ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

Robust Polypropylene Fabrics Super-Repelling Various Liquids: A Simple, Rapid and Scalable Fabrication Method by Solvent Swelling

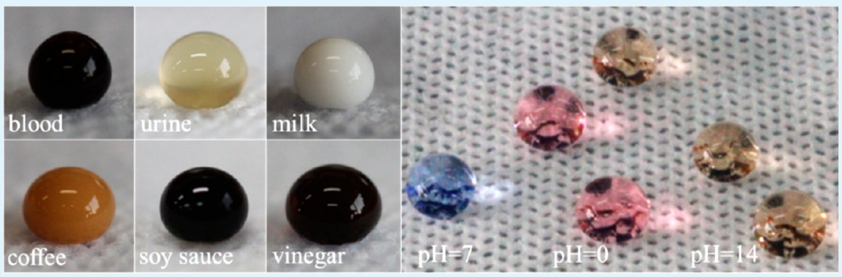
Tang Zhu,[†,‡] Chao Cai,[†,‡] Chunting Duan,[†,‡] Shuai Zhai,[†] Songmiao Liang,[§] Yan Jin,[§] Ning Zhao,*[,‡] and Jian Xu*[,‡]

[†]Beijing National Laboratory for Molecular Sciences, Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[‡]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[§]Vontron Technology Co., Ltd., Wudang District, Guiyang, Guizhou 550018, P. R. China

Supporting Information



ABSTRACT: A simple, rapid (10 s) and scalable method to fabricate superhydrophobic polypropylene (PP) fabrics is developed by swelling the fabrics in cyclohexane/heptane mixture at 80 °C. The recrystallization of the swollen macromolecules on the fiber surface contributes to the formation of submicron protuberances, which increase the surface roughness dramatically and result in superhydrophobic behavior. The superhydrophobic PP fabrics possess excellent repellency to blood, urine, milk, coffee, and other common liquids, and show good durability and robustness, such as remarkable resistances to water penetration, abrasion, acidic/alkaline solution, and boiling water. The excellent comprehensive performance of the superhydrophobic PP fabrics indicates their potential applications as oil/water separation materials, protective garments, diaper pads, or other medical and health supplies. This simple, fast and low cost method operating at a relatively low temperature is superior to other reported techniques for fabricating superhydrophobic PP materials as far as large scale manufacturing is considered. Moreover, the proposed method is applicable for preparing superhydrophobic PP films and sheets as well.

KEYWORDS: *fabrics, polypropylene, recrystallization, superhydrophobic, swelling*

1. INTRODUCTION

Superhydrophobic surfaces are those with a water contact angle (CA) over 150° and a small sliding angle (SA).[1] The superhydrophobic phenomena have been studied extensively since Barthlott demonstrated the self-cleaning effect of lotus leaf in 1997.[2,3] Many other functions such as friction reduction, anti-icing, antifog, anticorrosion can also be expected from the ultrawater-repellency.[4−12] Two factors should be considered when constructing a superhydrophobic surface: an appropriate surface roughness and a low surface energy.[13−22] So far, diverse methods and superhydrophobic materials have been reported, but cheap materials, simple and rapid preparing processes, robustness and durability of superhydrophobicity are still challenging for the practical applications.[23,24]

Polypropylene (PP), as one of the most widely used plastics, owns excellent comprehensive performances like nontoxicity, high strength and hardness, good wear resistance, eminent fatigue resistance, good chemical stability, and low price. PP products, such as fibers, films, sheets and pipes, are widely used in household appliances, automobiles, furniture, packaging industry and so on. To make a superhydrophobic PP surface can extend the application and performance of PP materials in many fields. Erbil et al. fabricated superhydrophobic gel-like PP coating from its solution by using a good/poor solvent mixture under a controlled drying temperature.[25] This good/poor solvent method is prevalent to fabricate superhydrophobic PP coatings.[26−28] However, superhydrophobic PP coatings can also be obtained by solution casting method without using the poor solvent, but the hydrophobicity was easily affected by the concentration of the polymer solution, the mass coated per unit area or the thickness of the coating etc.[29−31] Because of the high degree of crystallinity, PP is hard to dissolve. A high temperature (above 120 °C, in general) and long-term stirring are essential to make a uniform solution. Adding heterogeneous

Received: April 8, 2015
Accepted: June 10, 2015
Published: June 10, 2015

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

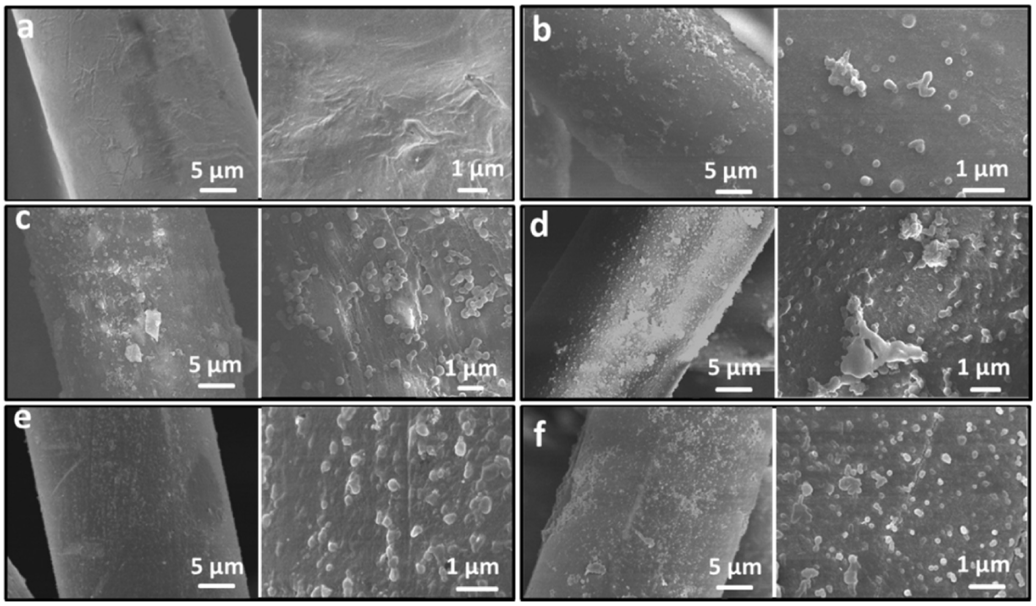


Figure 1. SEM images of the untreated PP nonwoven fabrics (a) and the fabrics treated by cyclohexane for 90 (b), 180 (c), and 300 min (d) at 70 °C and 30 (e) and 90 min (f) at 75 °C, respectively.

nucleating agents, such as halloysite nanotubes, zinc oxide nanoparticle, is another effective method to prepare superhydrophobic PP composite coatings.[32−35] These nanomaterials can accelerate the phase separation process and generate micronano multiscale structures. Templating or laminating exfoliation is a widely used technique to fabricate superhydrophobic PP materials.[36−39] For example, Hsu et al. constructed artificial Γ-shape hairs via membrane casting.[36] Similarly, template of PTFE-coated-sieves was used.[37] Transparent and superhydrophobic PP/HDPE materials were fabricated by laminating exfoliation method. This process is so instant that the materials can be delivered to customers as"peel and use".[38] Moreover, electrospinning i-PP solution or i-PP melt can obtain the superhydrophobic PP fabrics.[40,41] Besides, another methods were proposed. For example, Bekesi et al. prepared superhydrophobic PP surface via parallel laser processing followed by variothermal injection molding.[42] The technology combined injection molding with microworking robot was also introduced to construct PP micro/nano roughness.[43,44] By immersing H_2SO_4 etched PP fabrics in SiO_2/graphene oxide solution and then treating it with octyltrichlorosilane, a CA over 156° was achieved.[45] All these methods have been employed to prepare superhydrophobic PP materials successfully, but there are some disadvantages including the usage of the toxic chemicals, complicated and time-consuming processes, harsh fabricating conditions, specific equipment, high energy consumption, or unavailable for scale production.

Up to now, many of the reported superhydrophobic phenomena specially focused on the wettability of pure water.[46−50] However, other liquids in our daily life are ignored, such as milk, coffee, soy sauce, vinegar, blood and urine, which easily contaminate our clothes, table cloth, or bedclothes. Thus, it is of great significance to prepare the fabrics with the ability to repel the aforementioned liquids, especially for medical workers and those who cannot take care of themselves, like children, the elderly, and the patients.

In this research article, PP fabrics with the ability to super-repel a variety of liquids were fabricated by a solvent swelling method. The heated cyclohexane can swell PP molecules, and consequently submicron protuberances are generated through the recrystallization of the swollen polymer chains during the solvent evaporation process. The obtained superhydrophobicity demonstrates excellent durability and robustness, such as good resistances to water penetration, abrasion, acidic/alkaline solution and boiling water. Moreover, the solvent swelling method is simple, rapid, low toxic, and performed at a relatively low temperature, which make it suitable for large-scale fabrication.

2. EXPERIMENTAL SECTION

2.1. Materials. Commercially available PP nonwoven fabrics were used. The mean diameter of the fiber is about 19 μm (Supporting Information Figure S1a), and the thickness of the fabrics is about 332 μm (Supporting Information Figure S1b). Cyclohexane and chloroform of analytical grade were obtained from Beijing Chemical Works. Heptane of analytical grade was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. PP sheets were products of Deli Stationery Company (Ningbo, China). All chemicals were used as received without further purification.

2.2. Fabrication of Superhydrophobic PP Materials. Generally, 50 mL solvent in a 100 mL flask was heated to a desired temperature. PP nonwoven fabrics were immersed in the heated solvent for a certain time, and then were taken out to evaporate the residual solvent at ambient circumstance. Other PP materials were treated in similar ways.

2.3. Characterization. Water CA was characterized using a drop shape analysis instrument (KRÜSS DSA 100, Germany) at ambient temperature via a sessile drop method. A water droplet of 5 μL was employed. Each CA value was an average of five measurements made on different positions of the surface. Surface morphology was investigated by scanning electron microscope (SEM, JEOL-7500, Japan) operated at 5 kV. Differential scanning calorimetry (DSC) measurements were performed using DSC Q2000 TA Instruments-Waters LLC (America) at a heating/cooling rate of 10 °C/min in nitrogen atmosphere. Wide angle X-ray diffraction (WXRD) was performed by P2 X-ray polycrystal diffractometer (PANalytical, Holland). Cu was used as the anode material, the generator voltage was 40 kV, the tube current was 40 mA, and the scan angle (2θ) ranges from 5 to 40°. Tensile property was characterized by universal materials tester (INSTRON 3365, America) according to ISO 1184-

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

198 at a tensile rate of 50 mm/min in ambient circumstance. Resistance to water penetration-hydrostatic pressure was investigated by M018 (SDL, UK) according to ISO 811-1981, MOD. The hydrostatic pressure was applied dynamically with a water pressure rising rate of 60 cm H_2O/min. The value of the hydrostatic pressure was recorded when seepage emerged at three positions. Abrasion resistance measurement was carried out by felt using circular locus method and the hammer weighted 395 g. After 2000 times, contact angle and surface morphology were characterized again.

3. RESULTS AND DISCUSSION

3.1. Swelled by Cyclohexane. PP with a high degree of crystallinity is difficult to dissolve. Generally, the most frequently used solvents like xylene, decalin, and trichlorobenzene are highly toxic. However, cyclohexane, with low toxicity, can swell PP at a temperature higher than 60 °C.[51,52] Herein, cyclohexane was used to treat PP nonwoven fabrics. Figure 1a shows that the surface of the untreated PP fabrics is featureless. However, surface roughness of the fabrics increases after immersing the fibers in cyclohexane at 70 °C for a certain period of time. Several hundred nanometers' protuberances form on the fiber and some aggregations can also be observed (Figure 1b–d). In addition, the amount of the protuberances increases with prolonging the treating time (Figure 1b–d). The submicrometer sized protuberances get the surface roughness increase, and in combination with the inherent hydrophobicity of polypropylene (the surface tension is about 29.4 dyn/cm[53]), the water repellency of the fabrics is improved. As shown in Figure 2, water contact angle (CA) of the fabrics increases as

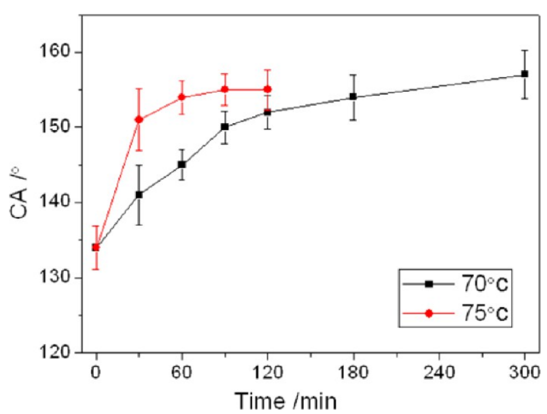


Figure 2. Water CAs of PP nonwoven fabrics treated by cyclohexane with different time at 70 and 75 °C, respectively.

the immersing time further increases, and the superhydrophobic PP fabrics with a CA larger than 150° can be obtained when the immersing time exceeds 90 min.

The preparing time of the superhydrophobic PP fabrics can be shortened by elevating the temperature. At 75 °C, the submicron protuberances also form on the fiber surface (Figure 1e and f). Compared to the morphology of the fibers treated at 70 °C, elevating temperature leads to the formation of large amount of protuberances in a shorter period of time (Figure 1e and f). The critical time to make the superhydrophobic PP fabrics decreases from 90 min (70 °C) to 30 min (75 °C) (Figure 2). This can be ascribed to the higher swelling degree of the fibers at the elevated temperature. Since more PP molecular chains would be swelled at the higher temperature in the same treating period, more protuberances can form through the recrystallization of the swollen macromolecules during the solvent evaporation process. Elevate the temperature to 80 °C, the critical time to prepare superhydrophobic PP fabrics can be shortened further. However, the fiber turns to be very porous (Figure S2a in the Supporting Information), and the mechanical strength decreases so dramatically that the fabrics can be easily torn up. This phenomenon indicates that certain amount of PP molecules could dissolve into the solvent at a too high temperature, resulting in the destruction of the integrity of the fabrics.

3.2. Swelled by Cyclohexane/Heptane Mixture. Taking the superhydrophobicity, mechanical strength and preparing time into account, the method is optimized. Heptane, having a less efficiency in swelling PP, was chosen to dilute cyclohexane. After immersing the fabrics in heptane at 80 °C for 120 min, the surface morphology of PP fabrics do not show detectable change (Figure S2b in the Supporting Information). Superhydrophobic PP fabrics can only be obtained by treatment in heptane at 95 °C for more than 100 min (Figure S3 in the Supporting Information). Submicron protuberances, grooves or holes form on the fibers, and the water CA increases as a result (Figure S3 in the Supporting Information). However, heptane is not the best choice for the fabrication of superhydrophobic PP fabrics because of the high temperature and long treating time. Herein, preferable preparation conditions for the superhydrophobic PP fabrics are proposed, that is using the mixture of cyclohexane and heptane. Two mixed solvents, that is, solvent A cyclohexane/heptane = 1/1 (volume ratio) and solvent B cyclohexane/heptane = 1/2 (volume ratio) were adopted at 80 °C. The SEM and CA images after treatment are shown in Figure 3. The SEM images demonstrate that a large

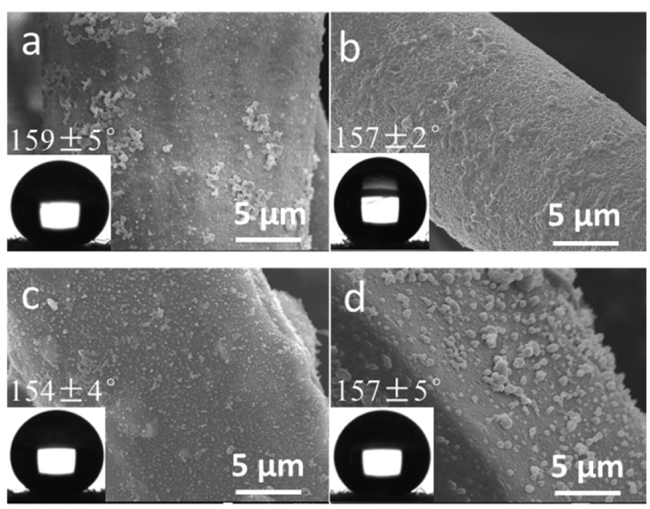


Figure 3. SEM images of PP fabrics treated by the mixed solvent A for 10 s (a) and 5 min (b), and by the mixed solvent B for 10 s (c) and 5 min (d) at 80 °C, respectively. The insets are the corresponding water CA images.

number of granular aggregations appear on the surface, and the CAs are higher than 150°. More interestingly, the mixed solvents do shorten the preparing time, and the superhydrophobicity can be achieved in 10 s. In addition, when the immersing time increases to 5 min, some grooves emerge on the surface of the fiber treated by solvent A (Figure 3b) while protuberances with larger size for the samples treated by solvent B (Figure 3d). The difference may be due to the fact

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

that solvent A with a higher concentration of cyclohexane may dissolve some PP molecules at 80 °C.

3.3. Repellency to Various Liquids. The resultant superhydrophobic PP fabrics show a CA over 150° and a small water sliding angle as well. A 5 μL water droplet sticks on the pristine PP fabrics surface even when the surface is upside down (Figure S4a in the Supporting Information). After treatment with the mixed solvent, the water droplet would slide off at a sliding angle of 23° (Figure S4b in the Supporting Information). When water droplets of about 80 μL were dropped on the fabrics tilted at an angle of about 10°, water droplets could easily roll off from the treated fabrics while adhere on the untreated fabrics (Supporting Information Figure S4c and Movie S1). Thus, the water repellency is improved after immersing the fabrics in the heated solvent for a very short time. Because of the increase of the surface roughness, air can be trapped into the microstructures as a solid−liquid barrier. The air cushion decreases the contact area between the droplet and surface and thus the liquid droplets can roll off easily.[54−59] The prepared superhydrophobic PP fabrics can also repel other liquids. Some liquids in daily life, such as milk, coffee, vinegar, and soy sauce, can rest on the surface in a sphere shape and can roll off easily with slight tilt or shake (Figure 4). Therefore, the fabrics show promising applications as garment, apron, table cloth and so on. Moreover, the superhydrophobic PP fabrics can also super-repel body fluids like blood and urine, which means they are potential to be applied as medical and health supplies, such as protective garments and diaper pads.

Figure 4. Digital photos of various liquid droplets of about 80 μL in volume resting on PP nonwoven fabrics treated by solvent B for 10 s at 80 °C.

3.4. Crystallization Behavior. The degree of crystallinity is calculated through the melting enthalpy ratio of the sample and 100% crystalline i-PP. The equilibrium enthalpy of fusion of 100% crystalline i-PP is 8.7 kJ/mol[60] and the corresponding melting enthalpy is 207 J/g. DSC results (Table 1 and Figure S5 in the Supporting Information) show that the crystallinity degrees of the pristine and superhydrophobic fabrics are 41.7% and 46.0%, respectively. The increase may be caused by the recrystallization occurred after the solvent treatment. However, the increment (4.3%) is slight because the immersing time is so short that only the polymer chains on the surface are swelled and recrystallized. In addition, from the WXRD patterns, several distinct diffraction peaks at 2θ values of approximately 13.9, 16.7, 18.4, 21.1, and 21.7 can be seen, corresponding to the (110), (040), (130) and overlapping (131) and (111) crystal planes, respectively (Figure 5a). They are typical characteristic peaks of α-crystal of PP.[61,62] The peak width at half-height of the characteristic peaks of (110), (040), (130) between the untreated and treated fabrics show no obvious variation, however, the intensity of the overlapping (131) and (111) peaks increases. The integral area indicates that the degree of the crystalline increases slightly, which is in agreement with DSC results. DSC and WXRD investigations confirm the occurrence of the recrystallization after the solvent treatment, which contributes to the formation of the microstructures on the fiber surface and the improved water repellency. However, the recrystallization occurred only on the fiber surface due to the short swelling time, and the integrity of the fabrics does not change. As a result, the mechanical properties of the fabrics largely remained after the solvent treatment. As shown in Figure 5b, the tensile strength of the superhydrophobic fabrics decreases by 18.2%, and the elongation increases by 39.1% after the solvent treatment. The decrease in the tensile strength may be the result of the recrystallization reducing the orientation of the polymer chains on the fiber surface and the formed rough microstructures acting as defects for the local stress concentration. The treated fabrics shrink to a certain degree owing to the existence of the internal stress during the fabrics preparation. Because of the shrinkage, the thickness of the fabrics increases from 331 to 422 μm (Supporting Information Figure S1c). Therefore, the increase of the elongation of the superhydrophobic PP fabrics is largely due to the shrinkage of the fabrics after the treatment. For the samples treated in cyclohexane at 70 °C, we do find that the degree of the crystallinity increases and the tensile strength decreases with the treating time, which corroborates our explanation (Supporting Information Figure S6).

3.5. Hydrostatic Pressure Measurement. Resistance to water penetration is important for waterproof fabrics. The test of resistance to water penetration was investigated by M018 (SDL, UK) according to ISO 811-1981, MOD. The hydrostatic pressure was applied dynamically with a water pressure rising rate of 60 cm H_2O/min and the value of the hydrostatic pressure was recorded when seepage emerged at three positions. As shown in Figure 6a, the hydrostatic pressure of the prepared superhydrophobic fabrics is 26.0 ± 2.5 cm water while that of the untreated fabrics is 10.8 ± 1.9 cm. The improvement can be ascribed to the rough structure on the fibers. Compared to the smooth fiber surface, the rough structure of the superhydrophobic fabrics can trap more air, which can resist water permeation. The "air layer effect" will disappear and the Cassie state will transform to Wenzel state when the pressure exceeds the threshold.[63−65]

Table 1. DSC Results of PP Fabrics before and after Treated by the Mixed Solvent B for 10 s at 80 °C

	melting temperature (°C)	crystallization temperature (°C)	melting enthalpy (J/g)	crystallization enthalpy (J/g)	degree of crystallinity (%)
before	163	119	86.3	95.5	41.7
after	163	120	95.3	107.1	46.0

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

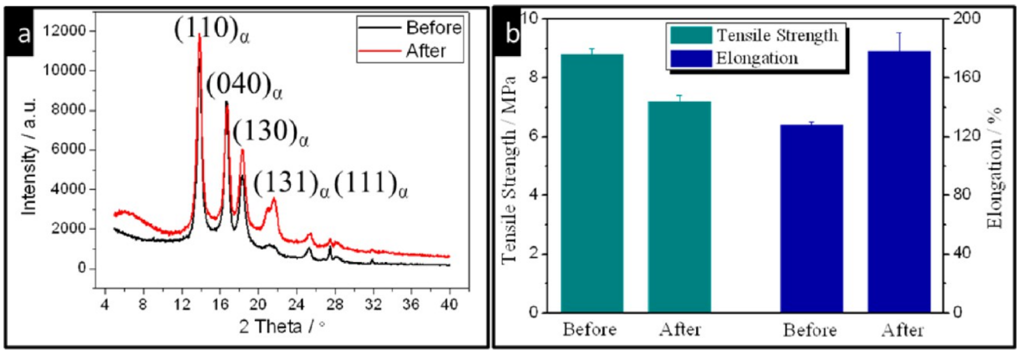


Figure 5. WXRD patterns (a) and mechanical properties (b) of PP fabrics before and after treated by the mixed solvent B for 10 s at 80 °C.

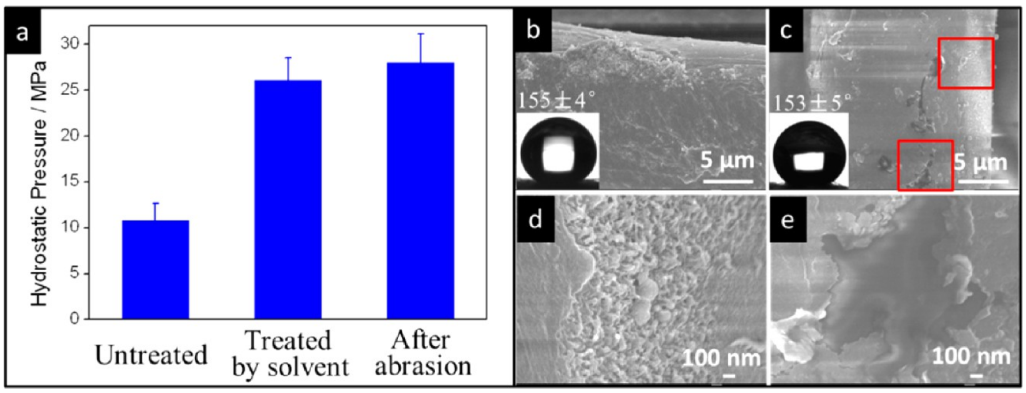


Figure 6. Hydrostatic pressure values of the PP fabrics: untreated and superhydrophobic fabrics before and after 2000 times abrasion (a). SEM images of the superhydrophobic fabrics before (b) and after (c) abrasion test. The high-magnification images of (c) show the retained protuberances (d), and the destruction of the protuberances (e), respectively. The insets are the corresponding water CA images.

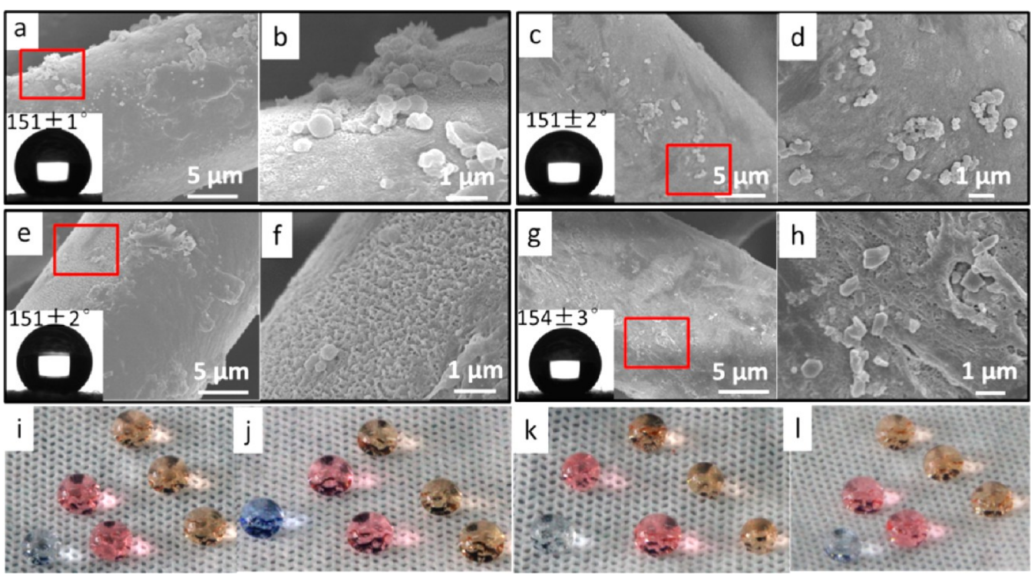


Figure 7. SEM and CA images of the superhydrophobic PP fabrics after immersed in aqueous solution of 1 mol/L HCl (a, b), 0.1 mol/L NaOH (c, d), and boiling water (e, f) for 24 h, and after exposure to the natural environment for 10 months (g, h). The high-magnification images of panels a, c, e, and g are shown in panels b, d, f, and h, respectively. The insets are the corresponding water CA images. The digital images (i–l) show the water droplets with different pH values setting on the fabrics after the corresponding treatment indicated in panels a–h. The pH values of the blue, pink, and orange water droplets are 7, 0, and 14, respectively.

3.6. Robustness and Durability of the Superhydrophobicity. The weakness of the superhydrophobicity limits the practical applications of the superhydrophobic materials. The abrasion test was carried out by felt using circular locus method with a hammer of 395 g. After abrasion 2000 times, water CA of the fabrics remains over 150° (Figure 6c). SEM images show that most of the protuberances are retained (Figure 6d) except some are worn off (Figure 6e). Since the microstructure retains, the hydrostatic pressure is about 28.0 ± 3.1 cm, comparable to that before the abrasion (Figure 6a).

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

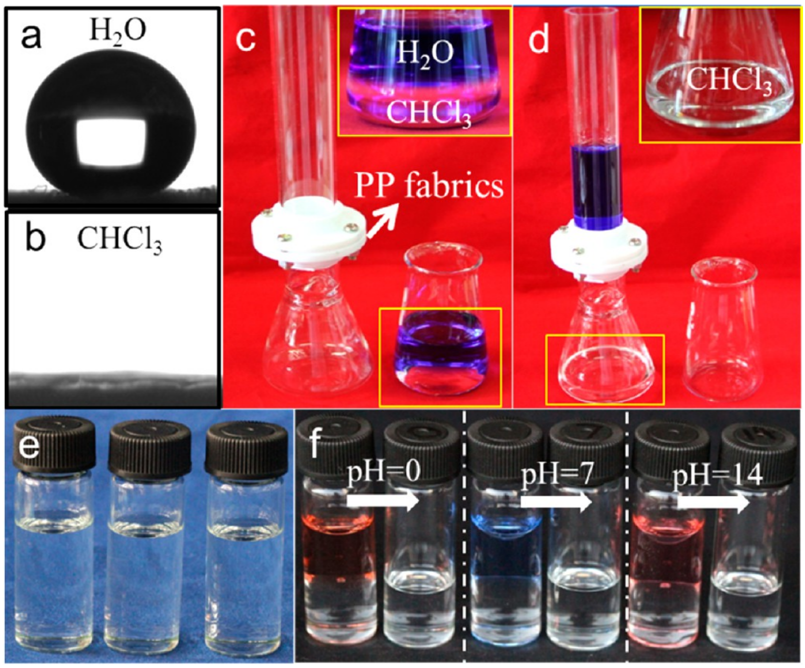


Figure 8. Contact angle images of water (a) and chloroform (b) on the superhydrophobic PP fabrics. Photographs show the oil/water separation using the superhydrophobic PP fabrics as the separation material (c, d). Photograph of the chloroform separated from water/chloroform mixture using the superhydrophobic PP fabrics after treated by 1 mol/L HCl aqueous solution or 0.1 mol/L NaOH aqueous solution or boiling water for 24 h, respectively (e). The separation of the oil/water mixtures with the water phases having different pH values (f). The water phase with different pH was dyed by ink with different colors.

The resistance to acidic/alkaline solution was tested by immersing the superhydrophobic fabrics in 1 mol/L HCl or 0.1 mol/L NaOH aqueous solution for 24 h. From Figure 7a–d, it can be seen that some of the microsized protuberances disappeared after the treatment compared with Figure 3c, however, most of the finer structures are retained. The reserved rough structures lead to the superhydrophobicity largely maintained, as a result, the water CAs only slightly decrease to 151 ± 1° and 151 ± 2°, and the sliding angles increase from 23 ± 5° to 57 ± 3° and 53 ± 5°, respectively. The good resistance to acid/alkali suggests the superhydrophobic fabrics can be used in harsh environment. Similar results can be found after immersing the superhydrophobic fabrics in boiling water for 24 h (Figure 7e, f). A water CA of 151 ± 2° and a sliding angle of 45 ± 3° were observed on the treated samples, implying the superhydrophobicity can be largely reserved after boiling sterilization. In addition, the fabrics are still superhydrophobic with a CA of 154 ± 3° after exposure to the natural environment for 10 months, as shown in Figure 7g and h. Water droplets with different pH values ranging from 0 to 14 can still rest on the surface in spherical shapes and slide off easily from the fabrics after the treatments as mentioned above, demonstrating the robustness of the superhydrophobicity (Figure 7i–l).

3.7. Oil/Water Separation. Oil spilling accidents have caused serious water pollution. The development of effective and cheap oil/water separation materials is urgent for treating the oily water. Recently, the materials with special wettability have been utilized to separate oil/water mixture.[66−73] The PP fabrics after treatment are simultaneously superhydrophobic and superoleophilic, with the water CA over 150° (Figure 8a), and oil CA of 0° (Figure 8b). The special wettability of the fabrics makes it repel water while allow the permeation of oil. A simple device for oil/water separation is designed, as shown in Figure 8c. The superhydrophobic fabrics are fixed in a PTFE valve to form a sandwich structure. After the mixture of chloroform and water was poured into the column, chloroform would pass through the fabrics while water (dyed blue) would be stored above the fabrics (Figure 8d and Supporting Information Movie S3). In addition, the flux of chloroform is about 76.4 ± 5.5 L/(m^2·s) in this device driven by gravity. However, the untreated PP fabrics cannot separate the oil/water mixture completely (Supporting Information Figure S7a and Movie S2) since it has lower resistance to hydrostatic pressure than that of the modified fabrics. Furthermore, oil/water mixture can be separated completely even the fabrics are treated either by 1 mol/L HCl, 0.1 mol/L NaOH aqueous solution or boiling water for 24 h (Figure 8e). Because of the robust superhydrophobicity of the as-prepared fabrics, it is potential to be applied in extreme environment conditions, like at high temperature or in strong acidic or alkaline circumstance. Figure 8f shows the separation of the oil/water mixtures with pH values of the water phases ranging from 0 to 14. It can be seen that pure oil can be collected from the mixtures.

4. CONCLUSIONS

In summary, superhydrophobic PP fabrics were facilely fabricated by a solvent swelling method. The fiber surface was swelled by heated solvent and then the swelled polymer chains recrystallized during the solvent evaporation process, leading to the formation of submicron protuberances. The superhydrophobic fabrics can repel various liquids, such as milk, coffee, vinegar, soy sauce, blood, and urine. Beyond that, the superhydrophobic fabrics exhibit excellent durability and resistance to water penetration, abrasion, acidic/alkaline solution and boiling water. These remarkable characteristics indicate potential applications as oil/water separation materials, protective garments, diaper pads or other medical and health

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003

supplies. Moreover, the method used here is facile, rapid, low cost, scalable, and versatile, thus it can be easily applied to prepare various types of superhydrophobic PP materials.

■ ASSOCIATED CONTENT

Supporting Information

SEM images of pristine PP fabrics, PP fabrics treated by solvent mixture B for 10 s at 80 °C, and by cyclohexane for 30 min or by heptane for 120 min at 80 °C, SEM images and water CA of PP fabrics treated by heptane for different time at 95 °C, water sliding angles of the pristine and the superhydrophobic fabrics, DSC results and mechanical properties, oil/water separation using the pristine and treated fabrics, SEM and CA images of the pristine and treated PP sheet, and movies showing water rolling behavior, oil/water separation using the untreated fabrics, and oil/water separation using the treated fabrics. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03056.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: zhaoning@iccas.ac.cn.
*E-mail: jxu@iccas.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from the Ministry of Science and Technology (2015DFG32320, 2012AA03A601, 2013CB933000) and the National Natural Science Foundation of China (21421061, 21474117).

■ REFERENCES

(1) Öner, D.; McCarthy, T. J. Ultrahydrophobic Surfaces. Effects of Topography Length Scales on Wettability. *Langmuir* **2000**, *16*, 7777−7782.
(2) Barthlott, W.; Neinhuis, C. Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces. *Planta* **1997**, *202*, 1−8.
(3) Neinhuis, C.; Barthlott, W. Characterization and Distribution of Water-Repellent, Self-Cleaning Plant Surfaces. *Ann. Bot.* **1997**, *79*, 667−677.
(4) Bhushan, B.; Jung, Y. C. Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-Cleaning, Low Adhesion, and Drag Reduction. *Prog. Mater. Sci.* **2011**, *56*, 1−108.
(5) Chen, J.; Dou, R.; Cui, D.; Zhang, Q.; Zhang, Y.; Xu, F.; Zhou, X.; Wang, J.; Song, Y.; Jiang, L. Robust Prototypical Anti-Icing Coatings with a Self-Lubricating Liquid Water Layer between Ice and Substrate. *ACS Appl. Mater. Interfaces* **2013**, *5*, 4026−4030.
(6) Chen, Y.; Zhang, Y.; Shi, L.; Li, J.; Xin, Y.; Yang, T.; Guo, Z. Transparent Superhydrophobic/Superhydrophilic Coatings for Self-Cleaning and Anti-Fogging. *Appl. Phys. Lett.* **2012**, *101*, 033701−033704.
(7) Farhadi, S.; Farzaneh, M.; Kulinich, S. A. Anti-Icing Performance of Superhydrophobic Surfaces. *Appl. Surf. Sci.* **2011**, *257*, 6264−6269.
(8) Fürstner, R.; Barthlott, W.; Neinhuis, C.; Walzel, P. Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces. *Langmuir* **2005**, *21*, 956−961.
(9) Guo, P.; Zheng, Y.; Wen, M.; Song, C.; Lin, Y.; Jiang, L. Icephobic/Anti-Icing Properties of Micro/Nanostructured Surfaces. *Adv. Mater.* **2012**, *24*, 2642−2648.
(10) Lai, Y.; Tang, Y.; Gong, J.; Gong, D.; Chi, L.; Lin, C.; Chen, Z. Transparent Superhydrophobic/Superhydrophilic TiO_2-Based Coatings for Self-Cleaning and Anti-Fogging. *J. Mater. Chem.* **2012**, *22*, 7420−7426.
(11) Liu, K.; Jiang, L. Bio-Inspired Self-Cleaning Surfaces. *Annu. Rev. Mater. Res.* **2012**, *42*, 231−263.
(12) Xu, W.; Song, J.; Sun, J.; Lu, Y.; Yu, Z. Rapid Fabrication of Large-Area, Corrosion-Resistant Superhydrophobic Mg Alloy Surfaces. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4404−4414.
(13) Feng, X. J.; Jiang, L. Design and Creation of Superwetting/Antiwetting Surfaces. *Adv. Mater.* **2006**, *18*, 3063−3078.
(14) Guo, Z.; Liu, W.; Su, B.-L. Superhydrophobic Surfaces: from Natural to Biomimetic to Functional. *J. Colloid Interface Sci.* **2011**, *353*, 335−355.
(15) Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces. *Chem. Soc. Rev.* **2007**, *36*, 1350−1368.
(16) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. Progess in Superhydrophobic Surface Development. *Soft Matter* **2008**, *4*, 224−240.
(17) Sun, T.; Feng, L.; Gao, X.; Jiang, L. Bioinspired Surfaces with Special Wettability. *Acc. Chem. Res.* **2005**, *38*, 644−652.
(18) Xue, C.-H.; Jia, S.-T.; Zhang, J.; Ma, J.-Z. Large-Area Fabrication of Superhydrophobic Surfaces for Practical Applications: An Overview. *Sci. Technol. Adv. Mater.* **2010**, *11*, 1−15.
(19) Yan, Y. Y.; Gao, N.; Barthlott, W. Mimicking Natural Superhydrophobic Surfaces and Grasping the Wetting Process: A Review on Recent Progress in Preparing Superhydrophobic Surfaces. *Adv. Colloid Interface Sci.* **2011**, *169*, 80−105.
(20) Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. Superhydrophobic Surfaces: From Structural Control to Functional Application. *J. Mater. Chem.* **2008**, *18*, 621−633.
(21) Zhang, Y.-L.; Xia, H.; Kim, E.; Sun, H.-B. Recent Developments in Superhydrophobic Surfaces with Unique Structural and Functional Properties. *Soft Matter* **2012**, *8*, 11217−11231.
(22) Zhao, N.; Xu, J.; Xie, Q.; Weng, L.; Guo, X.; Zhang, X.; Shi, L. Fabrication of Biomimetic Superhydrophobic Coating with a Micro-Nano-Binary Structure. *Macromol. Rapid Commun.* **2005**, *26*, 1075−1080.
(23) Zhang, X.; Zhao, N.; Liang, S.; Lu, X.; Li, X.; Xie, Q.; Zhang, X.; Xu, J. Facile Creation of Biomimetic Systems at the Interface and in Bulk. *Adv. Mater.* **2008**, *20*, 2938−2946.
(24) Zhao, N.; Wang, Z.; Cai, C.; Shen, H.; Liang, F.; Wang, D.; Wang, C.; Zhu, T.; Guo, J.; Wang, Y.; Liu, X.; Duan, C.; Wang, H.; Mao, Y.; Jia, X.; Dong, H.; Zhang, X.; Xu, J. Bioinspired Materials: from Low to High Dimensional Structure. *Adv. Mater.* **2014**, *26*, 6994−7017.
(25) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. Transformation of a Simple Plastic into a Superhydrophobic Surface. *Science* **2003**, *299*, 1377−1380.
(26) Franco, J. A.; Kentish, S. E.; Perera, J. M.; Stevens, G. W. Fabrication of a Superhydrophobic Polypropylene Membrane by Deposition of a Porous Crystalline Polypropylene Coating. *J. Membr. Sci.* **2008**, *318*, 107−113.
(27) He, M.; Wang, J.; Li, H.; Jin, X.; Wang, J.; Liu, B.; Song, Y. Super-Hydrophobic Film Retards Frost Formation. *Soft Matter* **2010**, *6*, 2396−2399.
(28) Hou, X.; Wang, X.; Zhu, Q.; Bao, J.; Mao, C.; Jiang, L.; Shen, J. Preparation of Polypropylene Superhydrophobic Surface and Its Blood Compatibility. *Colloids Surf., B* **2010**, *80*, 247−250.
(29) Rioboo, R.; Delattre, B.; Duvivier, D.; Vaillant, A.; De Coninck, J. Superhydrophobicity and Liquid Repellency of Solutions on Polypropylene. *Adv. Colloid Interface Sci.* **2012**, *175*, 1−10.
(30) Rioboo, R.; Voue, M.; Vaillant, A.; De Coninck, J. Drop Impact on Porous Superhydrophobic Polymer Surfaces. *Langmuir* **2008**, *24*, 14074−14077.
(31) Rioboo, R.; Voue, M.; Vaillant, A.; Seveno, D.; De Coninck, J.; Bondar, A. I.; Ivanov, D. A.; De Coninck, J. Superhydrophobic Surfaces from Various Polypropylenes. *Langmuir* **2008**, *24*, 9508−9514.
(32) Hejazi, I.; Hajalizadeh, B.; Seyfi, J.; Sadeghi, G. M. M.; Jafari, S. H.; Khonakdar, H. A. Role of Nanoparticles in Phase Separation and

Final Morphology of Superhydrophobic Polypropylene/Zinc Oxide Nanocomposite Surfaces. *Appl. Surf. Sci.* **2014**, *293*, 116−123.
(33) Liu, M.; Jia, Z.; Liu, F.; Jia, D.; Guo, B. Tailoring the Wettability of Polypropylene Surfaces with Halloysite Nanotubes. *J. Colloid Interface Sci.* **2010**, *350*, 186−193.
(34) Hou, W.; Mu, B.; Wang, Q. Studies on Wettability of Polypropylene/Methyl-Silicone Composite Film and Polypropylene Monolithic Material. *J. Colloid Interface Sci.* **2008**, *327*, 120−124.
(35) He, H.-M.; Gao, L.; Yang, X.-J.; Guo, W.-H.; Li, H.; Xie, T.; Yang, S.-K.; Wang, J.- P.; Zhang, Y.; Yang, X.-Y. Studies on the Superhydrophobic Properties of Polypropylene/Polydimethylsiloxane/Graphite Fluoride Composites. *J. Fluorine Chem.* **2013**, *156*, 158−163.
(36) Hsu, S. H.; Sigmund, W. M. Artificial Hairy Surfaces with a Nearly Perfect Hydrophobic Response. *Langmuir* **2010**, *26*, 1504−1506.
(37) Zhou, S.-S.; Guan, Z.-S.; Pang, Y. Fabrication of Polypropylene Super-Hydrophobic Surface Using PTFE-Coated-Sieves Template via Templating and Splitting Process. *Polym.-Plast. Technol. Eng.* **2012**, *51*, 845−848.
(38) Zhang, Z.-X.; Li, Y.; Ye, M.; Boonkerd, K.; Xin, Z.; Vollmer, D.; Kim, J. K.; Deng, X. Fabrication of Superhydrophobic Surface by a Laminating Exfoliation Method. *J. Mater. Chem. A* **2014**, *2*, 1268−1271.
(39) Ho, A. Y. Y.; Van, E. L.; Lim, C. T.; Natarajan, S.; Elmouelhi, N.; Low, H. Y.; Vyakarnam, M.; Cooper, K.; Rodriguez, I. Lotus Bioinspired Superhydrophobic, Self-Cleaning Surfaces from Hierarchically Assembled Templates. *J. Polym. Sci., Part B: Polym. Phys.* **2014**, *52*, 603−609.
(40) Cho, D.; Zhou, H.; Cho, Y.; Audus, D.; Joo, Y. L. Structural Properties and Superhydrophobicity of Electrospun Polypropylene Fibers from Solution and Melt. *Polymer* **2010**, *51*, 6005−6012.
(41) Patel, S. U.; Chase, G. G. Separation of Water Droplets From Water-in-Diesel Dispersion Using Superhydrophobic Polypropylene Fibrous Membranes. *Sep. Purif. Technol.* **2014**, *126*, 62−68.
(42) Bekesi, J.; Kaakkunen, J. J. J.; Michaeli, W.; Klaiber, F.; Schoengart, M.; Ihlemann, J.; Simon, P. Fast Fabrication of Super-Hydrophobic Surfaces on Polypropylene by Replication of Short-Pulse Laser Structured Molds. *Appl. Phys. A: Mater. Sci. Process.* **2010**, *99*, 691−695.
(43) Puukilainen, E.; Rasilainen, T.; Suvanto, M.; Pakkanen, T. A. Superhydrophobic Polyolefin Surfaces: Controlled Micro- and Nanostructures. *Langmuir* **2007**, *23*, 7263−7268.
(44) Rasilainen, T.; Suvanto, M.; Pakkanen, T. A. Anisotropically Microstructured and Micro/Nanostructured Polypropylene Surfaces. *Surf. Sci.* **2009**, *603*, 2240−2247.
(45) Jiang, G.; Hu, R.; Wang, X.; Xi, X.; Wang, R.; Wei, Z.; Li, X.; Tang, B. Preparation of Superhydrophobic and Superoleophilic Polypropylene Fibers with Application in Oil/Water Separation. *J. Text. Inst.* **2013**, *104*, 790−797.
(46) Kamegawa, T.; Shimizu, Y.; Yamashita, H. Superhydrophobic Surfaces with Photocatalytic Self-Cleaning Properties by Nanocomposite Coating of TiO_2 and Polytetrafluoroethylene. *Adv. Mater.* **2012**, *24*, 3697−3700.
(47) Lee, J.; Fearing, R. S. Wet Self-Cleaning of Superhydrophobic Microfiber Adhesives Formed from High Density Polyethylene. *Langmuir* **2012**, *28*, 15372−15377.
(48) Wisdom, K. M.; Watson, J. A.; Qu, X.; Liu, F.; Watson, G. S.; Chen, C.-H. Self-Cleaning of Superhydrophobic Surfaces by Self-Propelled Jumping Condensate. *Proc. Natl. Acad. Sci. U. S. A.* **2013**, *110*, 7992−7997.
(49) Bhushan, B.; Jung, Y. C.; Koch, K. Self-Cleaning Efficiency of Artificial Superhydrophobic Surfaces. *Langmuir* **2009**, *25*, 3240−3248.
(50) Zhang, X.; Guo, Y.; Zhang, Z.; Zhang, P. Self-Cleaning Superhydrophobic Surface Based on Titanium Dioxide Nanowires Combined with Polydimethylsiloxane. *Appl. Surf. Sci.* **2013**, *284*, 319−323.
(51) Kakugo, M.; Miyatake, T.; Naito, Y.; Mizunuma, K. Microtacticity Distribution of Polypropylenes Prepared with Heterogeneous Ziegler-Natta Catalysts. *Macromolecules* **1988**, *21*, 314−319.
(52) Ying, Q.; Xie, P.; Ye, M. A New Eluting Solvent for Gel-Permeation Chromatography of Isotactic Polypropylene. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 105−110.
(53) Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R.: *Polymer Handbook*; Wiley: New York, 1999; Vol. *VI*, p 525.
(54) Callies, M.; Quéré, D. On Water Repellency. *Soft Matter* **2005**, *1*, 55−61.
(55) Cassie, A.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546−551.
(56) Lafuma, A.; Quéré, D. Superhydrophobic States. *Nat. Mater.* **2003**, *2*, 457−460.
(57) Quéré, D. Non-Sticking Drops. *Rep. Prog. Phys.* **2005**, *68*, 2495.
(58) Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **2008**, *38*, 71−99.
(59) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.* **1936**, *28*, 988−994.
(60) Brandrup, J.; Immergut, E. H.; Grulke, E. A.; Abe, A.; Bloch, D. R. *Polymer Handbook*; Wiley: New York, 1999; Vol. *V*, p 23.
(61) Li, X.; Wu, H.; Huang, T.; Shi, Y.; Wang, Y.; Xiang, F.; Zhou, Z. Beta/Alpha Transformation of Beta-Polypropylene during Tensile Deformation: Effect of Crystalline Morphology. *Colloid Polym. Sci.* **2010**, *288*, 1539−1549.
(62) Luo, F.; Wang, K.; Ning, N.; Geng, C.; Deng, H.; Chen, F.; Fu, Q.; Qian, Y.; Zheng, D. Dependence of Mechanical Properties on Beta-Form Content and Crystalline Morphology for Beta-Nucleated Isotactic Polypropylene. *Polym. Adv. Technol.* **2011**, *22*, 2044−2054.
(63) Extrand, C. Repellency of the Lotus Leaf: Resistance to Water Intrusion under Hydrostatic Pressure. *Langmuir* **2011**, *27*, 6920−6925.
(64) Forsberg, P.; Nikolajeff, F.; Karlsson, M. Cassie−Wenzel and Wenzel−Cassie Transitions on Immersed Superhydrophobic Surfaces under Hydrostatic Pressure. *Soft Matter* **2011**, *7*, 104−109.
(65) Sheng, X.; Zhang, J. Air Layer on Superhydrophobic Surface Underwater. *Colloids Surf., A* **2011**, *377*, 374−378.
(66) Song, J.; Huang, S.; Lu, Y.; Bu, X.; Mates, J. E.; Ghosh, A.; Ganguly, R.; Carmalt, C. J.; Parkin, I. P.; Xu, W.; Megaridis, C. M. Self-Driven One-Step Oil Removal from Oil Spill on Water via Selective-Wettability Steel Mesh. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19858−19865.
(67) Huang, S. Mussel-Inspired One-Step Copolymerization to Engineer Hierarchically Structured Surface with Superhydrophobic Properties for Removing Oil from Water. *ACS Appl. Mater. Interfaces* **2014**, *6*, 17144−17150.
(68) Yang, H.-C.; Pi, J.-K.; Liao, K.-J.; Huang, H.; Wu, Q.-Y.; Huang, X.-J.; Xu, Z.-K. Silica-Decorated Polypropylene Microfiltration Membranes with a Mussel-Inspired Intermediate Layer for Oil-in-Water Emulsion Separation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 12566−12572.
(69) Cao, Y.; Liu, N.; Fu, C.; Li, K.; Tao, L.; Feng, L.; Wei, Y. Thermo and pH Dual-Responsive Materials for Controllable Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2026−2030.
(70) Xue, Z.; Cao, Y.; Liu, N.; Feng, L.; Jiang, L. Special Wettable Materials for Oil/Water Separation. *J. Mater. Chem. A* **2014**, *2*, 2445−2460.
(71) Zhu, Q.; Pan, Q.; Liu, F. Facile Removal and Collection of Oils from Water Surfaces through Superhydrophobic and Superoleophilic Sponges. *J. Phys. Chem. C* **2011**, *115*, 17464−17470.
(72) Ke, Q.; Jin, Y.; Jiang, P.; Yu, J. Oil/Water Separation Performances of Superhydrophobic and Superoleophilic Sponges. *Langmuir* **2014**, *30*, 13137−13142.
(73) Zhou, X.; Zhang, Z.; Xu, X.; Guo, F.; Zhu, X.; Men, X.; Ge, B. Robust and Durable Superhydrophobic Cotton Fabrics for Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208−7214.

DOI: 10.1021/acsami.5b03056
ACS Appl. Mater. Interfaces 2015, 7, 13996−14003