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## Photothermally actuated interfacial hydration for fast friction switch on hydrophilic polymer brushes modified PDMS sheet incorporated with Fe<sub>3</sub>O<sub>4</sub> nanoparticles

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**Near-infrared light triggered fast interfacial friction switch was achieved with polyelectrolyte brushes grafted PDMS embedded with Fe<sub>3</sub>O<sub>4</sub> nanoparticles, where *in situ* heating up of the photothermal Fe<sub>3</sub>O<sub>4</sub> nanoparticles in the polymer matrix changes the interface humidity and thereafter alters the hydration level of the interfacial polymer brushes.**

Friction is everywhere. It takes place between any rubbing surfaces including not only the moving parts in machines but also in our body and daily life when we are blinking, chewing, swallowing, walking, and driving for example.<sup>1</sup> Due to friction can lead to large amounts of energy lost, serious wear damages, or pains of biological body, antifriction becomes an everlasting topic that can be even dated to antiquity,<sup>1a</sup> which has resulted in many methods, materials and surfaces achieving lubrication in various fields including industry, manufacture, aerospace, and biomedical engineering, etc.<sup>2</sup> As a matter of fact, antifriction is not the only topic in tribology. Sometime high friction is desired, otherwise cars would not move or stop and people would not even stand on iced road. Therefore, the ability to regulate or switch interfacial friction is evidently quite attractive for many applications in biosensors, microfluidic devices, and intelligent devices and so on. That's why intelligent control of interfacial friction has attracted increasing attention currently.<sup>3</sup>

Essentially, friction between two contacted surfaces depends on their mutual interactions, including adhesion effects, electrostatic interaction, and hydrophobic interaction, etc.<sup>4</sup> Consequently, manipulating the interfacial interactions between sliding surfaces with external stimuli is a matter of course to achieve interfacial friction control and/or switch. To date, interfacial friction control has been realized by various

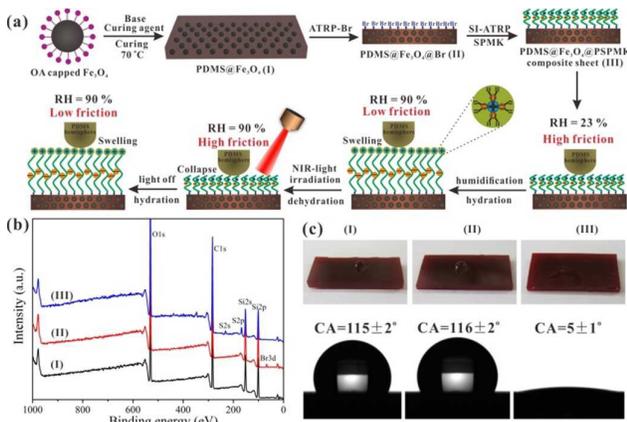
external stimuli such as temperature,<sup>5</sup> pH,<sup>6</sup> solvent,<sup>7</sup> electrolyte,<sup>8</sup> magnetic field,<sup>9</sup> potential field,<sup>10</sup> and UV light.<sup>11</sup> Despite the very recent achievements that the interfacial friction coefficient of polyelectrolyte brushes was dramatically tuned by at least three orders of magnitude (0.001~1) with counterions switching or it was multiply tuned with dual-stimuli, pH and temperature,<sup>5b, 6b, 8</sup> the switch of friction is time-consuming. The external stimuli need either ion exchange, solvent/solution switch, long time UV exposure, or heat up, which all cost time. The practical applications of these resultant friction switchable interfaces in intelligent technologies have thus been highly restricted. Therefore, how to realize the fast or real-time friction switch still remains a highly challenging topic.

Herein, we report for the first time a novel near-infrared (NIR) light based approach, which allows for achieving surfaces with fast friction switch between ultra-low (~0.02) to high level (>1.0). This approach is inspired by the previous findings that the interfacial hydration effect is crucial for aqueous lubrication.<sup>2b, 2c, 5a, 12</sup> Surfaces with good hydration effect exhibit an extremely low friction due to the fluidized hydration layer trapped on it, while conversely a high friction. Previously, we demonstrated that interfacial environments including temperature, pH, and humidity can be used to regulate the conformation of polymer chains at the interface and realize friction control of polyelectrolyte brushes and hydrogels by affecting the hydration effect.<sup>5, 6b, 12c</sup> Very recently, with the environmental humidity stimulus, we realized interfacial friction induced 'gecko feet'.<sup>13</sup> However, the regulation of surrounding environments is either time-consuming or difficult to precisely and quickly control.<sup>14</sup> Here, the key innovation is that Fe<sub>3</sub>O<sub>4</sub> nanoparticles was incorporated into the interfacial system, whose excellent near-infrared (NIR) photo-thermogenesis can locally change the *in situ* interface environments such as temperature to alter the hydration level of the interfacial polymer to realize fast friction switch. Fig. 1a shows the structure of fast friction switch system, i.e. poly(3-sulfopropyl methacrylate potassium salt) (PSPMK) grafted PDMS embedded with Fe<sub>3</sub>O<sub>4</sub> nanoparticles. Briefly, Fe<sub>3</sub>O<sub>4</sub>

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<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100039, China. Electronic Supplementary Information (ESI) available: Experimental details, high resolution XPS spectra, calculation method for photothermal conversion efficiency, and a video showing NIR light triggered friction switch controlling object motion. See DOI: 10.1039/x0xx00000x

nanoparticles were dispersed in PDMS matrix to serve as a good NIR-light absorber<sup>15</sup> and an elastic friction pair as well, and on which PSPMK polymer brushes were grafted through surface-initiated atom transfer radical polymerization (SI-ATRP) to act as a humidity-sensitive layer<sup>12a, 13</sup>. Details are described in Supporting Information.



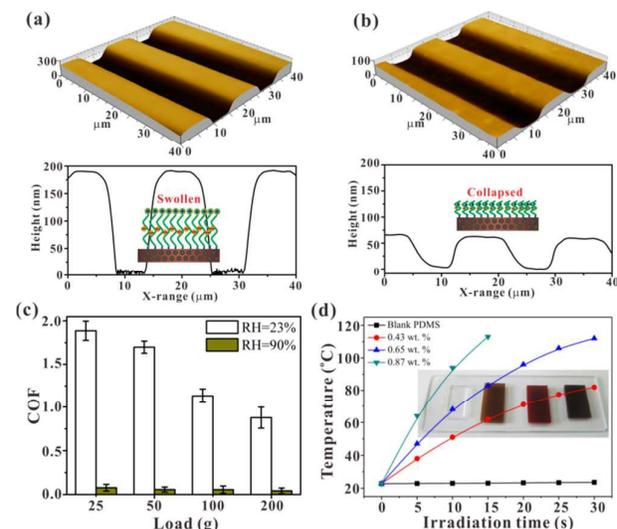
**Fig. 1** (a) Schematic illustration of the PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet fabrication and the dehydration/hydration interfacial friction switch triggered by NIR light.

The successful fabrication of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet was ascertained by XPS survey spectra (Fig. 1b) and high resolution spectra (Fig. S1), where the emergence of Br 3d signal (69 eV) indicated the successful assembly of the initiator on the PDMS@Fe<sub>3</sub>O<sub>4</sub> substrate and the evident S 2p (231 eV) and S 2s (167 eV) signals are assigned to the grafted PMPK brushes on the PDMS@Fe<sub>3</sub>O<sub>4</sub> substrate. The grafted PMPK polymer brushes enabled the surface's wettability changed from hydrophobicity to hydrophilicity (Fig. 1c). The water dropped on PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK spread out with the contact angle of ~5°, suggesting a superhydrophilic performance of the PMPK brushes, which is a prerequisite to achieve low friction in hydration lubrication.

The hydration performance of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK was then investigated with atomic force microscopy (AFM) probing the swelling-collapse behaviour of PMPK brushes to humidity. As observed by the AFM images, the thickness of PMPK brushes is 191 nm at 90% humidity (Fig. 2a), while only 63 nm at 23% (Fig. 2b). The >3 times of swelling ratio clearly illustrates that the polymer chains experienced a highly extended conformation because of the high level of hydration of PMPK brushes under wet condition. In addition, the polymer film with a definite thickness also indicates the coverage of PMPK polymer brushes on the substrate. Good hydration leads to low friction for hydration lubrication, and vice versa. The friction test shows that the COF of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK at 23% humidity is more than three orders of magnitude higher than that at 90% (Fig. 2c). This big difference reveals that friction switch is feasible for PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet once humidity is regulated. Compared with the surface COF of PDMS@Fe<sub>3</sub>O<sub>4</sub> substrate (Fig. S2), the hydration lubrication of PMPK brushes leads to

a much lower COF, which highlights the importance of PMPK brushes for our as-designed tribological system.

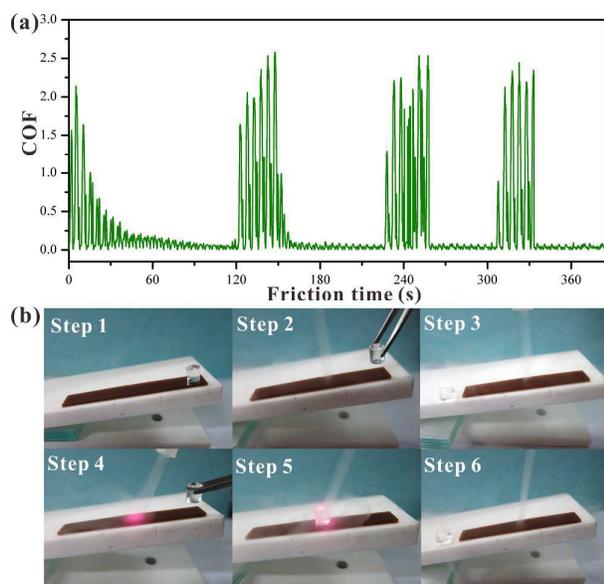
However, the surrounding humidity is difficult to precisely and quickly control.<sup>14</sup> Other than humidity control with entire environment, herein the NIR photothermogenesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was employed to locally decrease the humidity of PMPK brushes at a high humidity condition by in situ heating. Fig. 2d shows the temperature rise traces of the surface temperature of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK as a function of irradiation time. Under a continuous laser irradiation, the surface temperature of the PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet had a remarkable increase within seconds, while no obvious temperature increase was observed for PDMS@PSPMK sheet, indicating the buried Fe<sub>3</sub>O<sub>4</sub> nanoparticles can in situ heat up the surface when exposed to NIR laser because of its high photo-thermal conversion efficiency. The higher fraction of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles is, the faster of the surface temperature increase of the sheet is. Specifically, when the concentration of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was 0.87 %, the surface temperature of composite sheet reached ~100 °C with 10 sec NIR laser irradiation. The vigorous photothermal performance even resulted in a burn mark on the sheet. The photothermal conversion efficiency (PCE) was calculated (Eq. S1), which for our case is 30.64 % (Fe<sub>3</sub>O<sub>4</sub>: 0.65%, Irradiation time: 20 s). With the in situ heating up, it is expected that the local water will be evaporated rapidly leading to locally decreased humidity and thereby dehydrated PMPK brushes with high friction.



**Fig. 2** The AFM images of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK at humidity of 90 % (a) and 23% (b), and the surface COF and temperature changes to humidity (c) and NIR irradiation (d), respectively.

Fig. 3a is the friction test of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet at 90% humidity with NIR laser on/off. It can be seen that the PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet exhibited ultralow friction (COF ~0.02) under high humidity environment, yet high friction (COF >1.0) once irradiated by NIR laser. The friction increase is contributed to the dehydration of PMPK brushes due to the in situ heating of Fe<sub>3</sub>O<sub>4</sub> nanoparticles under NIR irradiation. Importantly, when the irradiation was turned off, the ultralow friction was quickly restored, resulted from the soon re-

hydration in the high humidity surrounding. With the ability of photothermogenesis-induced soon dehydration and re-hydration at high humidity environment, the PSPMK brushes grafted PDMS@Fe<sub>3</sub>O<sub>4</sub> sheet realized 'real-time' friction switch. Remarkably, the reversible friction switch can be cycled many times implying its high potentials in intelligent materials and technologies. For proof-of-concept purpose, a visual demonstration of the 'real-time' friction switchable PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet used to control the motion of object was conducted. As shown in Fig. 3b and Movie S1, on the inclined (~8.5°) PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet, a home-made PDMS cylinder stood still at the top at ambient due to the high friction between the PDMS cylinder and the sheet (Step 1). After wetting the sheet surface by a humidifier (Step 2), the cylinder quickly slid down (Step 3) because of the sharp friction decrease. However, after turning on the NIR laser (Step 4), it stopped suddenly just at the NIR laser irradiation spot during sliding (Step 5), where the friction was increased locally due to the NIR photothermal effect. Nonetheless, when the NIR-light was turned off, the PDMS cylinder began to move again (Step 6), indicating the PSPMK brushes re-absorbed water in high humidity environment and restored the low friction.



**Fig. 3** (a) The 'real-time' friction switch as a function of friction time under intermittent NIR light irradiation; (b) Proof-of-concept demonstration of NIR light-triggered friction switch of PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet for the motion control of objects. The inclined angle of the sheet is ~8.5°.

In conclusion, we have demonstrated a facile yet efficient NIR photothermogenesis strategy to realize efficient and fast interfacial friction switch. The key feature is the embedded Fe<sub>3</sub>O<sub>4</sub> nanoparticles with excellent photothermal effect as local nano-heater to heat the interface in situ, leading to the hydration/dehydration of the interfacial polymer and thus the interfacial friction switch. Due to directly acting on the interface, the NIR photothermogenesis strategy is more efficient, compared to conventional heating mode from

environment. The PDMS@Fe<sub>3</sub>O<sub>4</sub>@PSPMK sheet realized NIR light triggered real-time friction switch for the first time. The present NIR photothermogenesis induced real-time friction switch will find a practical way to design promising actuators and smart devices for intelligent materials in mechanical, electrical, engineering, and biomedical fields.

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