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## Multi-functional fluorinated ionic liquid infused slippery surfaces with dual-responsive wettability switching and self-repairing<sup>+</sup>

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Stimuli responsive slippery surfaces with controllable wettability have attracted much attention due to their potential application in many fields. However, most of these surfaces only adopted paraffin as the lubricant oil and achieved wettability transformation just by heating. In addition, the self-repairing properties of smart slippery surfaces have rarely been reported. Hence, challenges still remain in fabricating multiple responsive slippery surfaces based on other lubricants possessing self-repairing properties. Here, a smart slippery surface with controllable wettability was fabricated by using solid/liquid fluorinated ionic liquids (FILs) as lubricants and fluoropolymer films as the underlying substrates. The FIL, a thermo-responsive phase-transition material, was synthesized by ionic exchange and the substrate exhibited good self-repairing properties and magnetic-thermal and photo-thermal responses. By tuning the substrate temperature under light irradiation or magnetic field to change the phase state of the FIL, the surface could realize wettability conversion. Besides, the responsive temperature can be adjusted by tuning the melting temperature ( $T_{rn}$ ) of the FIL. The FIL was first synthesized and there was no report employing FILs as the lubricants to realize the wettability change of slippery surfaces. This work provided a new type of lubricant to prepare intelligent slippery surfaces, thus advancing the application of slippery surfaces in liquid transport devices.

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## 1. Introduction

Inspired by natural biointerfaces like lotus leaves,<sup>1,2</sup> rice leaves<sup>3-5</sup> and butterfly wings,<sup>5,6</sup> surfaces with adjustable wettability have attracted extensive research. The wettability of these surfaces will be changed when exposed to external stimuli such as humidity,<sup>7</sup> electric field,<sup>8,9</sup> magnetic field,<sup>10-12</sup> temperature,<sup>13-17</sup> *etc.* Such surfaces have been applied to no-loss liquid transportation,<sup>15,16,18,19</sup> water collection,<sup>17,20-22</sup> oil-water separation,<sup>7,18,23-25</sup> and dropwise condensation.<sup>26,27</sup> It is worth noting that the surface morphology and chemical characteristics are the two major factors which affect the change of surface wettability. Briefly, the chemical structure is changed with the migration or contraction of molecular segments. Many studies about poly(*N*-isopropyl acrylamide) have realized this conversion.<sup>28</sup> However, it's a big challenge to precisely control the adjustment of the surface microstructure.

Recently, a new kind of slippery liquid infused porous surface inspired by Nepenthes<sup>27,29-32</sup> supplies a new method to

overcome the above defects. For example, Hu's group<sup>33</sup> fabricated a silicon oil infused slippery surface based on multilayered biomimetic "tissue" by combining a poroelastic skin with artificial muscle. The morphology of this slippery surface could be finely tuned by a programmed voltage thus changing the droplet sliding motion on the surface. Besides, the slippery surface can be used to manipulate bubbles in an aqueous environment. Cao and his co-workers34 prepared a lubricant infused slippery surface based on super-hydrophobic substrates. The motion direction of underwater bubbles was finely regulated by adjusting the track width and sample shape. The porous substrates and the infused lubricants are two necessary conditions to fabricate a slippery surface. It should be emphasized that the performance will be altered with different substrates and diverse lubricants.9,16,30,35,36 However, according to the current studies, most smart slippery surfaces with controllable wettability based on the variation of the lubricant phase state only select paraffin as the lubricant. For instance, Seimei Shiratori and his co-workers16 prepared a temperature-driven slippery surface with controllable optical and wettability performances. The droplet motion and light transmittance on this surface could be regulated with the variation of temperature by altering the solid/liquid paraffin mixing ratio. Similarly, Heng's group<sup>15</sup> fabricated a thermally activated slippery surface with controllable droplet motion also based on paraffin. However, using paraffin as the lubricant will weaken the liquid repellency properties of the slippery

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surface due to its higher surface tension than fluorinated lubricant oil, such as perfluoroether and perfluorocarbon.<sup>29,37</sup> In addition, evaporation at high temperatures seems to be unavoidable for most organic lubricants. Hence, creating a new type of lubricant which has a suitable phase transfer temperature and good thermal stability is very significant to broaden the application of slippery surfaces.

Ionic liquids (ILs), as a novel type of solvent besides water and organic solvents, are completely composed of anions and cations. Owing to the weak interaction force between the large organic anions and cations,<sup>27,38</sup> ILs exhibit low melting points. Moreover, ILs have a very low vapor pressure and superb thermal stability. All of these are attractive features of ILs for using them as a new type of lubricant. The excellent high temperature stability promises a long life for slippery surfaces. Miranda's group<sup>38</sup> verified the stability of IL-infused slippery surfaces at high temperatures over 200 °C. However, studies about IL-infused slippery surfaces with reversible wettability, which was based on lubricant phase transfer to achieve the change of surface wettability, have never been reported. In addition, the currently reported smart responsive slippery surfaces mostly respond to a single stimulus like heating<sup>15,16</sup> and electric field.<sup>39,40</sup> Unfortunately, the conditions are more complex in practical application and the response often requires remote implementation. Fe<sub>3</sub>O<sub>4</sub>, as a type of magnetic nanomaterial, is capable of absorbing energy from sunlight and magnetic field and converting them to thermal energy.<sup>11,41,42</sup> Magnetically responsive switching has attracted widespread attention due to its remote controllability, excellent biocompatibility and double response to light irradiation and magnetic field. Furthermore, magnetic nanoparticles are capable of enhancing the mechanical properties of the obtained polymer. Hence, the addition of magnetic Fe<sub>3</sub>O<sub>4</sub> will result in a double responsive and robust smart surface. Besides, few studies have focused on the self-repairing properties of slippery surfaces, especially smart responsive slippery surfaces, owing to the limitation of the fabrication methods of substrates.

Herein, we present a magnetic-thermal and photo-thermal responsive solid/liquid FIL infused slippery surface (MPRS) with reversible wettability, on which the droplet motion can be smartly controlled by adjusting the substrate temperature. Briefly, when the temperature exceeded the  $T_{\rm m}$  of the FIL under light irradiation or magnetic field, the water droplets easily slid on the surface. Conversely, the droplets pinned on the surfaces if the temperature decreased below the  $T_{\rm m}$ . The  $T_{\rm m}$  of the FIL could be easily revised by using different cation groups. Besides, the surface showed good self-repairing performance, excellent stability and liquid repellency properties. The freezing time of the FIL-1H3M infused slippery surface was extended to 3605 s. These multi-functional intelligent materials could be applied in transport pipeline equipment for liquid transmission. The superb liquid repellency and anti-icing properties of MPRSs were capable of preventing the pipeline from blocking and freezing. Besides, once the hydrates and other substances were frozen in the pipeline under harsh situations, they could be melted under light irradiation or magnetic field through remote control and then the original transport performance of the

pipeline could be repaired. The self-repairing properties of MPRSs also promoted the materials' durability. It is worth mentioning that this is the first report about FIL-infused slippery surfaces with reversible wetting behavior and the FILs presented here have never been reported. These findings in this work provided a new type of lubricant to fabricate smart surfaces with regulatable wettability, which can be used in micro-fluidic and biomedical devices.

### 2. Experimental section

#### 2.1 Materials

2-Ethylhexyl acrylate (2-EHA), triethylamine, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), and azobisisobutyronitrile (AIBN, 99%) purity) were purchased from Aladdin Chemical Reagent Co., Ltd (China). Bis(2-methacryloyl)oxyethyl disulfide (BMOD) was obtained from Aldrich. 2-(Perfluorohexyl)ethyl acrylate (C<sub>6</sub>A) was synthesized as described in our previous work.43 1,3-Dimethylimidazolium chloride ([MMIm]Cl) was provided by Yuduo Biotechnology Co., Ltd (Shanghai, China). 1-Hexyl-3methylimidazolium chloride ([HMIm]Cl) was purchased from Moni Chem. Eng. Sci & Tech. Co., Ltd (Shanghai, China). 1-Ethylimidazole was provided by Macklin. Perfluorobutyl sulfonyl fluoride (C4F9SO2F) was provided by Hengxin Chemical Co., Ltd (Hubei, China). Ethyl bromide, ammonia solution (NH<sub>3</sub>·H<sub>2</sub>O, 25 wt%), ethanol absolute (C<sub>2</sub>H<sub>5</sub>OH, purity  $\geq$ 99.7%), and sulfuric acid ( $H_2SO_4$ , 98 wt%) were purchased from Sinopharm Chemical Regent Co., Ltd. All these reagents were used as received. Deionized water was used throughout the whole experiments.

#### 2.2 Synthesis of fluorinated ionic liquids

**1,3-Diethylimidazolium bromide ([EEIm]Br).** 1-Ethylimidazole was reacted with bromoethane in a 25 ml threenecked flask at 30  $^{\circ}$ C for 15 h. Then the excess solvent was removed by rotary evaporation at 25  $^{\circ}$ C followed by freezedrying for 24 h to obtain pure [EEIm]Br.

**Bis-perfluorobutyl sulfonimide potassium** (( $C_4F_9SO_2$ )<sub>2</sub>NK). First, 150 ml liquid ammonia was obtained in a three-necked flask by condensation. Then 40 g  $C_4F_9SO_2F$  was slowly injected into the flask *via* a peristaltic pump and reacted with the liquid ammonia for 3 h. It is noteworthy that liquid nitrogen was used for the whole process to cool down the temperature. Subsequently, the prepared intermediate was acidified with 50%  $H_2SO_4$  to form perfluorobutylsulfonamide ( $C_4F_9SO_2NH_2$ ) in anhydrous ether solution and then washed three times with distilled water and sublimated for purification at 80 °C.

Then,  $C_4F_9SO_2NH_2$ , triethylamine and  $CH_3CN$  were mixed in a 250 ml three-necked flask and stirred at 45 °C for 0.5 h.  $C_4F_9SO_2F$  was slowly dropped into the mixed solution and the temperature was raised to 80 °C for 24 h immediately, followed by heating the resulting orange solution to remove the solvent. Then, the products were dissolved in  $CH_2Cl_2$  solution and washed with distilled water three times. Finally, the dried outputs were acidified with 98%  $H_2SO_4$  and sublimed at 120 °C to yield diperfluorobutyl sulfonimide (( $C_4F_9SO_2)_2NH$ ). Then aqueous  $K_2CO_3$  was slowly added to the  $(C_4F_9SO_2)_2NH$  aqueous solution. During this process, a kind of white floc appeared, which was  $(C_4F_9SO_2)_2NK$ .

**FILs.** 1.86 g ( $C_4F_9SO_2$ )<sub>2</sub>NK and 20 ml CH<sub>3</sub>CN were blended in a 100 ml single-necked flask, followed by dropping [MMIm]Cl (or [EEIm]Br or [HMIm]Cl) which was dissolved with CH<sub>3</sub>CN in the mixture and reacted at 30 °C for 3 h. Then the FILs (FIL-1M3M, FIL-1E3E and FIL-1H3M) were synthesized by eliminating the residual solvent.

# 2.3 Preparation of magnetic-thermal and photo-thermal responsive slippery surfaces

The underlying substrate of the MPRSs was prepared by bulk polymerization. A typical copolymerization process is described as follows. Briefly, different contents of  $Fe_3O_4$  nanoparticles (0 wt%, 10 wt%, 30 wt%, and 50 wt%) were mixed with  $C_6A$ , 2-EHA and BMOD to obtain the mixed solution, and then dispersed by ultrasonic treatment for 10 min. Afterwards, the prepared solution was poured into a rectangular silicone mold and polymerized at 72 °C for 2 h to obtain the hybrid films (HFs-0, HFs-5, HFs-10, HFs-30, and HFs-50). Then, the as-prepared FILs were dropped onto the HFs to form slippery surfaces: MPRSs-1M3M, MPRSs-1E3E and MPRSs-1H3M ascribed to the FIL-1M3M, FIL-1E3E and FIL-1H3M, respectively. The  $Fe_3O_4$ nanoparticles were synthesized by previously reported methods.<sup>11,42</sup> Unless otherwise specified, the MPRSs used for the following measurements were based on HFs-30.

#### 2.4 Characterization

Chemical structure and physical properties. Fourier transform infrared (FT-IR) spectroscopy (Nicolet 5700) and <sup>19</sup>F-NMR (Bruker Advance DMX500, 25 °C) were used to analyze the chemical composition of the samples. A differential scanning calorimeter (DSC, TA-Q100, USA) was employed to test the  $T_{\rm m}$  of the FILs. The thermal stability of the FILs was measured using a thermogravimetric analyzer (TGA, TA-Q500, USA). The heating rate was 10 °C min<sup>-1</sup>.

Surface topography and wettability. The surface topography and surface roughness of the samples were characterized by field emission scanning microscopy (SEM, SU-8010, Japan) at an accelerating voltage of 20 kV and atomic force microscopy (AFM, TT2-AFM, USA) using a multimode in tapping mode, respectively. The scanning range was  $5 \times 5 \ \mu\text{m}^2$ . The contact angle (CA) was measured using an SDC-100 optical contact angle goniometer (SINDIN Co., Ltd., China). The average value was obtained by measuring at least five different positions on the same sample.

**Magnetic properties and magneto-thermal effects.** Magnetic studies of the samples were performed using a multi-functional vibrating sample magnetometer (J3426, UK) at 293 K. A homemade radio frequency (RF) induction heater<sup>44</sup> (power: 450 W) was employed for magneto-thermal experiments. The sample was fabricated in a Petri dish (diameter: 54 mm, height: 5 mm).

**Thermal stability measurement of lubricants.** The samples  $(2 \times 3 \text{ cm}^2)$  with three kinds of FILs were placed in an oven at

80  $^{\circ}\mathrm{C}$  for 10 days. The CA of the sample surface was then tested daily to evaluate the loss of the lubricant.

Anti-icing properties. An OCA instrument was used to observe the icing delay time (DT) of the water droplets (2 µl) on the sample surface. These specimens were placed on a Peltier cooling controller (PCC) to cool down the sample surface temperature and keep it at -15 °C, and the relative humidity (RH) was 45  $\pm$  5%. Then by photographing the shape of the water droplets at intervals, the DT was defined by the time at which the shape of the droplets changed. The anti-frosting performance was judged by the time when frost began to appear. The sample was putted on a PCC at -17 °C, RH 80  $\pm$  3%. The accumulation of water droplets on the surface of the sample was then recorded using a camera.

### 3. Results and discussion

#### 3.1 Preparation and characterization of the FILs

Scheme S1<sup>†</sup> illustrates the related reaction equation during the synthetic procedures of the FILs. The anion of the FILs was prepared by our previous work through the reaction of  $C_4F_9SO_2NH$  and  $K_2CO_3$ . The chemical structure of  $(C_4F_9SO_2)_2NH$  was verified by <sup>19</sup>F-NMR (Fig. S2a<sup>†</sup>). Then, the K<sup>+</sup> on  $(C_4F_9SO_2)_2NK$  was substituted by three kinds of cationic salts ([MMIm]Cl, [EEIm]Br, and [HMIm]Cl) and fluorinated ionic liquids were formed: FIL-1M3M, FIL-1E3E and FIL-1H3M, respectively. The corresponding <sup>19</sup>F-NMR spectra of the FILs are shown in Fig. S2b–d.<sup>†</sup> [EEIm]Br was synthesized by one-step replacement between 1-ethylimidazole and bromoethane. Its chemical structure is presented in Fig. S1.<sup>†</sup>

Fig. 1a shows the chemical composition of FIL-1H3M, FIL-1E3E and FIL-1M3M. The absorption peak appearing at about 3100 cm<sup>-1</sup> was assigned to the C-H stretching vibrations in the imidazole ring and the broad band at 746 cm<sup>-1</sup> corresponded to the C-H rocking bending vibrations in the imidazole ring. In addition, the signal of the carbon skeleton in the imidazole ring was observed around 1570 cm<sup>-1</sup> with little shift in different FILs due to the difference of alkyl groups in the imidazole ring. The absorption peaks at 1470  $\text{cm}^{-1}$ , 1454  $\text{cm}^{-1}$  and 1469  $\text{cm}^{-1}$  were primarily ascribed to the C-N stretching vibration in the imidazole ring and these peaks were overlapped with the C-H rocking bending vibrations in the alkyl group. All of these absorption peaks mentioned above confirmed that the imidazolyl cation salt successfully substituted the K<sup>+</sup> on (C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)<sub>2</sub>NK. Meanwhile, the characteristic groups in (C4F9SO2)2N<sup>-</sup> could also be observed from the FT-IR spectra. Specifically, the stretching vibration of the  $-SO_2$  group appeared at approximately 1573 cm<sup>-1</sup>. The broad band at 1139-1236 cm<sup>-1</sup> was assigned to the C-F and the absorption peak of the C-N stretching vibration in the alkyl group was discovered around 1077 cm<sup>-1</sup>. These results indicated that a fluorinated ionic liquid has been successfully synthesized.

The thermal stability of the FILs is shown in Fig. 1b. The initial decomposition temperatures  $(T_d)$  of the three FILs were all above 250 °C. Especially, the  $T_d$  of FIL-1H3M reached above 350 °C, thus demonstrating that the fluorinated ionic liquids prepared in this work possess outstanding thermal stability. The  $T_m$  of the FILs was measured by DSC to further prove the



iig. 1 FT-IR spectra (a) and TGA curves (b) of FIL-1H3M, FIL-1E3E and FIL-1M3M. DSC curves of FIL-1M3M (c) and FIL-1H3M (d).

transition temperature of the FILs from the solid to the liquid state. As shown in Fig. 1c, d and S3,† the  $T_{\rm m}$  of the FILs was 61.7 °C, -7.3 °C, -16.4 °C corresponding to FIL-1M3M, FIL-1E3E and FIL-1H3M, respectively. The wide difference in  $T_{\rm m}$  was caused by the different alkyl substituents on the imidazole ring.

To achieve smart control of droplet motion on these surfaces, FIL-1M3M with  $T_{\rm m}$  around 61.7 °C was selected as the lubricant to fabricate magneto-thermal and photo-thermal driven slippery surfaces. As shown in Scheme 1, FIL-1M3M could be reversibly transformed between the solid phase and the liquid phase by changing the temperature under light irradiation or magnetic field. Then the surface changed to be slippery from the hydrophobic state. FIL-1M3M was solid at room temperature and did not require a high temperature to melt, thus making the process flexible to control.

#### 3.2 Fabrication and characterization of MPRSs

The hybrid film used as the underlying substrate was fabricated by one-step solvent-free polymerization of  $C_6A$ , 2-EHA and  $Fe_3O_4$  nanoparticles, and BMOD was used as a cross-linking agent. The chemical structure of this polymer was characterized by FT-IR spectra presented in Fig. 2a. The broad band appearing at 1189–1079 cm<sup>-1</sup> was ascribed to the C-F stretching vibrations. The absorption peak of C=O was observed at  $1731 \text{ cm}^{-1}$  instead at  $1630 \text{ cm}^{-1}$  which indicated that the -CH= CH– group was completely polymerized. Besides, the characteristic peak of the Fe–O group could also be found at 808 cm<sup>-1</sup>. This revealed that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles existed in the bulk of the copolymer.

The enhancement effect of nanoparticles on the mechanical properties and surface roughness has been verified in many systems. This can also be found in this work. As shown in Fig. 2b and S6,† the compressive strength and surface CA increased with increasing content of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Besides, due to the photo-thermal effect and magneto-thermal effect of magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles, the surface temperature could respond to light irradiation or magnetic field. Considering the mechanical properties of the underlying substrate and the photo-thermal and magneto-thermal conversion efficiency of the nanoparticles, HFs-30 was selected for fabricating a slippery surface. The reversible disulfide bond endowed the substrates with good self-repairing properties. As shown in Fig. 2c, the cutting marks on the repaired matrix disappeared after healing at 72 °C for 4 h. The substrates showed good healing capability with 70% healing efficiency for fracture stress and 80% healing efficiency for fracture strain (Fig. S4<sup>†</sup>). In addition, the water droplet could move along the slippery surface after the surface was healed (Fig. S5<sup>†</sup>). It is believed that the reversible disulfide bonds were capable of re-connecting themselves together and then forming a new crosslinked network to repair the damaged section.45 Besides, the cut film could also be repaired under illumination or magnetic field ascribed to the magnetic and light heating efficiency of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The good self-repairing properties of the underlying substrates contributed to keeping the slippery surface stability for practical application.

Hereafter, the as-prepared FILs, as the lubricant oils, were dropped onto the hybrid films to form slippery surfaces. The specific fabrication processes and the change of the liquid



Scheme 1 Preparation procedure of MPRSs and the magnetic-thermal and photo-thermal responsive processes of the liquid drop motion.

droplet motion are illustrated in Scheme 1. In detail, when the temperature was lower than the  $T_{\rm m}$  of the FIL, the FIL was in the solid state and droplets would pin on the surface. At this time,

the surface was in the Wenzel state and strong. Under light irradiation or magnetic field, the surface temperature rose above the  $T_{\rm m}$  of the FIL and the hybrid film was covered by



Fig. 2 (a) FT-IR spectra of HFs-30. (b) Compressive stress-strain curve of the hybrid films with different contents of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. (c) Self-healing process of HFs-30.

liquid lubricants. Hence, the water droplet would slide down the surface.

The surface topography and surface roughness of HFs-30 and LMSs-30 were further investigated by SEM and AFM. As shown in Fig. 3a and b, the nanoparticles were evenly dispersed on the substrate and several microscopic bumps are present on the surface resulting in the micro-scale roughness with a RMS of 261 nm (Fig. 3d). These rough structures boosted the capillary action of the surface which promoted the storage capacity of the lubricants and contributed to keeping the high stability of the slippery surface. Moreover, the large amount of fluorinated groups contained in the FILs and hybrid films also increased the affinity between the lubricants and substrates. However, the compatibility between the FILs and HF substrates would be limited ascribed to the strong intermolecular force in the FILs.

As shown in Fig. 3e, the surface RMS roughness decreased to 8.78 nm and the structure of the hybrid film remained faintly visible (Fig. 3c) after the surface was covered by the solid FIL. Then the surface became highly smooth and defect-free, with a RMS roughness of 0.08 nm (Fig. 3f) at 65 °C. The surface topography observed from both SEM and AFM images was in good agreement with each other, thus demonstrating that the FIL permeated into the HF matrix and formed a molecular-scale smooth lubricant layer over the substrates. In addition, the CA decreased with the cover of the FIL from 119.81° to 87.88° owing to the reduction of the roughness and the introduction of

hydrophilic imidazole groups (Fig. 3g and h). And the surface CA further decreased to  $39.56^{\circ}$  when the temperature was above the  $T_{\rm m}$  of the FIL. Because the roughness of the FIL-infused surface decreased with the change of the FIL state, the contact area between the droplet and the surface increased.

#### 3.3 Liquid repellency and self-cleaning properties

The sliding motion of water droplets on the slippery surfaces recorded by the digital pictures is shown in Fig. S7.† A water droplet slipped on the surfaces covered by different FILs with a low tilting angle ( $\sim$ 5°) and left no traces. These results indicated that there was no replacement of the lubricants by water and the FIL was compatible with the substrates. More specifically, it took 3 s, 18 s, and 23 s for the droplets to slide down the surface of MPRSs-1M3M, MPRSs-1H3M and MPRSs-1E3E, respectively, which increased with increasing viscosity of the FILs. In addition, the sliding velocity of MPRSs-1M3M was tested at 65°, which reduced the viscosity of FIL-1M3M and then resulted in a faster sliding velocity.

Considering the practical application, several droplets with different polarities and a series of solutions constantly used in our daily life were selected to evaluate the liquid repellency performance of this slippery surface. As shown in Fig. 4a and e, the hexadecane and toluene droplets easily slid away the MPRSs-1H3M surface. The sliding rate of water droplets (7  $\mu$ l) could reach 5.78 mm s<sup>-1</sup>. However, honey droplets were



Fig. 3 SEM images of the HFs-30 cross section (a), HFs-30 surface (b) and MPRSs-1M3M surface (c) at 25 °C. 3D AFM height images of HFs-30 (d), and MPRSs-1M3M at 25 °C (e) and 65 °C (f). Contact angle photographs of HFs-30 (g), and MPRSs-1M3M at 25 °C (h) and 65 °C (i).



Fig. 4 (a) Sliding velocity of several droplets (7  $\mu$ l) on MPRSs-1H3M, tilt angle (TA): 25° and (b) evaporation stability of slippery surfaces at 80 °C for 10 days. (c) Snapshots showing the sliding of honey (i), soy sauce (ii) and coffee (iii) on MPRSs-1H3M, TA: 25°. (d) Self-cleaning tests by using silica particles (i) and copper(II) chloride dehydrate particles (CuCl<sub>2</sub>·2H<sub>2</sub>O) (ii) on MPRSs-1H3M, TA: 25°. (e) Snapshots of water (i), toluene (ii), dodecane (iii) and hexadecane (iv) droplets sliding down MPRSs-1H3M, TA: 25°.

difficult to move on most surfaces due to their high viscosity. In this work, the honey droplet left the surface in 10.34 s without no traces. And the coffee droplet slid down the surface in 3.77 s, thus indicating that the MPRSs were enough to prevent surface contamination by reagents. Besides, the liquid repellency of MPRSs-1M3M and MPRSs-1E3E was also measured adopting the same target pollutant. As shown in Fig. S8a and S9,† all liquid droplets could slip off MPRSs-1M3M and MPRSs-1E3E, and no track was left on their path. However, the sliding velocity of the droplets was very different on these three surfaces (Videos S1–S3†) caused by the discrepancy in the viscosity of the FILs, which increased with larger alkyl chains.

In addition, the self-cleaning properties were estimated by dirt-removal tests, using hydrophilic  $CuCl_2 \cdot 2H_2O$  and hydrophobic silica particles as model pollutants. Fig. 4d, S8b and c<sup>†</sup> show that some amounts of powders were pinned on the MPRSs. After water impact, SiO<sub>2</sub> particles floated on the water droplets and then slid down the slippery surface with the droplets. No trace was left and no obvious powder residue could be monitored on the impacted place. Besides, the  $CuCl_2 \cdot 2H_2O$ particles would be dissolved once they come into contact with water and then wiped away with water droplets because of their excellent solubility. Hence, the dirt could be completely removed by floating on the droplets or dissolution in water. These results suggested that the MPRSs were provided with superb self-cleaning properties.

Longevity is another important factor in practical application. In this work, the MPRSs exhibited excellent evaporation stability. At 80 °C for 10 days, there was no obvious change in the surface CA (Fig. 4b). Besides, the slipping velocity increased with increasing cycle times due to the reduction of lubricant oil viscous resistance. As shown in Fig. S10,† the slipping rate of MPRSs remained high and showed no trend of decline after 30 cycles. In addition, the MPRSs were capable of maintaining the surface slippery properties when the samples were placed vertically (Fig. S11<sup>†</sup>). The sliding velocity of the water droplet and mass of the MPRSs showed no changes after 1400 min. The significant stability of this slippery surface benefitted from the FILs' thermal stability and compatibility with the substrate. In general, the superb thermal stability of FILs and the selfrepairing properties of substrates ensure a long lifespan of MPRSs, thus promoting the practical application of smart slippery surfaces.

# 3.4 Magnetic-thermal and photo-thermal responses of MPRSs

To smartly control the droplet motion on the MPRSs, magnetic  $Fe_3O_4$  nanoparticles were mixed with the hybrid films to endow

their surfaces with magnetic-thermal and photo-thermal responses. As shown in Fig. 5a, the magnetization curves of the HFs were in an S-shape and without hysteresis, thus signifying that the MPRS wettability could be flexibly controlled due to the excellent paramagnetic properties of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Briefly, the magnetization saturation values were 56.5, 31.0, 13.0, and 0 emu g<sup>-1</sup> corresponding to HFs-50, HFs-30, HFs-10 and HFs-0, which increased with increasing loading of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. These results suggested that the hybrid films were easily manipulated under a magnetic field, thus promoting the conversion of magnetic energy to thermal energy.

Fig. S12<sup>†</sup> shows the typical device used to trigger heating of the hybrid films under a magnetic field. The heating effects of

the HFs were obtained after putting the samples under a magnetic field for 20 min. As shown in Fig. 5b, there was no heating effect generated for HFs-0, as no temperature change was observed within a reasonable error range. However, the temperature of the HFs-30 surface and HFs-50 surface increased by 17.8 °C and 22 °C. It was worth emphasizing that the operating power was 450 W, which was much lower than others' work.<sup>11</sup> The results indicated that the addition of magnetic nanoparticles could provide obvious magnetic heating performance for the hybrid films, which was beneficial for the smart control of the droplet motion on the slippery surfaces.

Fig. 5c presents the reversible switching of droplet motion on the MPRSs-1M3M surface, using water and hexadecane as the targets. The water droplet (3  $\mu$ l) was pinned on the surface



Fig. 5 (a) Hysteresis curves of HFs with different contents of  $Fe_3O_4$  nanoparticles. (b) The heating effects of HF surfaces under an alternative magnetic field for 20 min (power: 450 W), and the inset images show the water droplet motion on MPRSs-1M3M before (above) and after (below) applying the magnetic field. The thermo-controllable sliding motion of the water droplet (c) and hexadecane droplet (d) on the MPRSs-1M3M surface, TA: 9°, drop volume: 3  $\mu$ l.

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when  $T < T_{\rm m}$ . Because FIL-1M3M was solid, the low surface CA was not enough to make the droplet roll down the surface. After heating for a few seconds, the droplets started to slide on the surface, at this time,  $T > T_{\rm m}$ . Then the surface was cooled down, and the water droplet further slipped for a while and stopped sliding because time was needed for the liquid FIL-1M3M to completely solidify. The pinned droplet started to move again after reheating. The same sliding motion of the hexadecane droplet is presented in Fig. 5d. However, the CA and sliding rate of the hexadecane droplet were smaller than those of the water droplet on this slippery surface. This was caused by the difference in polarity and surface tension.

In addition, this smart surface could respond to light irradiation. The common experimental equipment for the photothermal response is presented in Fig. 6a. A sunlamp was selected as the heating source because it was more convenient than other sources and could be used in an actual environment. As shown in Fig. 6b, the surface temperature of HFs-30 increased by 20 °C under sunlamp irradiation for about 20 min and was unchanged for further irradiation. However, there was no significant change of the HFs-0 surface temperature after illumination for 60 min, thus revealing that the surface endowed with magnetic nanoparticles had good light heating efficiency. When the surfaces temperature was up to  $T_{\rm m}$  of the FIL under sunlamp irradiation, the CA of the MPRSs-1M3M surface changed to 39.56° from 88.78° as shown in the insets of Fig. 6b, which was caused by the change of the

FIL-1M3M state from solid to liquid. Meanwhile, the surface transformed to a slippery surface from the hydrophobic surface and resulted in the droplets being slipping off the surface instead of pinning. The controllable variation of surface CA and droplet motion on these surfaces promoted the application of smart slippery surfaces in medical equipment used for liquid transfer pipes. Besides, the reversible switching of the surface CA and the sliding speed of water droplets on the MPRSs-1M3M are demonstrated in Fig. 6c and d. At 25 °C, the water droplets pinned on the surface with a surface CA of 88°. After the surface temperature was increased to 65 °C, the water droplet began to slide on the surface with a speed of 35 mm  $s^{-1}$  and the surface CA decreased to 38.5°. Interestingly, no significant change of sliding velocity and surface CA was detected after 10 cycles, thus demonstrating that the slippery surface has excellent endurance properties.

#### 3.5 Anti-icing and anti-frosting properties

In this section, the anti-icing properties of MPRSs-1H3M were tested to evaluate its practical value under extreme conditions. The specimen was placed on a PCC device which was used to adjust the ambient temperature. At a constant temperature, a water droplet (2  $\mu$ l) was then dropped on the surface and the icing delay time was recorded. The DT of blank glass, rough solid HFs-30, flat solid MPRSs-1M3M and the HFs covered with silicone oil (MPRSs-Si) was also measured to compare anti-icing



Fig. 6 (a) Photo-thermal test device for absorbing light energy from a sunlamp, and the surface temperature was monitored using a non-contact infrared thermometer. (b) The heating effect of HFs-0 and HFs-30 under sunlamp irradiation (75 W). The CA (c) and sliding rate (d) changes on the MPRSs-1M3M at 25 °C and 65 °C for 10 cycles.

properties with those of MPRSs-1H3M, as silicone oil was constantly selected as the model lubricant to prepare slippery surfaces. Fig. 7c shows the variation of the individual water droplet shape on these samples during the whole freezing process. As we can see, the DT of uncoated glass was prolonged to 23 s, HFs-30 to 563 s, MPRSs-1M3M to 330 s, and MPRSs-1H3M to 3605 s (Fig. 7a), thus indicating that FIL-1H3M was prominent in delaying icing due to the high energy barrier of nucleation for water droplets. However, there was a huge difference in the DT of the slippery surfaces. The icing delay time of the MPRSs-Si surface was only extended to 662 s, which was much shorter than that of MPRSs-1H3M. Besides, the DT of the Teflon template was prolonged to 363 s (Fig. S13†), which was longer than the DT of MPRSs-1M3M, but shorter than the DT of HFs-30, because the roughness of the Teflon template surface was between that of MPRSs-1M3M and HFs-30. Moreover, the surface chemical composition was similar to that of the fluorinated surface. The presence of  $Fe_3O_4$  was capable of



**Fig. 7** (a) Icing delay time of different samples. (b) The time taken for frosting of four samples. (c) Snapshots of individual water droplets on samples during the whole freezing process. (d) Snapshots of the frosting experiment on the surfaces of glass, HFs-30, MPRSs-1M3M, and MPRSs-1H3M.

endowing the surface with good photo-thermal responsive deicing properties and creating a low-energy de-icing mechanism, which has been demonstrated in our previous work.<sup>11</sup> These results suggested that the FIL-1H3M infused slippery surfaces have excellent anti-icing properties.

In addition, the anti-frosting performance of this surface was also measured. As shown in Fig. 7b and d, there was a significant difference of the frosting state between these samples. For HFs-30, frost was very easy to deposit on it, because the rough surface provided many nucleation sites for frosting. The antifrosting time (AFT) was less than 10 min at -17 °C and the AFT of MPRSs-1M3M was extended to 30 min. This resulted from the reduction in the number of nucleation sites on the smooth surface of MPRSs-1M3M. But both surfaces were covered by a large amount of frost after 60 min, since the heat transfer rate of solid materials was faster than that of liquids. As for MPRSs-1H3M, the water droplet started to gather at the edge of the membrane after cooling for 30 min. Then the droplets coalesced and became larger. The AFT of this surface was prolonged by 100 min due to the reduced thermal conduction of liquids and the high energy barrier of nucleation for water droplets.

## 4. Conclusions

In this work, we successfully synthesized a magnetic-thermal and photo-thermal responsive slippery surface based on a new type of fluorinated ionic liquid and a fluorinated substrate with self-repairing properties. By altering the phase state of the FIL under light irradiation or magnetic field, the reversible wettability, from hydrophobic to slippery, and droplet motion, from pinning to sliding, were achieved. Besides, the responsive temperature could be controlled by using different substituent groups to synthesize FILs. In addition, the slippery surfaces presented good liquid repellency, self-cleaning properties and high stability. More interestingly, the freezing time of FIL-1H3M infused slippery surfaces was prolonged to 3605 s at -15 °C, which was 156 times that of the DT of glass. This work provides a new type of lubricant oil to fabricate a stable slippery surface with controllable wettability, thus promoting the application of slippery surfaces in microfluidic devices and biomedical systems.

## Conflicts of interest

None.

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