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Co-solvent induced nanoscale roughening in sustainable superhydrophobic coatings for versatile oil-water separation

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Abstract

Despite of the extensive effort made to construct a superhydrophobic surface in labs, achieving a short processing time and via a sustainable production route remains a challenge for practical applications. Here, with tetrahydrofuran and n-hexane as co-solvent, we demonstrate that roughness can be induced on polydimethylsiloxane (PDMS) coatings to achieve superhydrophobic coatings on different types of substrates including woven fabrics, non-woven fabrics, and melamine sponge. The sample constructed without adding particles exhibited excellent performance for versatile oil-water separation of mixtures of heavy oil and water, light oil and water, as well as oil-water emulsion. The best solvent proportioning and the corresponding forming mechanism were explored. Due to the great solubility of the PDMS in the co-solvent, the dipping solution exhibited a long-time stability. We believe that this

extremely easy dipping-curing method would open up a new direction for fabricating self-roughed superhydrophobic surface through adjusting the co-solvent composition. The developed method is fast and easily scalable for industrial applications.

Keyword: superhydrophobic, co-solvent, non-particle, fluorine-free, solvent- recycled, oil-in-water emulsion separation

1. Introduction

In the past decades, superhydrophobic surface with static contact angle (CA) larger than 150° and the dynamic slide angle (SA) smaller than 10° has drawn enormous attention due to its potential application in multifarious fields such as oil-water separation,^[1-5] self-cleaning,^[6-9] liquid drag-reduction,^[10-13] anti-icing,^[14-17] and so on.^[18-25] There is an inherent demand for creating surface roughness to achieve the superhydrophobic state, however, the created surface morphology was often easily damaged during use, leading to the loss of the superhydrophobic state and the functionality. Two methods have been proposed to solve this problem. One is to find harder materials to withstand the mechanical friction during the daily use. For example, Liu et al. fabricated superamphiphobic fabrics with the treatment of argon-plasma. The as-prepared cotton fabrics displayed robust mechanical strength and excellent durability after 3500 abrasion cycles. However, since plasma treatment and nanoparticles are used, this strategy obviously increases the materials and processing cost. The other is to simplify the processing steps and decrease the cost, so that when the surface is damaged, the property could be easily repaired by repeating

the fabrication process with a minimum time and cost involved.^[26-28] Based on the second strategy, methods like dip coating and spraying coating, using low-cost materials like CaCO_3 and soot have been introduced to reduce the processing time and cost.^[29, 30] **Qahtan et al. fabricated superhydrophobic films by spray coating of candle soot dispersion. The as-prepared surface was endowed prominent water jet resistance and thermally stability. But how to keep the dipping solution stable for a long duration remained as a big challenge.**

Though perfect superhydrophobic surface can be obtained through the above mentioned strategies, adding nanoparticles potentially poses a risk to human health.^[31, 32] Alternative materials and methods with no nanoparticles should be explored. Levkin et al. put forward a versatile porous polymer coating to fabricate superhydrophobic surfaces, while the complex raw materials and complicated procedures have restricted the practical usage.^[33]

Effort has been ongoing to search for ways to create superhydrophobic surface without the use of nanoparticles or fluorine-contained agent.^[34, 35] For example, by taking THF as solvent, water as non-solvent and PDMS as binder, a superhydrophobic surface was built through phase-separation.^[36] Though the whole process is very simple and the dipping-solution can be stored for a long time, there is still a need to further simplify the process and extend the shelf life of the solution. In this work, we make use of tetrahydrofuran (THF) and n-hexane as co-solvent, PDMS has been prepared as a fluorine-free superhydrophobic coating covering different kinds of substrates such as woven fabrics, non-woven fabrics, and melamine sponge. This

wide applicability for substrates enables versatile oil-water separation for heavy oil-water, light oil-water, as well as emulsion-water. The best solvent composition and the corresponding forming mechanism were investigated. Due to the great solubility of the PDMS in the co-solvent, the dipping solution exhibited a high stability. In addition, because the co-solvent was prepared just by blending the two solutions without any other pretreatment, the dipping solution could be recycled by adding PDMS. that the developed method will not only provide a low-cost process for producing superhydrophobic materials but also open up a new perspective on how to design a superhydrophobic surface for large scale production.

2. Experimental work

2.1. Materials and reagents

Different kinds of fabrics such as viscose, silk, nylon, polyester, acrylic, wool and ramie fabrics were obtained from Shanghai Textile Industry. THF (AR, 99%), n-hexane (AR, 95%), ethyl acetate (AR, 99.5%), NaOH, NaCl, methylene blue and oil red were obtained from Chinasun Speciality Products Co., Ltd. HCl (AR), toluene (AR, 99.5%) and dichloromethane (AR, 95%) were obtained from chinasun specialty products Co., Ltd. PDMS (Dow Corning 184) was purchased from Dow Corning Corporation. Melamine sponge, coffee powder and nonwoven fabric (polyester) were purchased from local stores. Sodium dodecyl sulfate (SDS) was bought from Shanghai Aladdin Biochemical Technology Co.,Ltd.

2.2. Preparation of superhydrophobic substrates

A series of THF and n-hexane co-solvents with the volume ratio ranging from 10:0 to 0:10 were first blended. Then PDMS (pre-polymer: curing agent = 10:1) was added, the concentration of PDMS was 1.0 v%. Subsequently different kinds of substrates were soaked into the dipping solution for 30 min and then baked at 120°C for 0.5 h in a drying oven.

2.3. Preparation of oil-water mixtures and oil-in-water emulsion

Three types of oil-water mixture: heavy oil, light oil, and emulsion .were prepared. Water (dyed with methylene blue, 100 ml) and dichloromethane (100 ml) were mixed together for preparing heavy oil-water mixture. And n-hexane (dyed by oil red, 3 ml) was poured into water (90 ml) to prepare light oil-water mixture. For the surfactant-free oil-in-water emulsion, toluene mixed with water in a volume ratio of 1:99 was first stirred vigorously for 30 min and then treated by 40 kHz ultrasonication for 1 h. Surfactant-stabilized oil-in-water emulsions were prepared through the same process with the addition of 0.1 g L⁻¹ SDS.

2.4. Characterization

The surface morphology was analysed by a field emission scanning electron microscope (FESEM, Hitachi S-4800). To observe the morphology of the modified fabric clearly, the resultant fabric is pre-coated with an ultra-thin Au nanoparticle. Energy-dispersive X-ray spectrometer (EDS), Fourier transform infrared (FTIR) spectroscopy (Nicolet 5700) and X-ray photoelectron spectrometer (XPS) (Kratos Axis-Ultra HAS) were used to observe the change of chemical bonding state and composition. Krüss DSA 100 (Krüss, Germany) apparatus was used to test the static

contact angle (CA) 3 times at 5 different places for each sample with the volume of water drop of 6 μl . The same instrument was used for dynamic contact angle (SA), measured at 3 different places with the volume of water drop of 15 μl . The adhesive force was measured by a surface tension meter (Dataphysics DCAT11) at three different places with the volume of water drop of 4 μl . An atomic force microscope (AFM, Dimension Loon, Bruker) was utilized to measure the surface roughness for both fabric (1 $\mu\text{m} \times 1 \mu\text{m}$) and mica plate (10 $\mu\text{m} \times 10 \mu\text{m}$). The elongation at break and tensile strength were measured by a universal testing machine INSTRON-3365. Air permeability and flexural rigidity were characterized by a digital air permeability instrument (YG461E-11), and fabric style instrument (KESFBAUTO-A), respectively. OLYMPUS BX51WI was employed for emulsion images. A UV-vis spectrophotometer (Hitachi, UV-1080, Japan) was employed to calculate the emulsion separation efficiency. The absorbance of pure water was assumed to be 0 in the calculation.

3. Result and discussion

3.1. Experimental analysis and anti-wetting mechanism

Scheme 1 illustrates the whole preparation process. The PDMS was first dissolved in the co-solvent composed by THF and n-hexane with different volume ratios from 10:0 to 0:10. The substrates were then dried in a drying oven at 120°C for 0.5 h. The corresponding contact angle was shown in Fig. 1, together with the adhesive force with water. With increasing n-hexane, the CA increased and the adhesive force decreased. When the volume ratio reached 3:7, the CA was as large as

$156.4 \pm 0.42^\circ$ and the corresponding adhesive force was $53.6 \pm 1.52 \mu\text{N}$. Then, further increase in n-hexane led to decrease in the contact angle. Because there were no other chemical components added in these solutions, the surface roughness of the PDMS coatings should be accountable for the difference. AFM was used to analyse the surface roughness for coated fibre (Fig. 2). The result proved the root mean square (RMS) roughness value increased from $4.84 \pm 0.10 \text{ nm}$ (pure THF) to $20.77 \pm 0.31 \text{ nm}$ when the volume ratio was 3:7, followed by a decrease to $10.00 \pm 0.44 \text{ nm}$ with further increase of n-hexane content which confirmed our conjecture. Despite this, the intricate surface microstructure of the cotton fibre makes it difficult to observe the morphology change caused by the PDMS coating. So we dropped 50 μL dipping solution on mica sheet. Fig. 3 was the corresponding AFM images. With increased n-hexane component, PDMS ‘islands’ appeared, the largest island appeared when n-hexane volume ratio was 70%, and the observed tendency was consistent with that for the fabric coatings.

Scheme 1. Schematic illustration of the procedures used to construct superhydrophobic substrates.

Figure 1. CA and adhesive force for fabric modified under different volume ratio of THF and n-hexane.

Figure 2. AFM roughness images under different conditions on cotton fabrics.

Figure 3. AFM roughness images under different conditions on the mica sheets.

THF and n-hexane are both known as good solvents for PDMS, however, a single component could not result in a excellent superhydrophobic surface. While once they were blended with a suitable ratio, surface roughness changed significantly, which has contributed to a larger contact angle. It will be interesting to explore the mechanism behind to identify a generalized principle for preparing suitable co-solvent.

We find that the change of the CA is consistent with the matching degree of solubility parameter (SP) for the co-solvent and PDMS. The SP for the co-solvent is calculated accordingly to the following equation:

$$m_s = \delta_1 s_1 + \delta_2 s_2$$

where m_s is the SP for the co-solvent, s_1 and s_2 are the SP of each component, and δ_1 , δ_2 are the corresponding volume ratio. The SPs are listed in table 1 (the s is revised considering the intermolecular interaction).^[37]

Table 1. The SPs of the different solvents and PDMS.

Solvent/Polymer	SP ((J/cm³)^{0.5})
n-hexane	13.77
THF	18.19
Ethyl acetate	16.90
PDMS	14.97

When the volume fraction of n-hexane is 70%, the SP of the co-solvent matched best with the PDMS, thus the best superhydrophobic property is realized. To further verify our theory, Ethyl acetate, another good solvent for PDMS, was chosen to blend with n-hexane as co-solvent. As shown in Fig. 4, the CA of the fabric is also consistent with the SP difference. The reason why co-solvent can endow the porous substrates with superhydrophobic property may be due to the different evaporation rate of each component. As known, the evaporation rate of the n-hexane is faster than THF. During the curing process, the solubility changed sharply and unevenly, result in a non-uniformly precipitation of PDMS. The crosslinking process and spreading process compete with each other, thus leading to different surface morphology under different so-solvent conditions.^[38, 39]

Figure 4. CA for fabric modified and the SP difference under different volume ratio for ethyl acetate and n-hexane.

Besides, due to the great solubility of the PDMS in the co-solvent, the dipping solution exhibited a long-time stability. The dipping solution can be stored for more than 10 weeks without sacrificing the property (Fig. S1). This is of great significance for the commercialization of the technology.

Figure 5. (a, b) SEM images of pristine cotton fibre and modified cotton fibre, the insert picture was the SA of droplet; (c, d) the elemental mapping for C, O and Si and the corresponding EDS spectrum of the modified cotton.

Modified cotton fabric prepared with 70% volumetric composition was chosen to characterize various kinds of properties. Fig. 5a and 5b are the SEM images for pristine cotton fibre and modified fibre. Though there exists natural veins on pristine cotton fibre, the surface of the modified one is rougher. The PDMS islands inhomogeneously cover the fibre surfaces. **It is noteworthy that besides the nanoscale roughness measured by AFM, some much larger islands also existed on modified fiber surface.** This is because more dipping solution can be held between the adjacent fibres due to the wicking effect. The co-existence of micro-scale-fibre and the nano-scale

PDMS islands has resulted in the hierarchical structure leading to a SA as low as $8.4 \pm 0.42^\circ$, similar to well-known lotus effect. [40, 41]

Figure 6. (a) FTIR spectra of pristine and PDMS modified cotton. (b) The wide XPS spectra of pristine and PDMS modified cotton. (c) High resolution C 1s spectrum of modified cotton fabric.

The elemental analysis of the modified fabric surface is given by EDS mapping in Fig. 5c, which indicates uniform coverage of the PDMS over the fibre). To further understand the surface chemistry, FTIR and XPS analyses were carried out. As displayed in Fig. 6a, compared with the pristine cotton, the stretching and bending vibration absorption peaks of -OH exhibited at 3430 cm^{-1} and 1650 cm^{-1} are from the water molecule and the -OH group of the cellulose. The stretching vibration peak of -CH₂ is provided by cellulose and PDMS. A series of stretching vibrations absorption peaks of -C-O at $1160\text{-}980 \text{ cm}^{-1}$ is mainly from corresponding groups of cellulose. Two new peaks at 800 cm^{-1} and 1260 cm^{-1} are the stretching vibration and bending

vibration of Si-C, indicating the coverage of PDMS. The same conclusion can also be confirmed by XPS survey spectra. The new peaks appeared at 100.1 eV and 150.5 eV represent the Si 2p and Si 2s, respectively (Fig. 6b). Charge referenced by C-C at 284.5 eV, high resolution C 1s spectrum of modified cotton fabric is carried out (Fig. 6c), five distinct peaks at 283.1 eV, 283.8 eV, 284.5 eV, 285.3 eV, 288.0 eV are for C-Si, C=C, -CH_x (C-C and -CH₃), C-O and C=O bonds, respectively.^[29] Furthermore, as shown in Fig. 5d, the content of PDMS is very low, that means it will take less raw materials to produce the superhydrophobic fabric, which means a low cost.

Figure 7. (a, b) The effect of abrasion and laundering times on CA for the superhydrophobic cotton surface with corresponding droplet images.

Table 2. The physical properties of pristine cotton fabric and as-modified cotton fabric

Property	Pristine cotton	Modified cotton
Tensile strength (N cm⁻¹)	468.95 ± 14.42 (warp)	452.44 ± 11.48 (warp)
	401.18 ± 15.05 (weft)	370.54 ± 9.30 (weft)
Elongation at break (%)	6.99 ± 0.23 (warp)	7.54 ± 0.12 (warp)

	19.35 ± 0.95 (weft)	22.05 ± 0.44 (weft)
	1244.1 (warp)	805.2 (warp)
Flexural rigidity (mg × mm)	400.0 (weft)	361.9 (weft)
	705.4 (total)	539.8 (total)
Air permeability (mm s⁻¹)	430.4	408.6

3.2. Physical and chemical durability

Though the PDMS content is low, as modified fabric exhibited an eminent mechanical stability. Using pristine cotton fabric as abrasion surface, the abrasion test was carried under 3.5 kPa pressure. The test was carried with speed of 3 cm s⁻¹ for a travel distance of 11 cm. Each a round trip was regarded as one abrasion cycle. As shown in Fig. 7a, the coated fabric can withstand 400 cycles of abrasion without sacrificing superhydrophobic property. Apart from this, the **accelerated laundry** test was also performed according to AATCC 61-2006 standard method 2A condition (**each cycle equals with 5 times of ordinary machine washing processes**). The superhydrophobic property could be preserved even after accelerated laundrying for 6 times (Fig. 7b). This guarantees the palmary stability during daily use. The chemical stability of the modified fabric was also estimated by immersing the as-prepared fabric into acid solution (HCl, pH=1), alkali solution (NaOH, pH=14), and salt solution (NaCl, 1 M) for 24 hours. As displayed in Fig. 8, the CA of the fabric did not change. Besides, the physic property of the fabric is retained due to the gentle fabrication process as listed in Table 2. It is remarkable that the air permeability of the

modified fabric is as good as pristine cotton fabric. We supposed this was because the space between the interlaced fibres could be reserved due to the small amount of PDMS attached on the surface.

Figure 8. The CA of the droplet for modified fabric before and after immersed into acid solution (HCl, pH=1), alkali solution (NaOH, pH=14), and salt solution (NaCl, 1 M) for 24 hours, the inset images are corresponding picture of droplets on the fabric.

Figure 9. The anti-fouling property (a) and self-cleaning process (b) of the pristine and modified

superhydrophobic cotton fabric.

3.3. Anti-fouling and self-cleaning ability

The superhydrophobic surface can endow the fabric with anti-fouling and self-cleaning properties. The pristine and modified cotton fabric was immersed into methylene blue solution (0.1 M). As displayed in Fig. 9a, the pristine cotton was dyed by the solution as soon as it is in contact with the water due to the hydrophilic nature. On contrast, for the modified fabric, no methylene blue solution was adhered on to the surface after submerging it deep into the solution. This observation not only proved the great anti-fouling property but also the ability against liquid pressure. Coffee powder was used to simulate the dust contamination. When water droplets were applied onto to the superhydrophobic surface, the coffee powder was dissolved in water and taken away by the rolling water, leaving many clear traces until the whole fabric was cleaned. While as for pristine fabric, the coffee powder dissolved in water and stained the fabric.

Figure 10. (a-c) Different kinds of substrates displayed superhydrophobic property after

modification. The substrates include woven fabrics, nonwoven fabric and melamine sponge. (d) Heavy oil-water separation process. (e) Light oil-water separation process.

3.4. Versatile oil-water separation

In most of previous reports, it is difficult to realize the versatile oil-water separation for oil-water mixtures and oil-water emulsion. This is because most of them need particular substrates or special methods.^[43, 44] The self-roughening strategy taken by the current work is easily adaptable for different kinds of fabrics including hydrophobic fibre like polyester or porous substrates such as melamine sponge (Fig. 10a-c). Taking advantage of these superhydrophobic substrates, versatile oil-water separations can be realized.

Firstly, superhydrophobic cotton fabrics were utilized to separate water and heavy oil (Fig. 10d). As a proof-of-concept study, the superhydrophobic cotton fabric was laid between two glass vessels. Water (dyed with methylene blue) and heavy oil (dichloromethane) were mixed together and then poured down into the upper vessel. The oil quickly infiltrated the superhydrophobic-superoleophilic fabric under the action of the gravity while the water was retained. The separation efficiency was calculated based on the volume change of the water. As shown in Fig. S2b, there was nearly no change for the volume of the water, which means the separation efficiency was ~100%. The same test was performed for 5 times (Fig. S2c). The result attests the excellent performance for repeated separation.

Nonwoven fabric made from polyester was chosen to absorb light oil (n-hexane, dyed by oil red) floating on the surface of water. The adsorption capacity was

guaranteed by porosity and the thickness of the fabric. As seen in Fig. 10e, the light oil was absorbed rapidly, while the water was repelled because of the superhydrophobic property of the fabric.

Figure 11. (a-c) The optical image for surfactant-free emulsions with corresponding micrographs before and after separation. (d-f) The optical image of surfactant-stabilized emulsions with corresponding micrographs before and after separation.

Melamine sponge was selected for separation of oil-water emulsion. The emulsion drops will emerge together when thrust into the porous structure of the sponge.^[45, 46] When the prepared sponges were placed into the emulsion with vigorous stirring, the solution gradually became transparent because the emulsion drops aggregated and were absorbed by the sponge. As exhibited in Fig. 11, plenty of emulsion drops suspended in the solution for both surfactant-free and surfactant-stabilized emulsions before the adsorption test. After being purified, the

amount of emulsion drops decreased sharply. The separation efficiency was characterized by calculating the light absorbance in visible region (300 nm to 800 nm). The results showed that the separation efficiency for surfactant-free and surfactant-stabilized emulsions was 97.02% and 94.89%, respectively (Fig. 12).

Figure 12. The absorbance of surfactant-free and surfactant-stabilized emulsions before and after purified by superhydrophobic sponge.

4. Conclusion

Using THF and n-hexane as co-solvent, PDMS could be self-roughened during the coating formation process, providing a non-particle route towards superhydrophobic surfaces for a wide range of substrates including woven fabrics, non-woven fabrics, and melamine sponge. The coatings with the best solvent composition and the corresponding forming mechanism were explored. The result shows that the superhydrophobic property of the fabric is related to the matching degree of SP for the co-solvent and PDMS. The higher the degree of matching, the better the superhydrophobic property. Due to the great solubility of the PDMS in co-solvent, the dipping solution exhibited a long-time stability. As a proof of concept, the PDMS coated fabrics and sponges were utilized for versatile oil-water separation

for heavy oil-water and light oil-water mixtures, and oil-water emulsion. We believe that this extremely easy dipping-curing method would open up a new direction for fabricating environmental-friendly, low-cost, and scalable superhydrophobic coatings for a range of industrial applications.

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Supporting information

Co-solvent induced roughening in fluorine-free superhydrophobic coatings for versatile oil-water separation

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Figure S1. (a) The images of the dipping solution for new prepared and after stored for 10 weeks. (b) The cotton fabric modified by the dipping solutions (new prepared and after stored for 10 weeks), the insert images are corresponding CA pictures.

Figure S2. The change for the volume of the water and oil before and filtrated for one

and five times. (a) the initial volume of the water and the heavy oil; (b) the volume of the water and the heavy oil after the mixture was filtrated for one time; (c) the volume of the water and the heavy oil after the mixture was filtrated for three times.