Electronic Supporting Information

Photothermally actuated interfacial hydration for fast friction switch

on hydrophilic polymer brushes modified PDMS sheet incorporated

with Fe₃O₄ nanoparticles

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1. Experimental Section

1.1 Materials

Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 98 %), Iron (II) chloride tetrahydrate (FeCl₂·4H₂O, 98 %), Oleic acid (OA, 99 %), ammonium hydroxide (NH₃·H₂O, 28-30%), anhydrous ethanol (AR), and sodium hydroxide (NaOH, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). and used as received. The base and curing agents of Sylgard 184 elastomer kit (Dow Corning) were purchased from J&K Chemical Ltd., and used as received. 3-Sulfopropyl methacrylate potassium salt (98%, SPMK), 2,2'-bipyridine (Bpy, 99%) and copper (I) bromide (CuBr) were purchased from TCI Co., Ltd. CuBr was purified by stirring overnight in acetic acid. For surface-initiated atom transform radical polymerization (SI-ATRP), the silane initiator 3-(trichlorosilyl)propyl-2-bromo-2-methylpropanoate and thiol ester initiator ω-mercaptoundecyl bromoisobutyrate were both synthesized in our lab according to previous strategies¹. Hexane and methanol were used as received. Deionized water was used in all the experiments. Gold film was prepared via thermal evaporation of 100 nm gold on silicon wafers with 5 nm Cr as the adhesive layer.

1.2 Synthesis of oleic acid capped Fe₃O₄ nanoparticles

The oleic acid capped Fe₃O₄ nanoparticles (OA-Fe₃O₄) were prepared through a modified chemical co-precipitation method, and then modified with oleic acid². Briefly, 0.1 mol of FeCl₃·6H₂O and 0.055 mol of FeCl₂·4H₂O were dissolved in a 500 mL glass flask filled with 150 mL deionized water. The solution was heated to 70 °C and then 70 mL of NH₃·H₂O was added to the flask under vigorous mechanical stirring to obtain black slurry. The mixture was left at 70 °C for 1 h. After 4 mL of oleic acid was added dropwise into the magnetic fluid under mechanical stirring, the mixture was left at 80 °C for 1 h. The OA-Fe₃O₄ nanoparticles were collected by a magnet and washed several times with ethanol/hexane alternately. Finally, the OA-Fe₃O₄ nanoparticles were dispersed in hexane, and the concentration was calculated to be 0.0173 g/mL.

1.3 Preparation of PDMS@Fe₃O₄ substrate

The base and curing agent of Sylgard 184 silicone elastomer were firstly mixed at a mass ratio of 10:1 in hexane, followed by the addition of the OA-Fe₃O₄ hexane dispersion. The mixture was stirred homogeneously, and poured into a home-made mold with a fluorinated silane substrate. Afterwards, the mixture was cured in an oven at 70 °C overnight. Finally, the PDMS@Fe₃O₄ substrate with the thickness of ~1.0

mm was obtained. By adjusting the addiction amount of OA-Fe₃O₄ hexane dispersion (2.0 mL, 3.0 mL and 4.0 mL), a series of composite substrates containing various concentrations (0.43 %, 0.65 % and 0.87%) of Fe₃O₄ nanoparticles were fabricated. Since the elastomer, curing agent, and OA-Fe₃O₄ nanoparticles all can be well dispersed in hexane, they can be mixed homogenously in hexane. After final thermal curing, the Fe₃O₄ nanoparticles were distributed uniformly in PDMS matrix.

1.4 Preparation of PSPMK brushes grafted PDMS@Fe₃O₄ composite sheet

PSPMK brushes grafted PDMS@Fe₃O₄ sheet was prepared by SI-ATRP. Firstly, chemical vapor deposition (CVD) was employed to anchor silane initiator on the PDMS@Fe₃O₄ substrate. The plasma oxidized PDMS@Fe₃O₄ substrate and a vial containing 10 μ L of 3-(trichlorosilyl)propyl 2-bromo-2-methylpropanoate were put into a vacuum desiccator. The chamber was pumped down to <1 mbar, and left under vacuum for 30 minutes. This process was cycled for 3 times. The initiator anchored PDMS@Fe₃O₄ substrate (PDMS@Fe₃O₄@Br) was obtained for further SI-ATRP. Typically, SPMK (1.5 g), 2,2'-bipyridyl (0.0628 g), 9 mL of methanol/H₂O (v:v = 2:1) were added into a test tube, which was then deoxygenated by bubbling nitrogen gas for 30 min. In the following, CuBr (0.0287 g) were added into the tube quickly. After 5 min of nitrogen gas bubbling, the PDMS@Fe₃O₄@Br was put into the tube for SI-ATRP. The polymerization was conducted under nitrogen protection for 2 h. The obtained PDMS@Fe₃O₄@PSPMK composite sheet was washed with deionized water and ethanol for further friction test. To facilitate the morphology investigation of PSPMK brushes at different humidity with atomic force microscopy (AFM), patterned PSPMK brushes grafted on gold substrate were synthesized by SI-ATRP initiated by ω-mercaptoundecyl bromoisobutyrate. The self-assembled monolayer (SAM) of thiol ester initiator was prepared by micro-contact printing. Briefly, a PDMS stamp was first immersed in the thiol ester initiator solution (5 mM ethanolic solution) for 30 seconds, then it was dried and made contact with the gold substrate for 15 seconds to print the initiator on gold substrate followed by gently wash with ethanol.

2. Characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Thermal scientific ESCALAB 250Xi X-ray photoelectron spectrometer. The binding energy was referenced to the C1s of contaminated carbon at 284.8 eV. The water contact angle on the as-made film was measured with a 5 μ L droplet of deionized water at ambient temperature with a DSA100 contact angle (CA) meter (Krüss Co., Germany). The average CA was obtained by measuring more than three different positions of the same sample. Atomic force microscopy (AFM) measurements were performed on an Agilent Technologies 5500AFM in tapping mode using a pyramidal Si tip (Veeco, RTESP). The sample platform was surrounded by a relative humidity controller. Imaging was performed under ambient condition (RH = 23%) and high humidity condition (RH = 90%).

The photothermal performance of PDMS@Fe₃O₄@PSPMK sheet was measured as follows. The composite sheet was irradiated by NIR laser at 808 nm (BST808-5-F,

Xi'an Best Laser Optronics co., LTD, China) at a power density of 1.7 W/cm^2 . The laser power was set at 1.34 W for the measurements. The area of the laser illumination spot on the composite sheet was 0.79 cm^2 . The surface temperature of the composite sheet was obtained by an infrared thermometer. When the surface temperature reached ~110 °C, a burn mark appeared on the sheet, and the irradiation was immediately turned off.

3. Friction test

The frictional tests were carried out in a ball-on-block configuration on a Universal Micro-Tribometer (UMT-2, CETR) under different humidity conditions. The distance of one sliding cycle was 10 mm, and the friction coe cient vs time plot was obtained. The contact between the frictional pair was achieved by pressing the upper running PDMS hemisphere against the lower stationary PDMS@Fe₃O₄@PSPMK sheet. The PDMS hemisphere with a diameter of 6 mm was prepared in a home-made mold using commercial silicone elastomer kit (SYLGARD 184, Dow Corning). Each friction test was repeated three times, and an average coefficient of friction (COF) was recorded. The relative humidity was adjusted by a relative humidity controller, and 808 nm NIR laser was employed to irradiate the surface of composite intermittently for photothermally mediated friction test. The normal load was 100 g. The laser power was set at 1.34 W for the measurements. The area of the laser illumination spot on the composite sheet was 0.79 cm².

4. The calculation method for photothermal conversion efficiency

The following formula was employed for calculating the photothermal conversion efficiency (PCE).

$$PCE (\%) = \frac{Heat \ quantity \ of \ composite \ sheet}{NIR \ light \ power \ X \ Irradiation \ time} X \ 100\%$$

$$=\frac{Cm\Delta T}{Pt}X\ 100\% = \frac{C\rho Sh(T2-T1)}{Pt}X\ 100\%$$
(S1)

where C is the specific heat capacity of PDMS (1.46 kJ/kg·K), m is the mass of composite sheet under NIR light irradiation, ΔT is the value of increased temperature, P is the NIR light power (1.34 W), t is the irradiation time, ρ is the mass density of PDMS (0.97 x 10³ kg/m³), S is the area of irradiation spot, h is the thickness of composite sheet, T2 is the temperature after a certain time irradiation, and T1 is the initial temperature (22.8 °C).

The photothermal conversion efficiency with the Fe_3O_4 concentration of 0.65 % after 20 s NIR light irradiation was chosen as a representative value. The S is 0.79 cm², the h is 1 mm, and the T2 is the 96.2 °C. After calculation, the PCE is 30.64 %.



Fig. S1 High resolution XPS spectrum in (a) Br 3d region of PDMS@Fe₃O₄@Br and

(b) S 2p region of PDMS@Fe₃O₄@PSPMK.



Fig. S2 Surface COF for PDMS@Fe₃O₄ substrate as a function of normal load at

different humidity conditions.

Movie S1 Demonstration of NIR light trigger 'real-time' friction switch of PDMS@Fe₃O₄@PSPMK for motion control of objects.

References

- (a) M. Husseman, E. E. Malmström, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell and C. J. Hawker, *Macromolecules*, 1999, **32**, 1424; (b) D. M. Jones, A. A. Brown and W. T. S. Huck, *Langmuir*, 2002, **18**, 1265.
- (a) X. Li, H. Li, G. Liu, Z. Deng, S. Wu, P. Li, Z. Xu, H. Xu and P. K. Chu, *Biomaterials*, 2012, 33, 3013; (b) H. Zhu, Y. Shang, W. Wang, Y. Zhou, P. Li, K. Yan, S. Wu, K. W. Yeung, Z. Xu, H. Xu and P. K. Chu, *Small*, 2013, 9, 2991.