Supplemental information for

Reversibly Electro-controllable Polymer Brush for Electro-switchable Friction

Hulie Zeng, Yong Zhang, Sifeng Mao, Hizuru, Nakajima and Katsumi Uchiyama**

Department of Applied Chemistry, Graduate School of Urban Environmental Sciences Tokyo Metropolitan University, Minamiohsawa, Hachioji, Tokyo 192-0397, Japan

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* *Corresponding author: H. Zeng (zeng-hulie@tmu.ac.jp) and K. Uchiyama (uchiyama-katsumi@tmu.ac.jp)*

I Supporting movie

Movie M recoded the motion of a small plastic piece manipulated by the electro-switchable friction. The small black plastic piece was held between two faced ITO glass substrates those modified with poly-AHPS branched brushes after supplied a voltage of -0.4 V for 5 min. Then, the charging voltage was shifted to +0.4 V, and the movie started.

II Experimental

II. 1 Procedure to synthesize poly-AHPS branched brushes on ITO glass

Indium tin oxide (ITO) glass slide was firstly cut to 2×2 cm square, and then immersed into RCA1 solution (NH_4OH:H_2O_2:H_2O=1:1:1) *(Warning: This solution is highly reactive and extreme precautions must be taken upon its use.)* at 60 °C for 60 min with gentle stirring. The slide was then rinsed by ultrapure water and degassed for 15 min. Following this, the ITO glass slide was immersed into 5% (v/v) (3-aminopropyl)triethoxysilane (APTES) in chloroform at 50 °C for 60 min. After the ITO glass slide was further cleaned in pure chloroform in an ultrasonic cleaner for 10 min to remove unreacted APTES, it was dried by nitrogen gas. Further surface modification to the ITO glass slide was performed with an initiator by immersing it into a chemical mixture including 1.2% (w/v) 4,4'-azobic(4-cyanovaleric acid) (ACV), 1.0% (w/v) benzotriazol-1-yloxy-tris(dimethylamino)phosphoniumnexafluorophosphoate (BOP), 0.5% (w/v) 1-hydroxy-benzotriazole (HoBt), 0.8% (v/v) N,N'-diisopropylethylamine (DIEA) in dimethylformamide (DMF) at room temperature for 24 hours. After cleaned by DMF, it was immersed in 10% (v/v) 2-acrylamido-2-methylpropane sulfonic acid (AHPS) in methanol to perform the graft polymerization at 60 °C for 18 hours (Fig. S1).

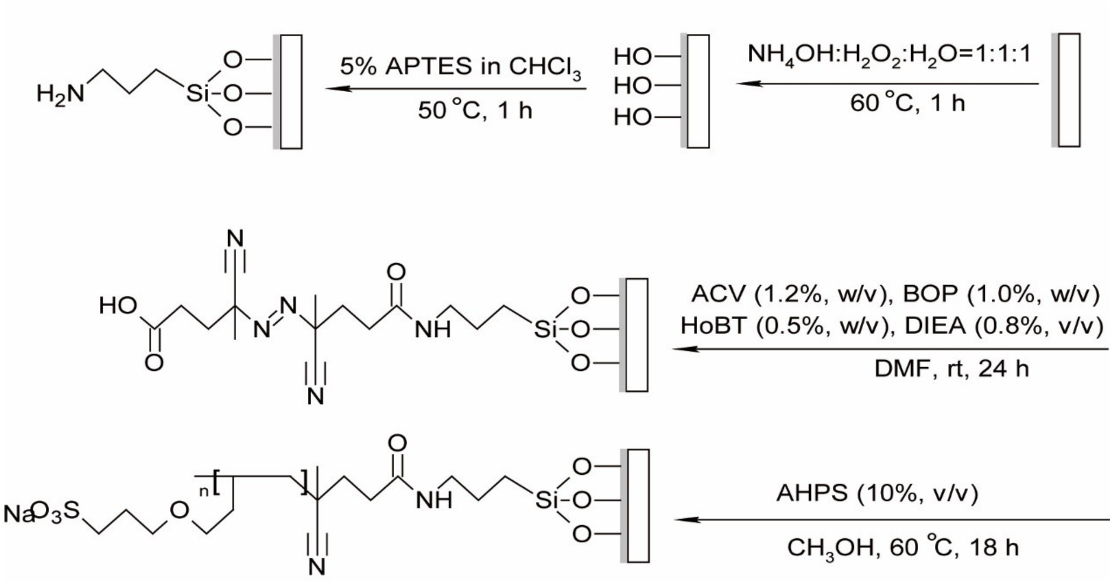

Figure S1: Procedure to synthesize poly-AHPS branched brushes on ITO glass.

II. 2 Contact angle measurement

The poly-AHPS polymer branched brushes modified ITO glass substrate was immersed in 0.1 M KCl solution and applied with either +0.4 V or -0.4 V (Ag/AgCl electrode was the reference.) for 5 min at room temperature to obtain the stretched or rolled status of the polymer branched brushes. The slide was then immersed in pure water and dipped for 3 times to wash away the residual KCl. Following this, the substrate was blown dry by an air duster. Finally, it was set on a horizontal stage to measure the static contact angle by gently dropping a 5 μL of water on the surface of the substrate.

II. 3 AFM and DFM observation

The poly-AHPS branched brushes modified ITO glass substrate at 2×2 cm^2 square was immersed in 0.1 M KCl solution and applied with either +0.4 V or -0.4 V (Ag/AgCl electrode was the reference electrode.) for 5 min at room temperature to obtain the stretched or rolled status of the polymer branched brushes. The substrate was then immersed in pure water and dipped for 3 times to wash away the residual KCl. Following this, the matrix was gently dried by a filter paper, and set on the sample stage to measure the appearance of poly-AHPS branched brushes by AFM or DFM.

II. 4 ATR-IR observation

Indium tin oxide (ITO) glass slide was cut to 4×4 cm square, and modified with the poly-AHPS branched brushes for the ATR-IR observation. The ATR-IR with tunable incident angle was utilized for the observation of poly-AHPS modified ITO glass, while Ge crystal and 67° of incident angle were adopted. The stretched and rolled poly-AHPS branched brushes were obtained by respectively charging them with -0.4 V or +0.4 V (Ag/AgCl electrode was the reference electrode.) for 5 min.

II. 5 X ray photoelectron spectroscopy (XPS) observation

To match the sample stage of XPS, the ITO glass slide was cut to 1×1 cm^2 square, and modified with the poly-AHPS branched brushes for the XPS observation of the status of the poly-AHPS branched brushes after negatively charged or positively charged. To inspect the effect of each step of the synthesis of poly-AHPS on ITO glass slides, the slides that were treated with different steps of synthesis were evaluated by performing the XPS measurement. For example, one slide was evaluated after finishing the first step of the synthesis, the second after finishing two steps of the synthesis, and so on.

The XPS spectra of the stretched and the rolled poly-AHPS branched brushes were measured after the poly-AHPS branched brushes modified ITO glass substrate was charged with -0.4 V or +0.4 V for 5 min, respectively.

The Spectra were acquired by a JPS-9010MX photoelectron spectrometer, equipped with an Mg Kα source (10mA, 10KV). The pass energy of 50eV was used for all of the spectra of the specimens.

II. 6 Preparation of the substrate for DFM observation to measure the height profile of the poly-AHPS branched brushes

Around 70 nm depth of chromium metal layer was vacuum evaporated on the 2×2 cm^2 square of ITO glass slide, and then half of the Cr coating on the ITO glass slide was removed by the Cr itching solution (50 mL of Cr itching solution included 8.334 g ammonium ceric nitrate, 2.166 mL of 60% hypochlorous acid.). After that, the ITO glass slide was utilized for the modification of the poly-AHPS branched brushes.

Finally, the half Cr layer on the ITO glass was removed by the above Cr itching solution to obtain the half modified poly-AHPS branched brushes ITO glass substrate for DFM observation. The stretched and rolled poly-AHPS branched brushes were obtained by respectively charging them with -0.4 V or +0.4 V (Ag/AgCl electrode was the reference electrode.) for 5 min.

II. 7 Measurement of kinetic friction

Two ITO glasses were respectively cut into 2×2 cm^2 square and 4×4 cm^2 square to modify with poly-AHPS branched brushes layer for the measurement of kinetic friction. One ITO glass substrate modified with poly-AHPS branched brushes was mounted and fixed at a stage. The other ITO glass substrate modified with poly-AHPS branched brushes was set upon the fixed ITO glass substrate, and connected with a light spring and then a syringe pump. All parts of the setup excepting the light spring and the syringe pump, were set in a transparent bottle that filled with saturated potassium sulfate solution at the bottom to obtain a surrounding of the humidity of 97% (Fig. S2). The syringe pump was connected with the upper movable ITO substrate by a copper thread through a tiny hole on the side well of the transparent bottle. The pulling linear velocity of the syringe pump could be read via the pulling volume in a certain time. Meanwhile, the loading stress on the two faced substrates could be obtained by the weight of iron block, and the kinetic friction could be read by the lengthened length of the light spring.

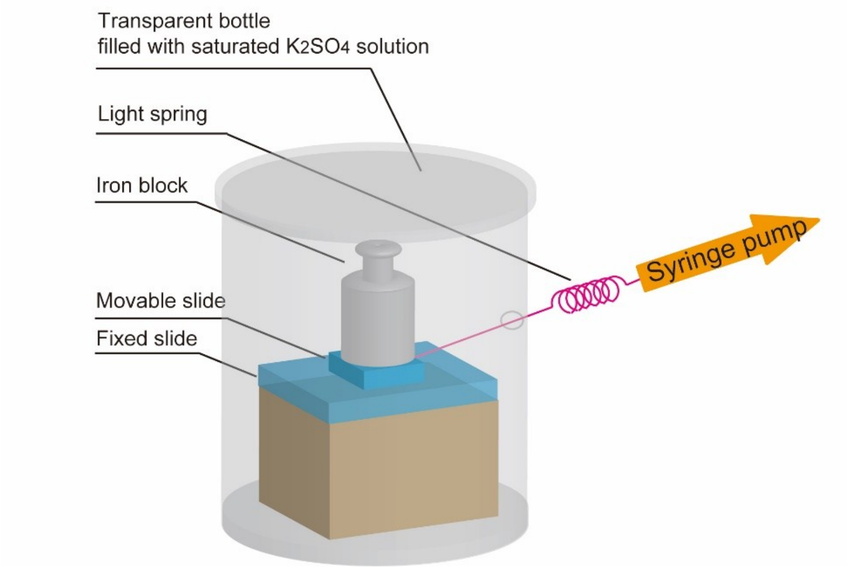

Figure S2: Setup to measure the kinetic friction between two faced substrates sliding at face to face mode.

III Supporting discussions

III 1 Characterization of process to preparing poly-AHPS branched polymer brushes by XPS

The ITO glass was first treated with RCA1 solution to generate hydroxyl groups (i) as the activated spots; and then modified with amino group-terminated molecular layer (ii) by APTES. Following this, it was connected with carboxyl group-terminated azide initiator (iii). Finally, it was grafted and polymerized with sulfonic group-terminated polymer branched brushes (iv) as shown in Fig. S1.

To evaluate the performance of each step of the preparation of poly-AHPS branched brushes on ITO glass slides, and to inspect the successful modification of poly-AHPS branched brushes, a X ray photoelectron spectroscopy (XPS) was utilized to identify the surface chemical structure for each step (Fig. S3). At stage i, the generation of hydroxyl groups on ITO glass slides replaces the In_2O_3 and SnO_2 evidenced by the significant decrease at the peak corresponding to In3d at 450.3 eV, while the broad peak of O1s around 537.2 eV corresponding to the original In_2O_3 and SnO_2 fade away, and the O1s peak at 537.6 eV verifies the generated hydroxyl groups. At stage ii, the introduction of APTES on the ITO glass induces the peak of N1s at 404.8 eV for the appearance of amino group at the top of ITO glass. The introduction of methylene of APTES also induces a slight shift in the peak of C1s from 290.7 eV to 290.6 eV, which probably corresponds to carbonic dusty. At stage iii, the introduction of azide initiator with longer chains almost conceals the core level of In3d at 450.3 eV. The introduction of carboxyl group of the azide initiator also announces the lower binding energy shift of C1s from 290.6 eV to 290.4 eV. At the final stage iv, the introduction of poly-AHPS long branched brushes results in the lower binding energy shifting of C1s at 290.0 eV which allowed the carbon atom to contact the sulfonic group. The appearance of the sulfonic group of the poly-AHPS branched brushes induces the lower binding energy shift of O1s to 536.7 eV. The remarkable evidence of the modification of poly-AHPS is that the S2p core level at 173.4 eV just appears at this stage. Therefore, the fluctuations of In3d, C1s, N1s, O1s and S2p at the five states primarily confirm the propelling of the modification in Fig. S1.

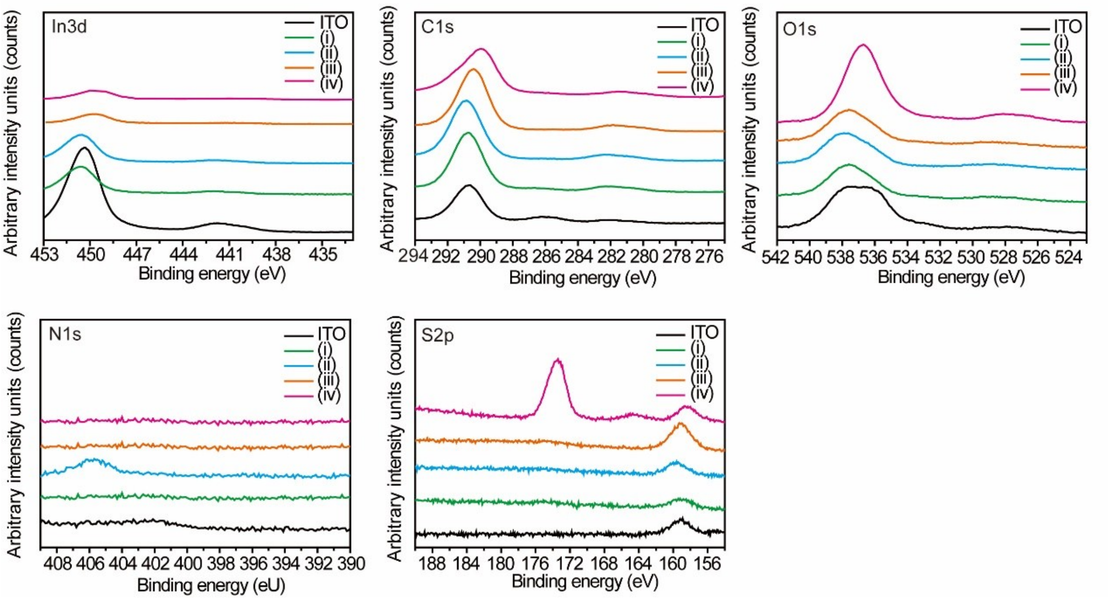

Figure S3: Inspection of the procedure to synthesize the poly-AHPS branched brushes on ITO glass substrate by XPS.

III. 2 Characterization of poly-AHPS branched brushes modified ITO glass substrate by CV

The successful modification of poly-AHPS branched brushes on ITO glass was also electro-chemically characterized by the cyclic voltammetric curves. The responded current of the ITO glass substrate tends to keep zero displaying strong characteristics of capacitance in black dash due to the high electrical conduction of blank ITO glass, however, the responded current of the poly-AHPS branched brushes modified ITO glass shown by the black line is proportional to the applied electrical potential implying the strong characteristics of resistance (Fig. S4).

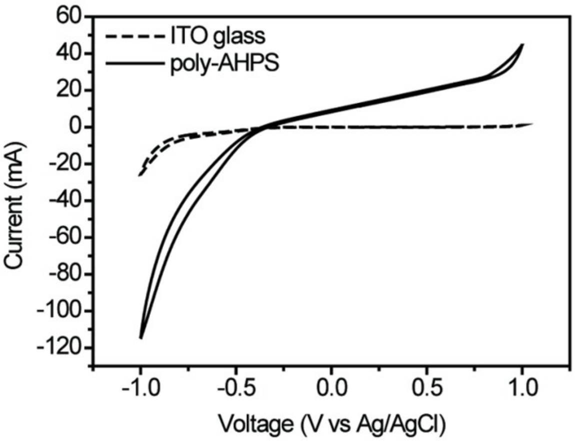

Figure S4: Cyclic voltammetric curves of blank ITO glass (black dush) and poly-AHPS branched brushes modified ITO glass (black line). The electrolyte solution was 0.1 M KCl, and the scan speed was 50 mV/s. The reference electrode was Ag/AgCl electrode.

III 3 Optimization of pulling velocity in kinetic friction measurement

To obtain the stable and reasonable pulling velocity to carry out the kinetic friction measurements in the experiment, the kinetic friction of two faced glass slide substrates those modified with poly-AHPS branched brushes was measured under different loading stress. The stable friction could be obtained as high as 5.77mm/s pulling velocity under the loading stress of 0.273N and 0.368N (Fig. S5), so that pulling velocity of 5.77 mm/s was selected in the measurement of kinetic friction in the experiments.

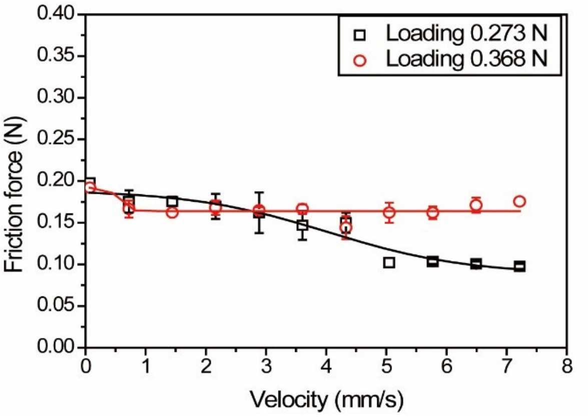

Figure S5: The relationship between the kinetic friction and pulling velocity of the two faced ITO glass substrates modified with poly-AHPS branched brushes layer. The measurements were carried out under a humidity of 97%.