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Selective, Spontaneous One-Way Oil-Transport Fabrics and Their Novel Use for Gauging Liquid Surface Tension

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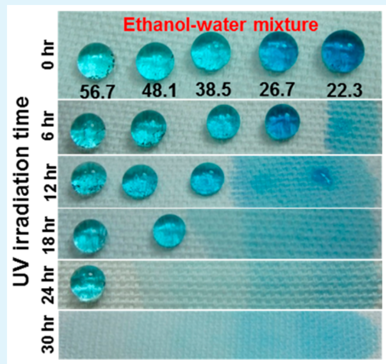
Supporting Information

ABSTRACT: Thin porous materials that can spontaneously transport oil fluids just in a single direction have great potential for making energy-saving functional membranes. However, there is little data for the preparation and functionalities of this smart material. Here, we report a novel method to prepare one-way oil-transport fabrics and their application in detecting liquid surface tension. This functional fabric was prepared by a two-step coating process to apply flowerlike ZnO nanorods, fluorinated decyl polyhedral oligomeric silsesquioxanes, and hydrolyzed fluorinated alkylsilane on a fabric substrate. Upon one-sided UV irradiation, the coated fabric shows a one-way transport feature that allows oil fluid transport automatically from the unirradiated side to the UV-irradiated surface, but it stops fluid transport in the opposite direction. The fabric still maintains high superhydrophobicity after UV treatment. The one-way fluid transport takes place only for the oil fluids with a specific surface tension value, and the fluid selectivity is dependent on the UV treatment time. Changing the UV irradiation time from 6 to 30 h broadened the one-way transport for fluids with surface tension from around 22.3 mN/m to a range of 22.3−56.7 mN/m. We further proved that this selective one-way oil transport can be used to estimate the surface tension of a liquid simply by observing its transport feature on a series of fabrics with different one-way oil-transport selectivities. To our knowledge, this is the first example to use one-way fluid-transport materials for testing the liquid surface tension. It may open up further theoretical studies and the development of novel fluid sensors.



KEYWORDS: *one-way fluid transport, directional fluid transport, liquid transport, fabric, sensor, surface tension, coating*

■ INTRODUCTION

Spontaneous, one-way fluid transport is highly desirable for various applications from water harvesting, microfluidics, and membrane separation to functional clothing and defense. Such a "smart" property has been reported mainly on open solid surfaces,[1−6] single filaments,[7−13] and thin porous materials.[14−19] On open solid surfaces, one-way fluid transport is often driven by opposite wettability in the adjacent areas. A typical example is a Stenocara Beetle's back, which contains an array of hydrophilic bumps on a hydrophobic surface.[1] When tiny water droplets attach to the surface, they move into the hydrophilic areas. A similar moisture movement was reported on spider silk, which has alterations of the surface hydrophilicity/hydrophobicity and diameter along the silk length.[7] On the basis of Nature's examples, one-way water-transport films and filaments have been developed for water-harvesting purposes.[2−6,9−13]

One-way liquid transport through a porous material was mainly reported on fabrics and nanofibrous membranes.[14−19] In theory, liquid transport through a porous structure is more complicated than that on an open solid surface or filament because liquid in a porous structure often receives capillary action. According to Young's equation, the capillary force (P_c) formed in a cylindrical capillary channel can be calculated as $P_c = -[(2\gamma \cos \theta)/r]$ (where θ is Young's contact angle (CA) of the channel wall, γ is the liquid surface tension, and r is the cylinder radius). When the pore is hydrophilic (i.e., $\theta < 90°$), a positive capillary force forms to draw the liquid into the capillary channel, whereas the liquid will be repelled off a hydrophobic channel (i.e., $\theta > 90°$) because of the negative capillary force. It is generally known that liquid does not spread into a porous structure if it is not wettable. However, our and other researchers' recent studies have indicated that a single-layer fibrous membrane consisting of a hydrophobic layer on one side and a hydrophilic layer on the other could allow liquid water to penetrate across the nonwetting layer and wick into the wettable matrix, whereas an external force has to be applied to enable liquid transport in the opposite direction.[14,16−19] Such an unexpected one-way water transport could proactively move sweat off the body side, hence improving perspiration, useful for making sportswear and soldiers' uniform garments.

Oil transport in one direction could even be more useful because of the diversity of oil fluids (e.g., organic fluids, fuels, and low-melting-point chemicals) and their wide use in daily life and industry. However, one-way oil transport and its functionality have not been well studied until very recently by

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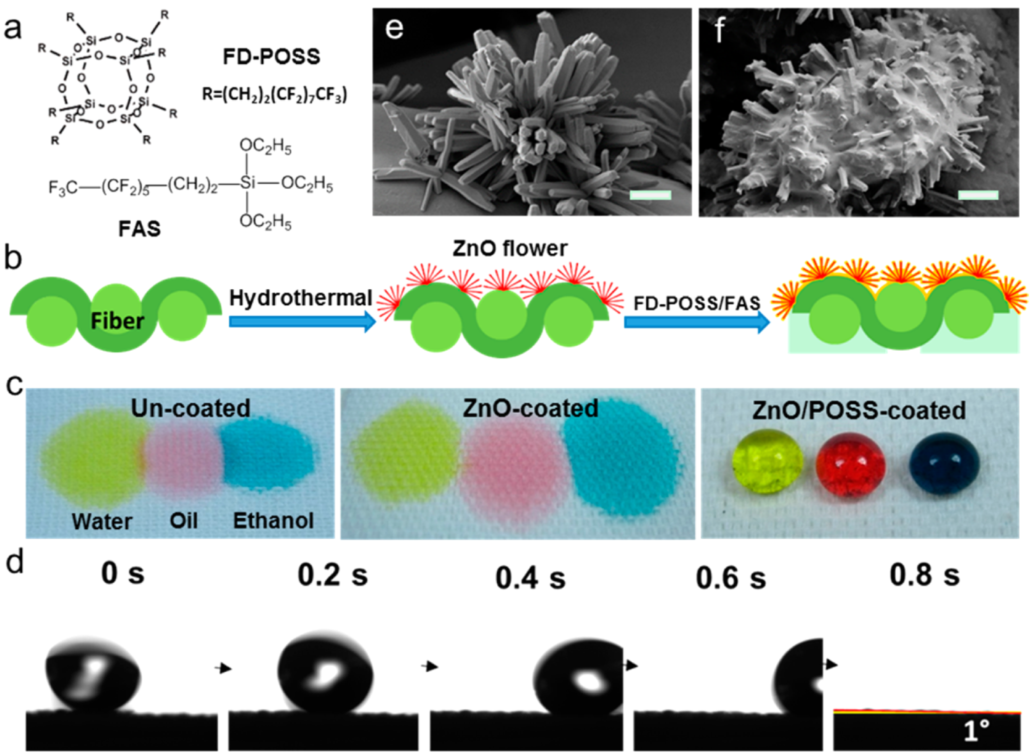

Figure 1. (a) Chemical structures of the coating materials, (b) coating procedure, (c) photographs of yellow-colored water, red-colored cooking oil, and blue-colored ethanol (volume 35 μL) on cotton fabrics, (d) still frames taken from a video to show a water droplet (5 μL) sliding off a 1°-tilted ZnO/POSS-coated fabric. SEM images of the cotton fabric (e) after ZnO treatment and (f) after both ZnO and FD-POSS/FAS treatment (scale bar in the SEM images, 2 μm).

our group.[18,19] Previously, we have reported a one-way oil-transport fibrous membrane and proven its unique ability to enhance oil−water separation. Tian et al.[20] also reported underwater one-way oil transport.

Here we report a novel one-way oil-transport fabric that is prepared using a two-step coating technique and subsequent UV treatment. The treated fabric shows a novel one-way oil-transport ability that allows oil fluid to transport automatically from the UV-unirradiated side to the UV-irradiated surface, but it stops fluid transport in the opposite direction. The one-way oil-transport fabric still maintains high superhydrophobicity. We have also found that this one-way fluid-transport ability is selective to oil fluids with specific surface tension, and the selectivity is dependent on the UV treatment time. Changing the UV irradiation time from 6 to 30 h broadens the one-way transport for fluids with surface tension from around 22.3 mN/m to a range of 22.3−56.7 mN/m. We further proved that this selective one-way oil transport can be used to estimate the surface tension of a liquid simply by observing its transport feature on a series of fabrics with different one-way transport selectivities. To our knowledge, this is the first example to use one-way fluid-transport materials for testing the liquid surface tension. It may open up further theoretical studies and the development of novel fluid sensors.

EXPERIMENTAL SECTION

Materials. Zinc acetate dihydrate, 1*H*,1*H*,2*H*,2*H*-(perfluorodecyl)-triethoxysilane ($C_{16}H_{19}F_{17}O_3Si$), ethanol (AR), glycerol, ethylene glycol, hexadecane, silicone oil, *n*-octane, methanol, *n*-decane, and aqueous ammonia solution (concentration, 28%) were obtained from Aldrich. Cooking oil was purchased from a local supermarket. (Tridecafluorooctyl)triethoxysilane (Dynasylan F 8261) was supplied by Degussa. Commercial cotton fabric (weaving weft double, 165 g/m^2, thickness = 460 μm) was purchased from a local supermarket. The cotton fabric sample was cleaned by ultrasonication in isopropyl alcohol for 15 min, then rinsed with isopropyl alcohol, and finally dried at 120 °C for 1 h.

Synthesis of a Zinc Hydroxide Ammonia Solution (Solution A). A total of 3.4 g of a 25% ammonia solution was added dropwise into a solution of 5.5 g of zinc acetate dihydrate in 100 g of water. After the addition of ammonia, the mixture was stirred at room temperature for 2 h. The white precipitate was filtered and washed with copious water. The wet cake was transferred to a 500 mL flask. A 10% ammonia solution was added into the flask to make the total weight of the wet cake and ammonia solution 200 g. The mixture was stirred until the solution became clear. The total solid content in the solution was around 1%.

Preparation of a Fluorinated Decyl Polyhedral Oligomeric Silsesquioxane (FD-POSS) Containing Solution (Solution B). FD-POSS was synthesized using a previously described method.[21,22] In brief, FD-POSS (1.0 g) was dissolved in fluorinated alkylsilane (FAS; 5.0 g) to form a clear viscous solution, which was then dispersed in 100 mL of ethanol.

Coating Treatment of Cotton Fabrics. A two-step process was employed for the coating treatment of cotton fabrics. In step 1, cotton fabric was soaked in 180 mL of solution A. The mixture was kept at 95 °C in an oven for 4 h until two-thirds of the water evaporated. Slightly yellow ZnO rods grew on the fabric. After rinsing with water twice, the fabric was dried again at 120 °C for 1 h. In step 2, solution B was directly applied to ZnO-coated fabric using a dip-coating method. The coated fabric samples were finally dried at 140 °C for 30 min.

Formation of a One-Way Oil-Transport Fabric. A piece of fabric sample after coating with ZnO and FD-POSS/FAS was irradiated by a UV pencil lamp (Spectroline, model 11SC-1 short-wave UV lamp) at a distance of 5 mm. The UV lamp at such a distance has an intensity of 38 mW/cm^2 (254 nm). After irradiation, the fabric showed a one-way transport effect to oil fluids.

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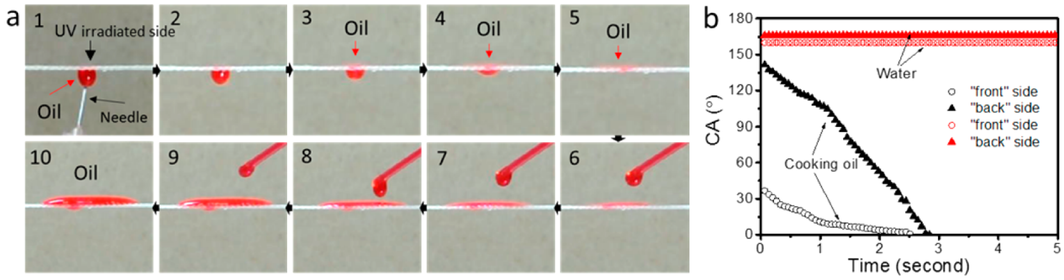

Figure 2. (a) Still frames taken from a video to show the dropping of red-dyed cooking oil onto the UV-irradiated "front" and "back" surfaces. (b) CA changes during the dropping of water or cooking oil onto the one-way oil-transport fabric. (Sample: ZnO/POSS-coated fabric, one-side UV irradiation for 14 h.)

Characterizations. Electron microscopic images were taken by scanning electron microscopy (SEM; Leo 1530, Gemini/Zeiss, Oberkochen). Transmission electron microscopy (JEM-200 CX JEOL, Seike Instruments) was used to observe the coating layer. Fourier transform infrared (FTIR) spectra were measured on an FTIR spectrophotometer (Bruker Optics, Ettlingen) in attenuated total reflectance mode. X-ray photoelectron spectrometry (XPS) spectra were collected on a VG ESCALAB 220-iXL XPS spectrometer with a monochromated AL Kα source (1486.6 eV) using samples of ca. 3 mm^2 in size. The obtained XPS spectra were analyzed by *CasaXPS* software. CAs were measured using a commercial contact-angle meter (KSV CAM101 Instruments Ltd.) using water droplets of 13 μL volume. Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu Ka radiation (40 kV and 40 mA) monochromatized with a graphite sample monochromator over the 2θ range of 5−85°. Crystalline phases were identified using the ICDD-JCPDS powder diffraction database. Initial analysis was performed on the collected XRD data for each sample using the Bruker XRD search match program EVA.

RESULTS AND DISCUSSION

Parts a and b of Figure 1 show the chemical structures of the coating material and the procedure for the two-step coating treatment. In the first step, ZnO was hydrothermally grown on the fabric substrate. An ethanol suspension of FD-POSS and FAS was then applied to the ZnO-coated fabric through a dip-coating technique. Figure 1c shows photographs of water, cooking oil, and pure ethanol (all in 35 μL) dropped on the cotton fabrics. Both uncoated and ZnO-coated fabrics were wettable to these liquids. However, the ZnO-coated fabric after coating with FD-POSS/FAS (also abbreviated as "POSS" in this paper) became highly repellent to all of the liquids (Figure 1c).

The untreated and ZnO-coated fabrics had a CA of 0° to water, cooking oil, and ethanol. The ZnO/POSS-treated fabric had CAs of 166 ± 1.3°, 156 ± 1.9°, and 146 ± 1.4° to water, cooking oil, and ethanol, respectively. The sliding angle (SA) was used to characterize CA hysteresis of the ZnO/POSS-coated fabric. It was interesting to note that the coated fabric had a SA as low as 1° to water. Water (volume 5 μL) moved rapidly off the fabric when it was tilted by only 1° (Figure 1d). In comparison, the fabric showed larger SAs to cooking oil and ethanol (18° and 35°, respectively). This was ascribed to their low surface tension (32.0 and 22.3 mN/m for cooking oil and ethanol, respectively). Further the CA test using liquids of different surface tensions indicated that the ZnO/POSS-coated fabric had a superamphiphobic surface with a CA above 150° to the liquids of surface tension greater than 26.7 mN/m (see detailed results in the Supporting Information).

Parts e and f of Figure 1 show the SEM images of coated cotton fabrics. Flowerlike nanorods were formed on the fiber surface after hydrothermal treatment (Figure 1e). The nanorods were around 4−5 μm in length and 200−400 nm in diameter. They evenly covered the entire fabric surface (see more SEM images in the Supporting Information). The XRD test indicated that the ZnO nanorods were in the crystal form of bulk ZnO wurtzite (Supporting Information). For the ZnO/POSS-coated fabric, some resin-like material was observed to accumulate in the middle part of the ZnO flowers (Figure 1f).

Atomic force microscopy (AFM) imaging was employed to measure the roughness of the coated fibers (see the results in the Supporting Information). After ZnO coating, the root-mean-square (rms) roughness increased from 8 to 342 nm. The FD-POSS/FAS coating treatment slightly reduced the rms to 306 nm.

Cotton contains hydroxyl groups on the fiber surface. These allow ZnO to interact with cotton through hydrogen bonding (e.g., between the oxygen atom of ZnO and the hydroxyl group of cotton) apart from physical absorption.[23,24] The silane heads of FAS can react with the hydroxyl groups on both the cotton and ZnO surface, making ZnO/POSS stably cover on both surfaces. As confirmed by XPS measurement, FD-POSS/FAS covers the entire surface of the flowerlike ZnO nanorods (see the Supporting Information).

The formation of a superamphiphobic surface on the cotton fabric after ZnO and FD-POSS/FAS treatments can be explained by the increased surface roughness and reduced surface free energy. Cotton and ZnO are intrinsically hydrophilic; however, the FD-POSS/FAS coating considerably lowers the surface energy. Our previous study indicated that the fabric coated with FD-POSS/FAS alone can have a superhydrophobic surface.[25,26] Here, ZnO nanorods in the coating layer increase the surface roughness, leading to enhanced liquid repellency.

To prepare a one-way oil-transport fabric, we used strong UV light to irradiate the ZnO/POSS-coated fabric on only one side. After 14 h of irradiation, the directly irradiated surface (also referred to as the "front" surface in this paper) changed the CA from 156° to 0° for cooking oil, but the surface still maintained its water CA at 160° (with a SA lower than 10°). This suggests that UV treatment turns the "front" surface from superamphiphobic to oleophilic but superhydrophobic. After UV irradiation, the surface maintained the superhydrophobic oleophilic feature for a long time at room temperature (Supporting Information).

When cooking oil was dropped on the fabric surface, which did not directly receive UV irradiation (also referred to as the "back" surface in this paper), it penetrated through the fabric and spread onto the "front" surface. Figure 2a shows a series of frames taken from a video to show oil transport. To avoid

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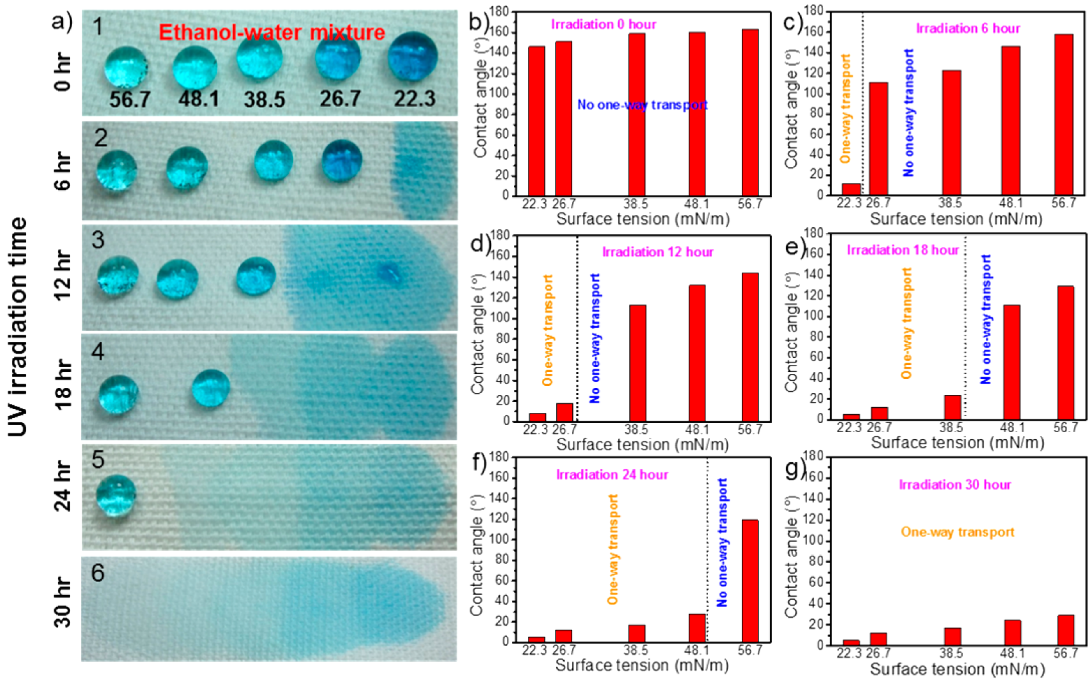

Figure 3. (a) Ethanol−water mixtures with different surface tension values on the ZnO/POSS-coated fabric after UV irradiation for different periods of time (the liquids are dropped on the "back" surface for the UV-irradiated samples). (b−g) Ethanol−water CAs on the "front" surface of the corresponding fabrics. [The data in part a1 indicate the surface tension (mN/m) at 20 °C.]

Table 1. Demonstration of the Sensor Ability To Test the Surface Tension[a]

liquid	actual surface tension (mN/m, 20 °C)	UV-irradiated time (h) on the fabric: 0	6	12	18	24	30	tested surface tension (mN/m)
silicone oil	21.5	×	√	√	√	√	√	$\gamma < 22.3$
ethanol	22.3	×	√	√	√	√	√	$\gamma < 22.3$
hexadecane	27.5	×	×	√	√	√	√	$22.3 < \gamma < 27.5$
cooking oil	32	×	×	×	√	√	√	$27.5 < \gamma < 38.5$
ethylene glycol	47.3	×	×	×	×	√	√	$38.5 < \gamma < 48.1$
glycerol	63.4	×	×	×	×	×	√	$48.1 < \gamma < 63.4$
water	72.8	×	×	×	×	×	×	$\gamma > 63.4$
allowable one-way transport liquid surface tension upper limit			22.3	27.5	38.5	48.1	63.4	

[a] √ = one-way liquid transport. × = nontransport on both sides.

effects from gravity, oil was fed upward to attach to the bottom surface (i.e., the "back" surface) of a horizontally laid fabric sample. Once the oil fluid contacted the fabric, it moved up to penetrate through the fabric and then spread onto the top layer (Figure 2a, entries 1−5). However, when oil was dropped onto the top surface (i.e., the "front" surface), it just spread onto the surface layer without penetrating through the fabric (Figure 2a, entries 6−10). These results clearly indicate that the ZnO/POSS-coated fabric after one-side UV irradiation shows a one-way oil-transport ability.

Figure 2b shows the CA change during the dropping of cooking oil onto the UV-irradiated ZnO/POSS fabric. When cooling oil was dropped onto the "back" side, its CA changed to zero within 3 s because of its penetration through the fabric. When cooking oil was dropped onto the "front" surface, the CA changed from 36° to 0° in 2.5 s. Although the "front" side had an oleophilic surface after UV irradiation, the "back" surface still maintained a high initial CA to cooking oil.

It is known that an ethanol−water mixture can have different surface tension values, in the range of 22.3−56.7 mN/m (at 20 °C), depending on the ethanol concentration.[27] By using a series of ethanol−water mixtures with different surface tensions, we examined the effect of the UV irradiation time on the one-way oil-transport feature.

Figure 3 shows the dropping of a series of ethanol−water mixtures that have different surface tensions (see the mixing conditions in the Supporting Information) onto the ZnO/POSS-coated fabrics. Without UV irradiation, the ZnO/POSS-coated fabric was highly repellent to all of the ethanol−water mixtures. All of the liquid drops can remain stable on the fabric with a large CA value (see data in Figure 3b). There was no difference between the two fabric sides. For the coated fabric after 6 h of UV irradiation, it allowed pure ethanol (surface tension 22.3 mN/m) to have the one-way transport feature, whereas the fabric prevented the ethanol−water mixtures studied from penetrating on both sides. The fabric "front" surface showed a CA above 110° for all of the ethanol−water mixtures (Figure 3c). For the ZnO/POSS-coated fabric irradiated by UV light for 12 h, it showed one-way transport to an ethanol−water mixture [3:5 (v/v); surface tension 26.7

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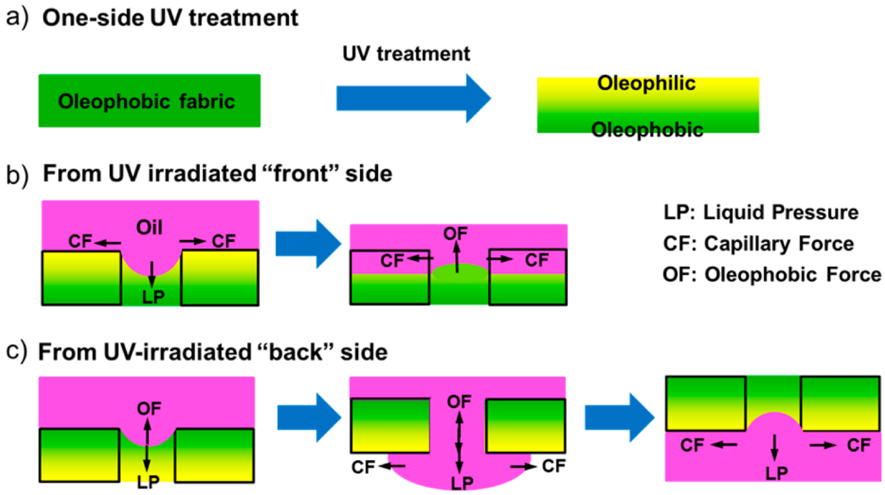

Figure 4. Proposed one-way oil-transport mechanism.

mN/m] besides pure ethanol. The fabric "front" surface was still highly repellent to other ethanol−water mixtures (Figure 3d). These results suggest that increasing the UV irradiation time from 6 to 12 h leads to one-way transport to more oil fluids with surface tension broadened to a range of 22.3−26.7 mN/m. Longer UV irradiation, e.g., 18, 24, and 30 h, further extended the upper limit of the surface tension to 38.5, 48.1, and 56.7 mN/m, respectively (Figure 3e−g).

The above results also suggest that the surface tension of a liquid can be estimated by observing its transport performance on a series of the ZnO/POSS-coated fabrics that are UV-irradiated for different periods of time. To prove this, we tested glycerol (surface tension 63.4 mN/m), ethylene glycol (47.3 mN/m), cooking oil (32.0 mN/m), hexadecane (27.5 mN/m), and silicone oil (21.5 mN/m) on the fabrics. Table 1 lists the test result, which is very close to the actual data. By fine-tuning the UV irradiation time, a finer testing range could be attained, leading to higher sensitivity. The minimum liquid surface tension measurable by this technique is 22.7 mN/m (methanol) with an experimental error of less than 1.2 mN/m.

The surface tension of liquid has been conventionally measured by some methods such as measuring the tension formed between liquid and a solid object (e.g., ring, needle, and plate), the liquid drop dimension (e.g., diameter, geometry, volume), the maximum pressure of air bubbles in the liquid, capillary rise, or resonant oscillations of the liquid drop. Recently, Burgess et al.[28] reported a novel three-dimensional photonic crystal showing wetting selectivity to fluids. However, the use of a fibrous membrane to measure the liquid surface tension has not be reported in research literature. Our work should be the first example for using a one-way fluid-transport fabric to test the liquid properties.

To find out the source of the surface property change after UV irradiation, we performed FTIR and XPS studies on the ZnO/POSS-coated fabric. After UV irradiation, the "front" surface showed considerably reduced vibration intensity at 1190 and 1470 cm^{-1}, which correspond to C−F vibrations. Meanwhile, a new peak occurred at around 1690 cm^{-1}, indicating the formation of C═O bonds. However, the peaks in the wavenumber range of 3300−1500 cm^{-1} had little change. This suggests that C−F bonds on the "front" surface are converted into carbonyl groups. The XPS spectra confirmed that the atomic content of the F element reduced by 55.80% on the "front" surface of the UV-irradiated fabric, accompanied by the occurrence of carbonyl groups (see detailed XPS results in the Supporting Information). These surface chemistry changes can be ascribed to the photodegradation effect of ZnO nanorods.[29−32] Because carbonyl groups have higher polarity than C−F, the replacement of C−F with carbonyl would increase the surface free energy.

Despite the change of the surface chemistry on the "front" surface, the "back" side, which did not receive direct UV irradiation, shows surface features almost identical with those of the unirradiated sample. ZnO has strong absorption to UV light, and its coating on the fabric blocks UV-light penetration through the fabric. The UV-light intensity should have a gradient decay along the fabric thickness. This would lead to variation in the surface chemistry with depth after UV irradiation, and an oleophilicity-to-oleophobicity gradient along the fabric thickness, i.e., from the UV-irradiated "front" to "back" surfaces, would form.

On the basis of these results, we proposed the one-way oil-transport mechanism. The ZnO/POSS-coated fabric after one-side UV irradiation shows a gradient change from oleophilicity to oleophobicity across the thickness. As a result, the oil fluid can spread on the oleophilic side (i.e., UV-irradiated "front" surface) but not on the oleophobic surface (i.e., UV-irradiated "back" side) because of the high oleophobicity. When oil is dropped on the oleophobic surface, it moves across the nonwetting barrier layer and spreads into the oleophilic zone (Figure 4), which is similar to that for water transport on a fabric with a superhydrophobicity-to-hydrophilicity gradient across the thickness.[14,16−19] The UV-irradiation time affects the oleophilicity-to-oleophobicity gradient profile. This should be the main reason leading to the selectivity of the one-way oil-transport property.

■ CONCLUSION

We have proven that a fabric, after being coated with ZnO nanorods and a low-surface-energy substance (e.g., FD-POSS and FAS) and further irradiated by strong UV light on one fabric side, shows an interesting one-way oil-transport ability. Such a one-way oil-transport function is selective to oil fluids with specific surface tension, and the fluid selectivity is dependent on the UV treatment time. Through observation of the transport performance of a liquid fluid on a series of

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fabrics that show different one-way oil-transport selectivity, the surface tension of the oil fluid is estimated successfully. Our work on a one-way oil-transport fabric may open up further theoretical studies and the development of novel fluid sensors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05678.

CAs and SAs, SEM and AFM images, XRD patterns, FTIR and XPS spectra, photographs, and surface tension data (PDF)

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Notes

The authors declare no competing financial interest.

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