic transition of PET fabric treated in a deep eutectic solvent of choline chloride and oxalic acid. *Polymer* 234, 124246. <https://doi.org/10.1016/j.polymer.2021.124246>.

Zhou, H., Wang, H., Niu, H., Zhao, Y., Xu, Z., and Lin, T. (2017). A waterborne coating system for

preparing robust, self-healing, superamphiphobic surfaces. *Adv. Funct. Mater.* 27, 1604261. <https://doi.org/10.1002/adfm.201604261>.

Zhou, H., Wang, H.X., Niu, H.T., Gestos, A., and Lin, T. (2013). Robust, self-healing superamphiphobic fabrics prepared by two-step coating of fluoro-containing polymer, fluoroalkyl silane, and modified silica nanoparticles. *Adv. Fun. Mater.* 23, 1664–1670. <https://doi.org/10.1002/adfm.201202030>.

Zimmermann, J., Reifler, F.A., Fortunato, G., Gerhardt, L.C., and Seeger, S. (2008). A simple, one step approach to durable and robust superhydrophobic textiles. *Adv. Fun. Mater.* 18, 3662–3669. <https://doi.org/10.1002/adfm.200800755>.

STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
PET fabric	Beverly, Shanghai, China	single side weft knitted, 75D/72F, 24 yarn per cm in weft direction and 28 yarn per cm in warp direction
Hexadecyltrimethoxysilane	Gelest Inc.	CAS: 16,415-12-6
1,1,2H,2H-perfluorodecyltriethoxysilane	Gelest Inc.	CAS: 101,947-16-4
(3-glycidyloxy propyl)trimethoxysilane	Gelest Inc.	CAS: 2530-83-8
SiO ₂	Maikun Chemical Co. Ltd., Shanghai, China	10-20 nm in diameter
HCl	China National Medicines Co. Ltd.	36-38%, CAS: 7647-01-0
Zelan R3 (fluoro-free)	Changzhou Sconia Trading Co., Ltd.	Industrial products
PF206 (fluorinated)	Anhui Sinograce Chem Co., Ltd.	Industrial products
Others		
Adobe photoshop CS5	Adobe Systems Incorporated	https://www.adobe.com/products/photoshop.html
Origin 8.0	OriginLab Corporation	https://www.originlab.com/

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Junping Zhang (jpzhang@licp.cas.cn).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All data used in the study are included in this publication and would be made available upon request.

Any additional information required to reanalyze the data reported in this paper is available from the [lead contact](#) upon request.

This paper does not report original code.

EXPERIMENTAL MODEL AND SUBJECT DETAILS

Our study does not use experimental models typical in the life sciences.

METHODS DETAILS

Preparation of Superhydrophobic PET@HD@FD fabrics

0.2 g of SiO₂ nanoparticles, 0.9 mL of HDTMS, 0.2 mL of GPTMS and 0.25 mL of HCl were added in turn into a conical flask containing 50 mL of deionized water. The mixture was ultrasonicated for 5 min and stirred at room temperature for 1 h to form the uniform SiO₂@HD-POS emulsion. Then, the PET fabrics were immersed in the emulsion for 10 min and cured at 140°C in an oven for 2 h to form the PET@HD fabrics.

0.5 g of SiO₂ nanoparticles, 0.75 mL of PFDTES, 0.4 mL of GPTMS and 0.25 mL of HCl were added in turn into a conical flask containing 50 mL of deionized water. The mixture was ultrasonicated for 5 min and stirred at room temperature for 4 h to form the uniform SiO₂@FD-POS emulsion. Then, the PET@HD fabrics were immersed in the emulsion for 10 min and cured at 140°C in an oven for 4 h to obtain the PET@HD@FD fabrics.

Preparation of superhydrophobic fabrics using commercial reagents

10 mL of Zelan R3 was added into a 500 mL beaker containing 190 mL of deionized water. Then, the PET fabric was immersed in the emulsion for 10 min and cured at 140°C for 4 h to form the superhydrophobic Z-PET fabric. The superhydrophobic P-PET fabric was prepared via the same procedure using PF206.

Measurement of WSA

For the fabric surface is macroscopically uneven, the traditional contact angle measurement is unable to accurately evaluate wettability of superhydrophobic fabrics. Therefore, the WSA was employed to evaluate superhydrophobicity of the fabrics instead of contact angle and sliding angle according to previous studies (Wu et al., 2013; Zhang and Seeger, 2011; Zimmermann et al., 2008). A minimum of five places were tested for each sample and the average values with standard errors were reported.

Evaluation of abrasion and washing durability

The abrasion durability of the superhydrophobic fabrics was tested using a Matindale tester (YK2354, Dongguan Yaoke Instrument Equipment Co. Ltd., China) according to the standard of ASTM 4966 (Zhou et al., 2017). The abrasion test was carried out at 12 kPa, which is usually used to evaluate fabrics for heavy duty upholstery usages. A standard fabric was employed as the abradant.

The washing durability of the superhydrophobic fabrics was evaluated according to the AATCC 61-2006 2B test method. The fabric (5 cm × 15 cm) was put in the container together with 150 mL of tag solution containing 0.15 wt% detergent and 50 stainless steel balls. The fabric was washed for 45 min at 49°C with a stirring speed of 40 rpm. This standard washing procedure (45 min) has the same effect as five cycles of home machine laundering. Then, the fabric was rinsed with deionized water and dried at 60°C for 30 min.

After the abrasion and washing tests, the changes in the WSA of the superhydrophobic fabrics were recorded to evaluate their abrasion and washing durability.

Evaluation of self-cleaning performance

First, the fabrics (5 × 15 cm) were contaminated with three square stains (2 × 2 cm) by spraying 130 μL of blue-black ink evenly onto them, and then dried at room temperature for 30 min. The fabrics were also contaminated by other ways, such as impact of 1.0 mL of blue-black ink from 80 cm height onto the 45° tilting fabrics and pressing 0.5 g of tomato sauce under 15 kPa on the fabrics.

The contaminated fabrics were washed according to the AATCC 61-2006 2B test method but without any detergent. 150 mL of deionized water and 50 stainless steel balls 6 mm in diameter together with the fabric were put into a standard washing machine (YK-062, Dongguan Yaoke Instrument Equipment Co. Ltd., China) and washed for 5 min at 49°C with a stirring speed of 40 rpm. Then, the laundry water was replaced with deionized water and the fabric was further washed for another 4 min. Finally, the self-cleaned fabric was rinsed with deionized water, and then dried at 60°C for 30 min. This standard washing procedure (9 min) is equivalent to one cycle of home machine laundering.

The color parameters of the pristine, contaminated and self-cleaned fabrics were evaluated using the CIE 1976 $L^*a^*b^*$ colorimetric method with a Color-Eye automatic differential colorimeter (X-Rite, Ci 7800), where L^* is the color lightness (0 for black and 100 for white), a^* is the red (+)/green (−) axis, and b^* is the yellow (+)/blue (−) axis (Wang et al., 2021). The changes in L^* , a^* and b^* values were used to evaluate self-cleaning performance of the fabrics.

Evaluation of pressure-resistance

The pressure-resistance of the superhydrophobic fabrics was evaluated via various tests as shown below.

- (i) Hydrostatic pressure-resistance: The fabrics were kept at 1.0 m depth in deionized water. After a period of time, the fabrics were taken out of water and their appearance was checked (wet or dry). If the fabrics remained dry, the instant WSA of the fabrics was immediately recorded after being taken out of water (without drying).

- (ii) Water impalement resistance: The water impalement resistance of the fabrics was studied by letting water droplets (10 μL) impact the 45° tilted fabrics from different release height. The maximum release height of water droplets the fabrics can withstand, i.e., no impalement, was recorded.
- (iii) Laundry shearing resistance: The fabrics were washed according to the AATCC 61-2006 2B test method but without any detergent. During washing, the fabrics were sheared with the 50 stainless steel balls. After being washed for a period of time, the fabrics were taken out of water and their appearance was checked (wet or dry). If the fabrics remained dry, the instant WSA of the fabrics was immediately recorded after being taken out of water (without drying).
- (iv) Squeezing & shearing resistance: The squeezing & shearing resistance of the fabrics was evaluated using a Matindale tester according to the standard of ASTM 4966. (Zhou et al., 2017) Two pieces of the same fabrics were fixed on the Matindale tester and an ink droplet (20 μL) was put between the fabrics. The droplet was squeezed & sheared under 9 kPa for 10 cycles. After the test, the appearance of the fabrics was checked.

Evaluation of vapor-resistance

A 250 mL beaker was covered by a plastic sheet with a 2 × 2 cm hole at the center and the fabric was kept 2 cm above the hole. Then, the water (~200 mL) in the beaker was boiled on a heating plate to generate hot vapor (~90°C). After being exposed to the hot vapor for 5 min, the weight increase of the fabric was recorded and its appearance was checked (wet or dry). If the fabric remained dry, the instant WSA of the fabric was immediately recorded after being taken out of the vapor (without drying).

Characterization

The micrographs of the samples were taken using a field emission SEM (JSM-6701F, JEOL). Before SEM observation, all samples were coated with a layer of gold film. The elemental maps of the samples were obtained using an EDS of SEM. FTIR spectra of samples were recorded using a Thermo Nicolet Nexus TM spectrophotometer in the range of 4,000-400 cm^{-1} using KBr pellets. ATR-FTIR spectra of samples were collected using a Fourier transform infrared spectrometer (Nicolet 5700). The surface chemical composition of samples was analyzed via XPS using a VG ESCALAB 250 Xi spectrometer equipped with a monochromated AlKa X-ray radiation source and a hemispherical electron analyzer. The spectra were recorded in the constant pass energy mode with a value of 100 eV, and all binding energies were calibrated using the C 1s peak at 284.6 eV as the reference. The adhesive force of droplets (9 μL) on the fabrics was measured by a high-sensitivity microelectromechanical balance system (Dataphysics DCAT11, Germany). The tensile strength of the fabrics was measured using a universal testing machine (CMT4304, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China) equipped with a 1000 N load cell at room temperature. The air permeability of the fabrics was measured by a digital fabric air permeability tester (GH-461E, Guangzhou Chuangda Instrument Co., Ltd. Guangzhou, China).

QUANTIFICATION AND STATISTICAL ANALYSIS

The statistical results of WSA, L^* , b^* and adhesion force were tested from 5 different places of each sample. The statistical results of weight change was tested 5 times for each sample.