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Supporting Information

Repeatedly Regenerating Mechanically Robust Polymer Brushes from Persistent Initiator Coating (PIC)

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Experimental Procedures

Material

Glass slides (Sailboat, China) of 25 mm × 60 mm. Silica wafers (thickness 400 ± 10 um, diameter 100 mm, Suzhou rui materials semiconductor Co, Ltd). α-bromoisobutyryl bromide (98%, J&K). (3-aminopropyl)tiethoxysilane (APTES, 99%, Sigma-Aldrich). 3-sulfopropyl methacrylate potassium salt (SPMA, 97%, J&K Chemical Co. Ltd). Methyl methacrylate (MMA, 99%, J&K Chemical Co. Ltd). Styrene (99.5%, J&K Chemical Co. Ltd). 1H,1H-Pentadecafluorooctylacrylate (PFOA, 97%, J&K Chemical Co. Ltd). Tetraethyl orthosilicate (AR, Sinopharm Chemical Reagent Co. Ltd). Copper (II) chloride dihydrate (99%, Sinopharm Chemical Reagent Co. Ltd). N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin). Ascorbic acid (AA, Sinopharm Chem-ical Reagent Co. Ltd). All other chemicals and solvents were purchased from commercial sources and used as received without further purification.

Characterization

The thickness of the polymer layer was measured using a spectroscopic ellipsometer (Gaertner model L116E) equipped with a He −Ne laser source (λ = 632.8 nm) at a fixed angle of incidence of 50°. The refractive index of polymer film was 1.5. DSA-100 optical contact angle meter (Krüss Company, Germany) was used to measure contact angles (CAs). The probe liquid was a droplet of deion-ized water (5 μL) to obtain the static contact angle. The chemical composition about the sample was obtained by X-ray photoelectron spectroscopy (XPS), and the measurement was carried out on an ESCALAB 250xi spectrometer (Thermon Scientific, USA) by using Al Kα radiation. The binding energy of C 1s (284.8 eV) was used as the reference. The etching voltage of Ar+ gun was 3000eV, and the etching time was 50s, 100s, 150s, 200s, and 250s respectively. The morphology of surfaces with different modifications was analyzed by an atomic force microscope (AFM) (Agilent 5500) in tapping mode with a commercially available type-II MAC lever. 1H NMR spectra were measured on a Varian Unity Inova 400 FT NMR spectrometer operated at 400 MHz.

Preparation of the ATRP initiator (APTES-Br)

APTES–Br was prepared by following previous method.[1] APTES (10 mL, 43 mmol) and triethylamine (7.8 mL, 57 mmol) were added in dry $CHCl_2$ (200 mL) under the protection of nitrogen. The mixed solution was placed in an ice water bath, and α-bromoiso-butyryl bromide (5.55 mL, 51 mmol) was added dropwise at 0 °C. After completing the addition, the mixture was stirred at 0 °C for further 30 min, and then warmed to 25 °C and stirred overnight. The mixture was filtered, concentrated in vacuo to give APTES–Br.

Preparation of PIC

5ml tetraethoxysilane and 625μL APTES-Br was added into 25ml ethanol, then 0.5ml nitric acid was added into the above ethanol solution under agitate intensely, and allowed the solution to stand for at least 24 hours before usage. This precursor solution was then dipping coating (pulling rate was 20mm/min) on a clean glass slide that was treated with oxygen plasma for 2 minutes to remove organic pollutants. After dried in the 80 ˚C air oven for 2h, the PIC layer was deposited on the surface.

Preparation of APTES-Br monolayer (mAPTES -Br) layer by CVD

As a control, the APTES-Br monolayer (mAPTES -Br) layer was also prepared on glass slide by chemical vapor deposition (CVD).[2-3] The glass slide was placed in ethanol solution, ultrasonic treated for 0.5h and dried with dust-free cloth, then it was treated with oxygen plasma for 2min. Then, put the cleaned glass slide into a vacuum dryer with 20ul APTES-Br. After vacuumizing for 20 min, it was placed in the oven and baked for 0.5 H. And then repeat the process twice times. Finally, the glass slide was repeatedly washed with ethanol and deionized water, and then dried with nitrogen to obtain APTES-Br monolayer (mAPTES-Br) layer on the glass slide.

SI-ATRP of SPMA from PIC or CVD Substrates

pSPMA brushes were prepared through an ARGET-ATRP process on each PIC and mAPTES-Br layer by following previous method.[4-5] SPMA (2g), Water (5mL), $CuCl_2$ $2H_2O$(8mg,) and PMEDTA (10 µL) were added in a glass bottle, and then stirred vigorously until the monomer and catalyst were completely dissolved. AA (88 mg) was then added to this solution and stirred for ~2 min to activate the catalyst. The reactant molar ratio was $[AA] / [Cu^{2+}] / [PMEDTA] = 10:1:1$. After that, divide the mixed solution into two parts and pour into the flasks that contain PIC and mAPTES-Br covered substrates, respectively. Finally, the substrates were removed out after 6 hours, washed with deionized water for several times and dried with nitrogen.

SI-ATRP of hydrophobic monomer from PIC or CVD Substrates

MMA/Styrene/PFOA (5 mL), DMF (10 mL), $CuCl_2$ $2H_2O$ (16 mg,) and PMEDTA (50 µL) were added in a glass bottle, and then stirred vigorously until the catalyst were completely dissolved. AA (176 mg) was added to 2 ml DMF and sonicated until complete dissolution. This solution was then added to the ATRP reaction solution and stirred for ~2 min to activate the catalyst. After that, pour the mixed solution into the flasks that contain PIC or mAPTES-Br covered substrates and placed it in an oven at 80°C. Finally, the substrates were removed out after 6 hours, washed with DMF for several times and then put it into a fluorine solvent and sonicate for 5 min and dried with nitrogen.

Friction Test

The wear resistance was measured by an abrasion tester (Model 339). Polyester cloth was used as the upper friction pair in the experiment. In the wear resistance test, the glass slides modified with PIC were subjected to different cycles of reciprocating dry friction under a load of 10N. The contact angle of the surface was measured, and compared with that of the glass slides modified with mAPTES-Br under the same conditions. The surfaces of PIC after 0, 5000, 10000, 15000 and 20000 friction cycles were selected to test the content of bromine initiator on the surface. The wear resistance test of polymer brush is consistent with the above process except the test was carried out in water surrounding.

The friction coefficient was conducted using a conventional ball-on-desk reciprocating friction tester (MFT-R4000, Huahui Co. Ltd). Elastomeric poly(dimethylsiloxane) (PDMS) hemispheres with a diameter of 6 mm act as an upper friction pair in this experiment. The PDMS hemispheres were prepared by a commercial silicone elastomer kit (SYLGARD 184 silicone elastomer base and curing agents, Dow Corning). A polystyrene 96-well cell culture plate with round-shaped well (diameter 6 mm, Dow corning) was used as a mold to prepared PDMS pins ([base] / [curing agents] = 10:1). The mixtures were put into the mold after removing bubbles and then incubated in an 80 °C oven for 3 h to obtain PDMS hemispheres. The load was regulated by applying weights. All friction experiments were carried out in water surrounding.

Properties of Re-initiated Polymerization

The processes of renewable performance test of surface wettability, friction performance and chemical composition were basically the same. The pSPMA polymer brushes on the surface modified with PIC was rubbed back and forth for 20000 times on an abrasion tester, and then its surface properties were tested. After that, the worn substrate was put into the reaction solution, sealed and reacted for 6 hours, then removed out the substrate and washed with deionized water, flushed with nitrogen, and the surface properties were tested again. The process was repeated several times and compared with the CVD surface under the same conditions.

Preparation of Large-Scale PIC Formed on Substrates by Spray-Coating Process.

The PIC layer was coated on the mirror (20×20 cm^2) by spraying method. First, the PIC solution was diluted with ethanol to reduce its viscosity. Then, the mixed solution was sprayed on a clean mirror (half of the mirror is covered with white paper for comparison). After ethanol volatilization, the mirror is put into the oven at 80 °C for 2 h to obtain the mirror modified with large-scale PIC.

SI-ATRP of pSPMA polymer brushes Grafted from Large-Scale PIC Substrates

The method of open-air SI-ATRP on PIC-covered surface was improved on the basis of the conventional ARGET-ATRP. The identical precursor solution of SI-ATRP for PSPMA (8mL, 0.02 mL/cm^2) was carefully poured on one end of the mirror. Then, a PET film of the same size was gently covered on the mirror from this side, and then kept undisturbed at room temperature for 2h in air. After this, the mirror was repeatedly washed with deionized water and dried with nitrogen. The obtained mirror was used for CA and antifogging test.

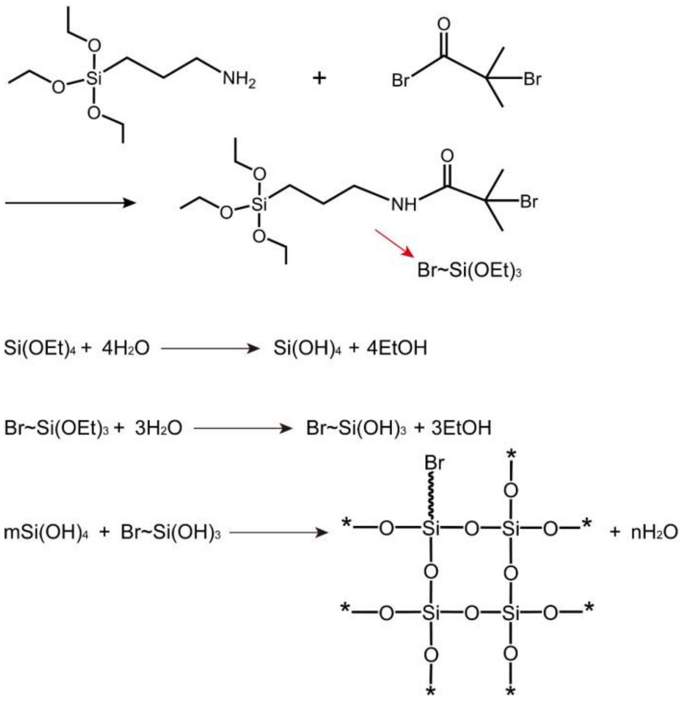

Figure S1. The preparation reaction equations of APTES-Br and PIC.

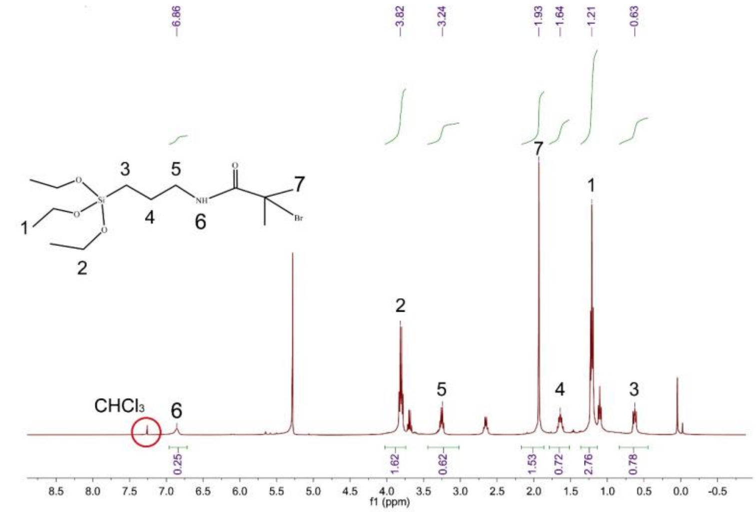

Figure S2. The 1H NMR of the APTES-Br.

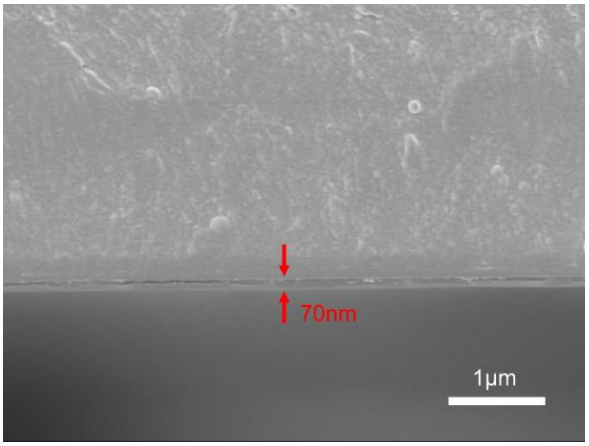

Figure S3. The SEM image of PIC.

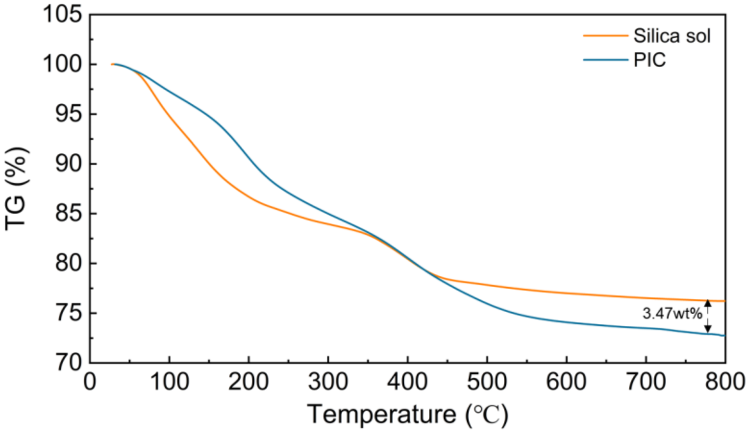

Figure S4. The TG curve of PIC.

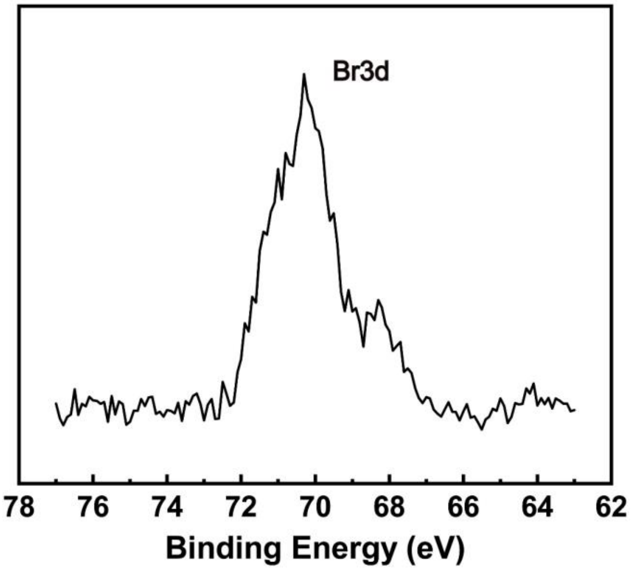

Figure S5. The high resolution XPS of Br 3d on the PIC surface.

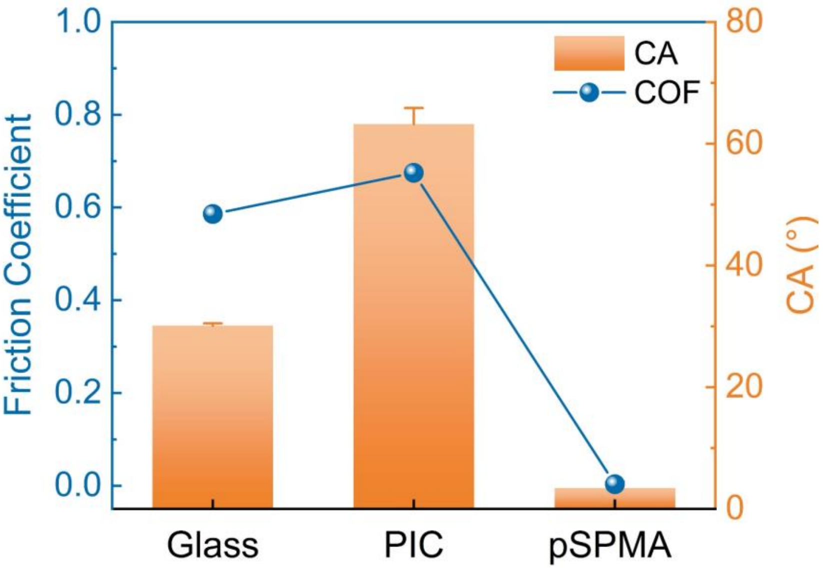

Figure S6. The friction coefficient (3N, 2Hz, against PDMS ball in aqueous solution) and water contact angle of substrate surfaces at different preparation stage.

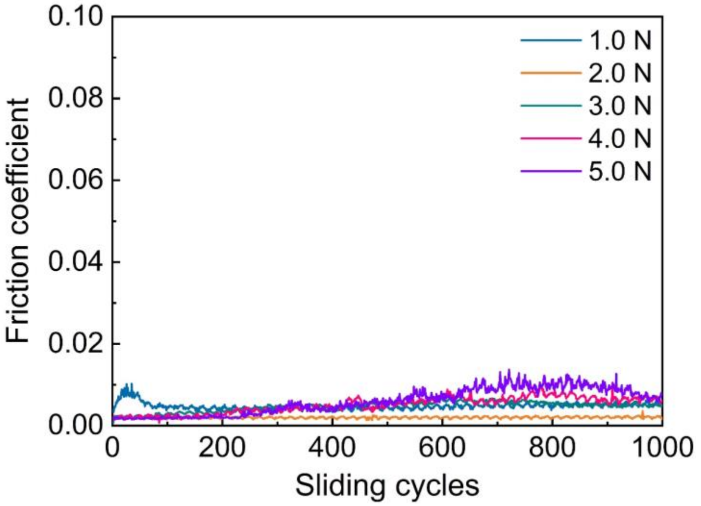

Figure S7. The changes of friction coefficient on the PIC-pSPMA surface under different load (2Hz, against PDMS ball in aqueous solution).

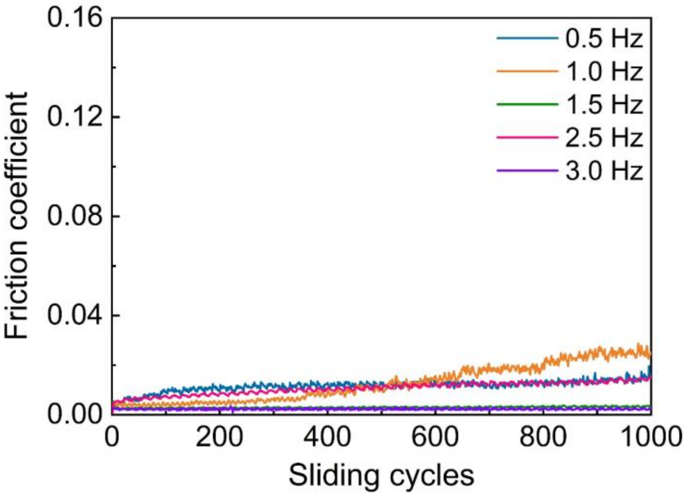

Figure S8. The changes of friction coefficient on the PIC-pSPMA surface under different frequency (3N, against PDMS ball in aqueous solution).

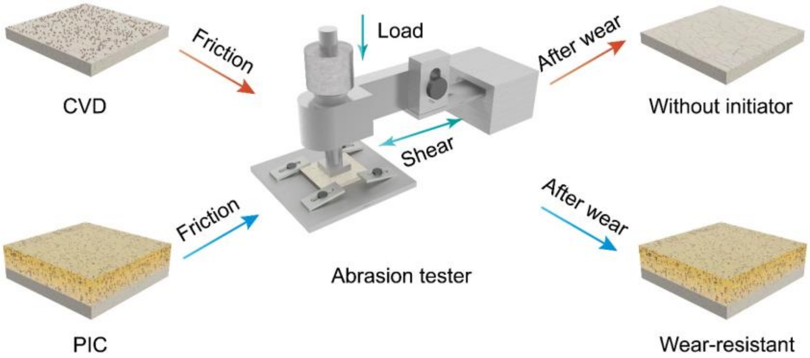

Figure S9. The schematic wear resistance of the PIC and CVD initiator surfaces

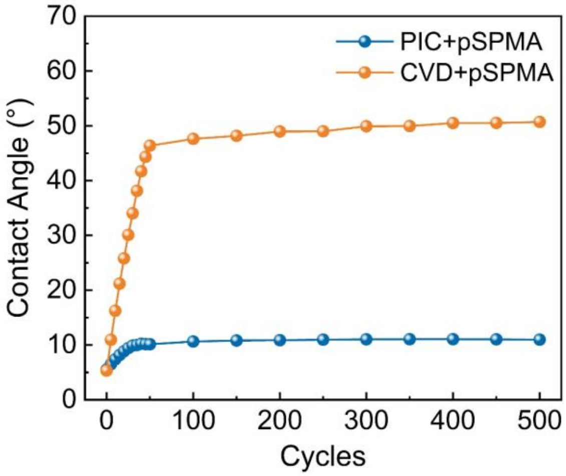

Figure S10. The changes of contact angles on PIC+pSPMA and CVD+pSPMA surfaces in 500 short cycles (25kPa, against polyester fiber in aqueous solution).

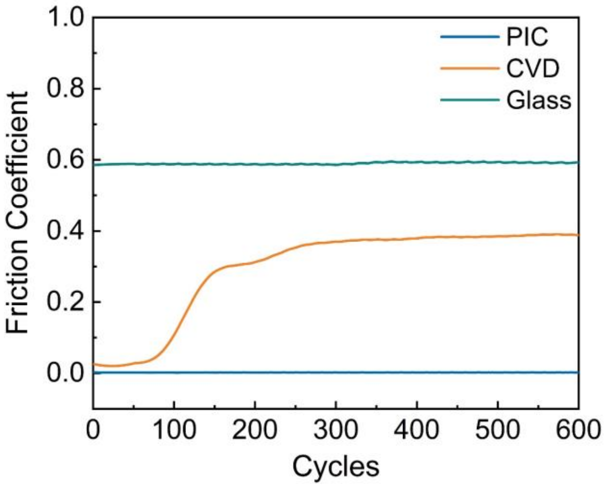

Figure S11. The changes of COF on PIC-pSPMA, CVD-pSPMA and Glass surfaces in 600 short cycles (3N, 2Hz, against PDMS ball in aqueous solution).

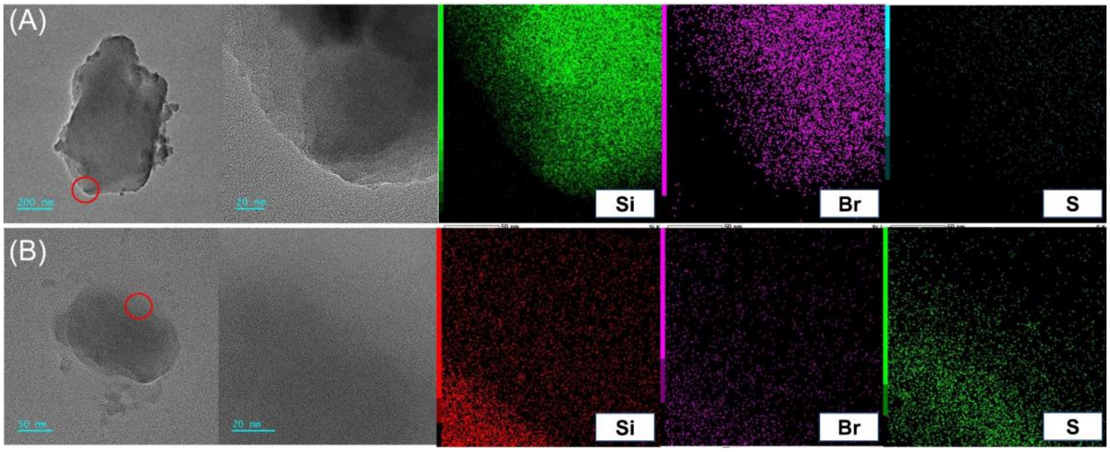

Figure S12. The TEM image of PIC (A) and PIC-pSPMA (B).

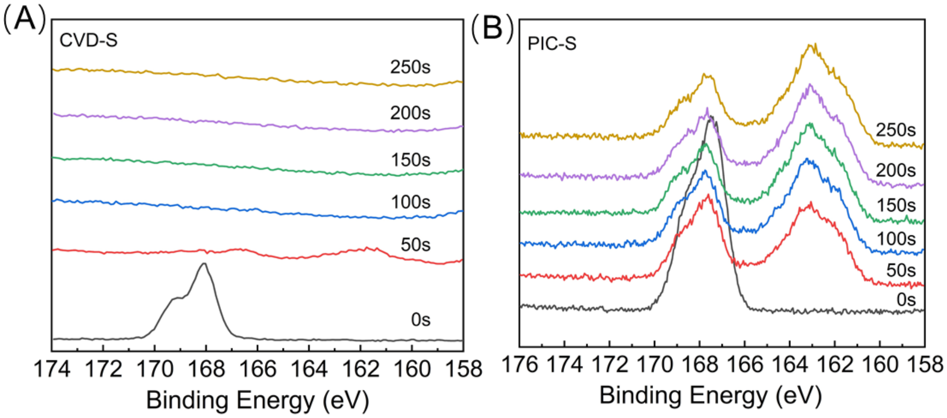

Figure S13. The S element XPS spectra of the different Ar+ bombardment time on (A) CVD- pSPMA surface and (B) PIC-pSPMA surfaces

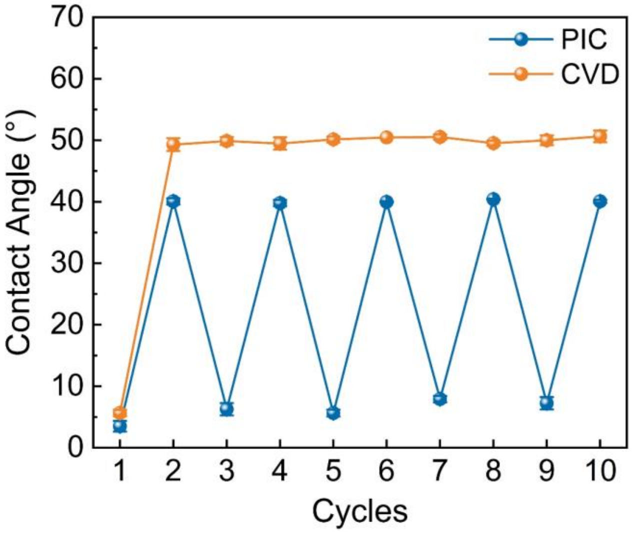

Figure S14. The reversible contact angle change on PIC and CVD surface with wear-repair process (25kPa, 20000 cycles, against polyester fiber in aqueous solution).

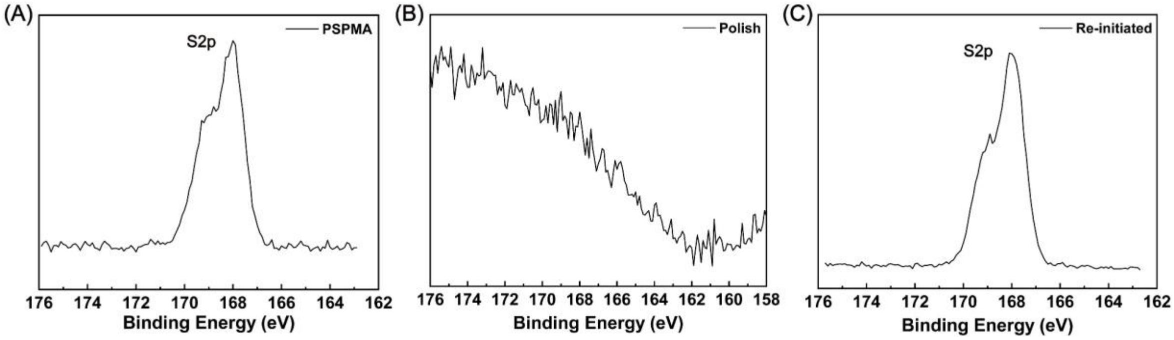

Figure S15. The XPS fine spectrum of S element with wear-repair process on the PIC surface.

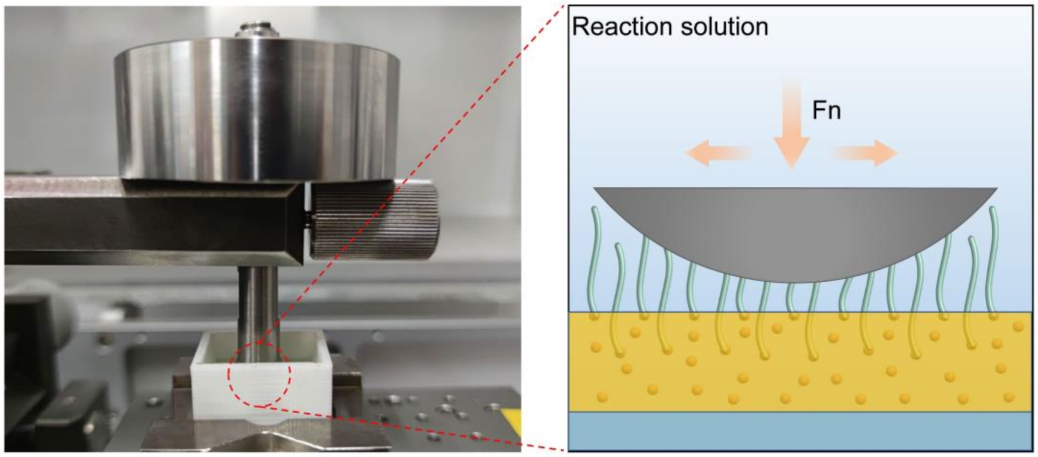

Figure S16. The schematic of friction test on PIC+pSPMA surface in the reaction solution.

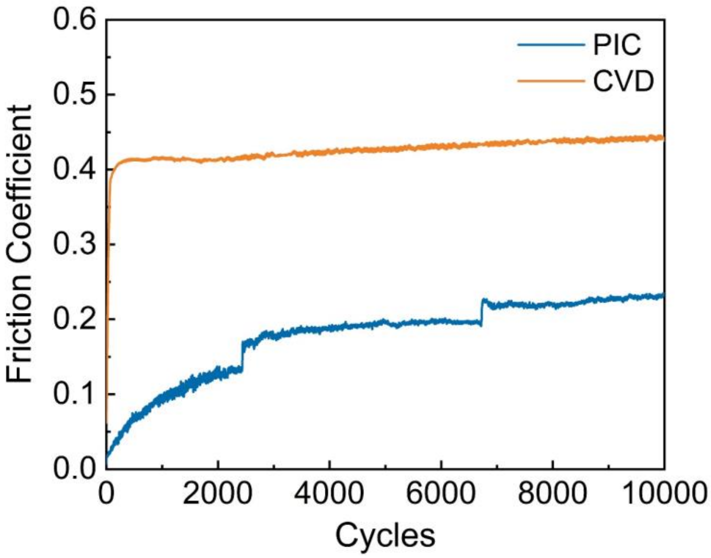

Figure S17. The changes of the friction coefficient of lubricating layer surfaces with or without silica sol layer in aqueous solution (5N, 2Hz, against PDMS ball).

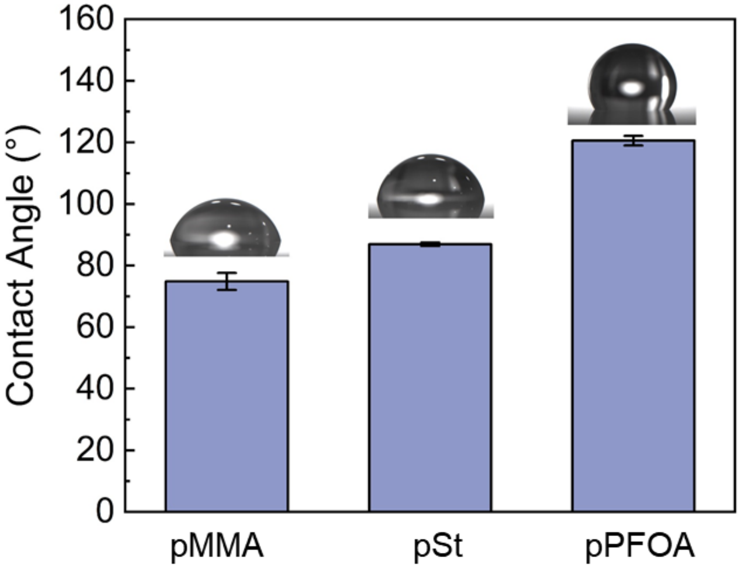

Figure S18. The changes of water contact angle of PIC grafted with different monomers.

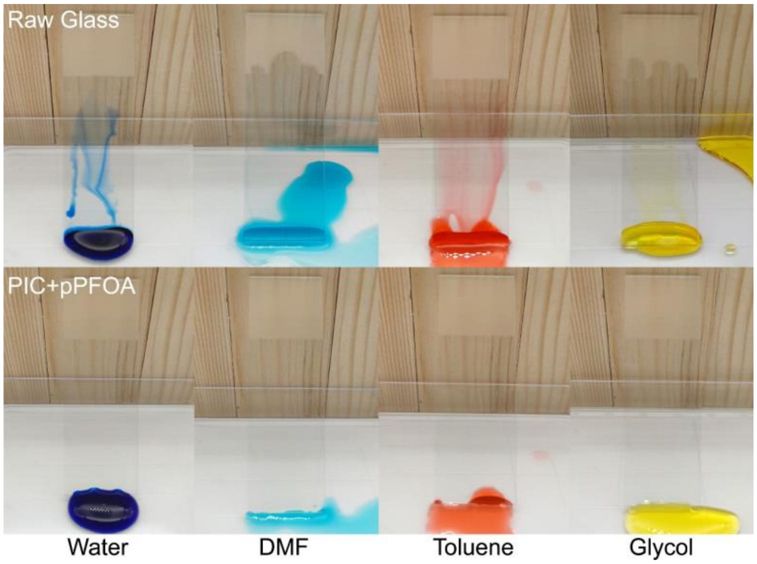

Figure 19. Water/DMF/Toluene/Glycol droplet sliding off from raw glass surface and PIC-pPFOA surface.

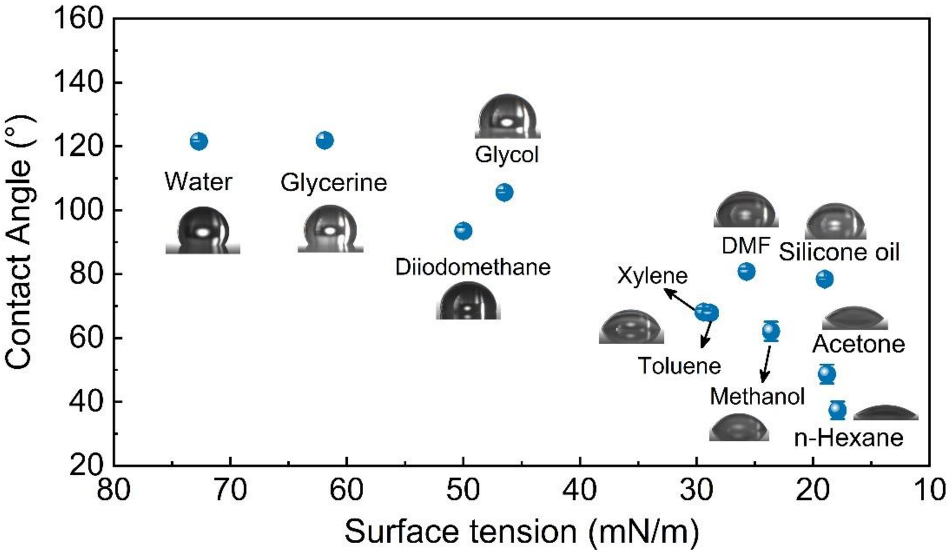

Figure S20. The contact angle of various organic liquid on the PIC+pPFOA surfaces.

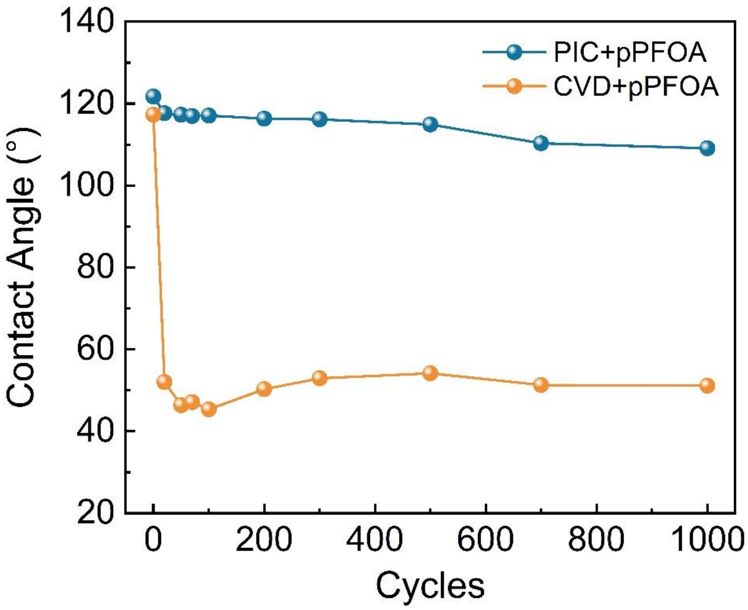

Figure S21. The changes of contact angles on PIC and CVD surface grafted with pPFOA brushes in 1000 cycles (25kPa, against polyester fiber).

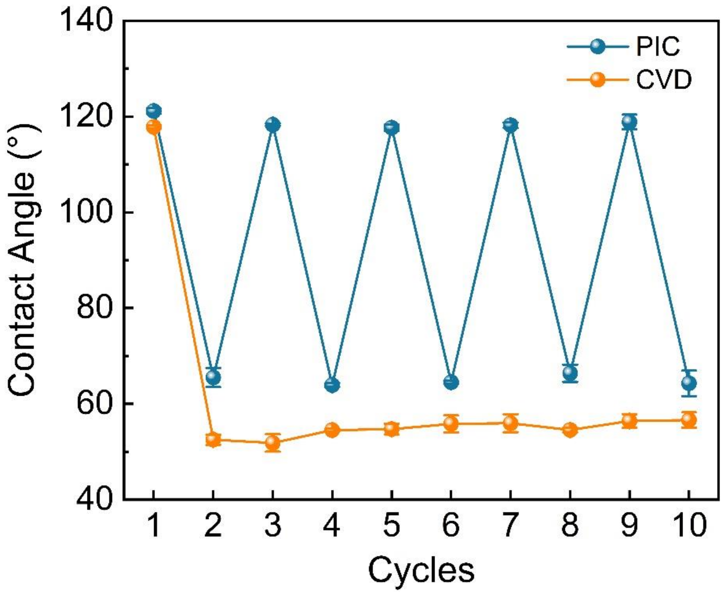

Figure S22. The reversible contact angle change on PIC and CVD surface with wear-repair process (25kPa, 20000 cycles, against polyester fiber).

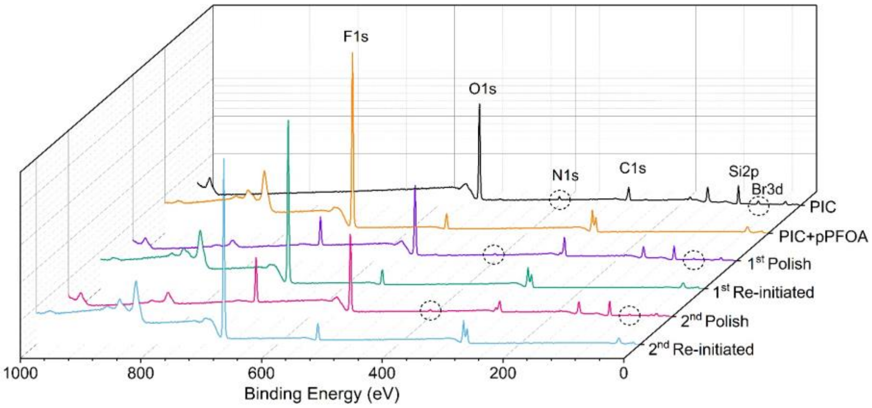

Figure S23. The changes of chemical composition of the surfaces during the wear-repair process.

References

1. Sun, Y. B.; Ding, X. B.; Zheng, Z. H.; Cheng, X.; Hu, X. H.; Peng, Y. X., Surface initiated ATRP in the synthesis of iron oxide/polystyrene core/shell nanoparticles. *Eur. Polym. J.* **2007,** *43* (3), 762-772.

2. Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J., Controlled synthesis of polymer brushes by "Living" free radical polymerization techniques. *Macromolecules* **1999,** *32* (5), 1424-1431.

3. Jones, D. M.; Brown, A. A.; Huck, W. T. S., Surface-initiated polymerizations in aqueous media: Effect of initiator density. *Langmuir* **2002,** *18* (4), 1265-1269.

4. Min, K.; Gao, H. F.; Matyjaszewski, K., Use of ascorbic acid as reducing agent for synthesis of well-defined polymers by ARGET ATRP. *Macromolecules* **2007,** *40* (6), 1789-1791.

5. Sato, T.; Dunderdale, G. J.; Urata, C.; Hozumi, A., Sol–Gel Preparation of Initiator Layers for Surface-Initiated ATRP: Large-Scale Formation of Polymer Brushes Is Not a Dream. *Macromolecules* **2018,** *51* (24), 10065-10073.