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Supporting Information

A Smart Surface with Switchable Wettability by an Ionic Liquid

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1. Materials: (100) oriented smooth silicon wafers (n-type) were purchased from Beijing Jade Bird Yuan Core Micro System Technology Co., LTD. Silicon microposts (SiMPs) were obtained by lithography etching. Phenylethyl methacrylate (PhEtMA, >98%) was purchased from Jinan Yudong Technology Development Co., LTD. Sulfuric acid (98%, AR), Hydrogen peroxide (30%, AR), Nitric acid (65%, AR), Hydrofluoric acid (≥40%, GR), Dichloromethane (AR), Acetic acid (AR), Ethanol (AR), Acetone (AR), Tetrahydrofuran (THF, AR), Methanol (AR) and Pyridine (AR) were purchased from Beijing Chemical Works. Silver nitrate (99.9%) was purchased from Alfa Aesar. 3-Aminopropyltrimethoxysilane (ATMS, NH2, 97%), 3-Aminopropyltriethoxysilane (APTES, 97%), y-(methacryloxypropyl)trimethoxysilane(COOC, 97%), n-Hexyltrichlorosilane (C6, 97%), Dodecyltrichlorosilane (C12, 95%), Trimethoxy(3,3,3trifluoropropyl)silane (C3F3, 97%), Perfluorohexylethyltrichlorosilane (C8F13, 97%), 1H,1H,2H,2H-perfluorodecyltrimethoxysilane (PFDMS, 97%), Anisole (99%), Copper (II) bromide (CuBr₂, 99%), 1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amid ([EMIm][NTf₂], 99%), Methyl methacrylate (MMA, 99%), Styrene (St, 99.5%) and Methyl 2bromopropionate (98.0%) were purchased from J&K Scientific. Copper (I) bromide (CuBr, 99.999%), Pentamethyldiethylenetriamine (PMDETA, 99%), Bromoisobutyryl bromide (98%), Polystyrene (PSt, M_w = 192000) and Poly(methyl methacrylate) (PMMA, M_w = 2000) were obtained from Sigma-Aldrich Co. All the reagents were used without further modification unless specially mentioned.



Figure S1. scanning electron microscopy (SEM) image of the SiMPs. The width of the posts is 10 μ m, and the spacing between the posts is 5 μ m.



PPhEtMA-co-PFDMS mixed molecular brush

Figure S2. Schematic representation of chemical processes for preparation of poly(phenylethyl methacrylate) and PFDMS (PPhEtMA-co-PFDMS) mixed molecular brushes-modified silicon substrate. It is a combination of silane chemisty and subsequent surface-initiated atom-transfer radical polymerization. The molar content of PPhEtMA and PFDMS is refer to x and y.



Figure S3. Atomic force microscopy (AFM) phase images show that smooth silicon wafers modified with mixed brushes (b, c) is heterogeneous, while that modified with pure PPhEtMA or PFDMS (a, d) is relatively homogenous.

2. Preparation of pure PMMA, PSt and PPhEtMA molecular brush modified surfaces by surface-initiated atom-transfer radical polymerization: The silicon substrates were pretreated as described above, and then were immersed in solutions containing 5% APTES in ethanol (v:v) (adjusting pH at 4.5-5.5 by acetic acid) for 2 h, and then washed with ethanol before further crosslinking in oven at 120°C for 0.5 h. Subsequently, initiator bromoisobutyryl bromide was introduced on the surfaces. Polymerization of PMMA was achieved by immersing the silicon substrate into a degassed solution of MMA (10 mL) in anisole (10 mL) containing CuBr (9.6 mg, 0.067 mmol), CuBr₂ (1.5 mg, 0.0067 mmol) and PMDETA (17.3 µL, 0.083 mmol), and the homogeneous reaction solution was degassed three times using freeze-pump-thaw cycles, and then carried out at 60°C under nitrogen atmosphere for 6 h. After washing with anisole and acetone, the substrates were dried with a flow of nitrogen. PSt and PPhEtMA modified surfaces were also prepared in a similar manner, except that St or PhEtMA was used as the monomer instead of MMA. For the polymerization of St, the reaction was carried out at 100°C for 24 h, and for PhEtMA, the reaction was carried out at 40°C for 6 h (Figure S4).¹



Figure S4. Schematic representation of PMMA, PSt and PPhEtMA molecular brush formation on silicon substrates via silane chemistry and subsequent surface-initiated atom-transfer radical polymerization.

X-ray photoelectron spectroscopy (XPS) results demonstrate the successful modification of each polymer on the substrate (Figure S5). The C1s core level spectra of PMMA, PSt and PPhEtMA are decomposed into several peaks to demonstrate the successful modification of the surfaces (Figure S5). For PMMA-modified surface, four peaks with binding energies of 284.6, 285.3, 286.6, and 288.6 eV are attributed to the presence of <u>C</u>-(C,H), <u>C</u>-COO, <u>C</u>-O and COO species respectively (Figure S5a). While for PSt grafted surface, proportion of peak areal for <u>C</u>-(C,H) (284.8 eV) increases, and a small shake-up peak appears at 292 eV due to $\Pi - \Pi^*$ transitions in the aromatic ring, which is a result of the present of PSt chains on the surface (Figure S5b). As the chemical structure of PPhEtMA is a combination of PMMA and PSt. PPhEtMA-modified surface shows all peaks for PMMA and PSt, and the proportion of peak areal for C-(C,H) (284.7 eV) is larger than PMMA-modified surface due to the increasement of C-(C,H) species in PPhEtMA (Figure S5c). The detection of peaks for C-CON, C-N (285.7 eV) and CON(287.9 eV) on PSt-grafted surface may result from the low reactivity of St, which leads to a short molecular chain on the surface, so these peaks can't be shielded. These results are in accordance with previous reports.^{2,3}

AFM images show that smooth silicon wafers modified with brushes of PMMA, PSt and PPhEtMA are relatively homogenous with very low surface roughness (Figure S6).



Figure S5. High-resolution C1s peaks obtained by XPS on PMMA (a), PSt (b) and PPhEtMA (c) modified surfaces, respectively.



Figure S6. AFM images show that smooth silicon wafers modified with brushes of PMMA, PSt and PPhEtMA are relatively homogenous with very low surface roughness.

3. Synthesis of PPhEtMA by atom-transfer radical polymerization: Polymer of PPhEtMA was synthesized by the atom-transfer radical polymerization method using methyl 2-bromopropionate as the initiator. CuBr (56 mg, 0.4 mmol), PMDETA (83.5 μ L, 0.4 mmol), PhEtMA (32 mL), and methyl 2-bromopropionate (45 μ L, 0.4 mmol) were dissolved in anisole (15 mL). Then, the solution was degassed three times by freeze-pump-thaw cycles, and polymerization was carried out at 40°C for 8 h.⁴ The product was purified by reprecipitation using THF as a good solvent and methanol as a poor solvent, and then dried for 24 h at 80°C under a vacuum condition. The molecular weight value for the as-prepared polymer was

obtained from gel permeation chromatograph (GPC) measurements. The result shows that the number average molecular weight M_n was 10806 Da and M_w/M_n was 1.49.

4. Compatibility of PMMA, PSt and PPhEtMA with [EMIm][NTf₂]: To demonstrate the compatibility of PMMA, PSt and PPhEtMA with [EMIm][NTf₂], we mixed 0.5 wt% polymer with [EMIm][NTf₂]. Figure S7 shows the optical images of the three mixtures at 20°C and 100°C. We can see that PMMA is soluble in [EMIm][NTf₂] at 20°C and 100°C (Figure S7a), while PSt is insoluble at 20°C and 100°C (Figure S7b). PPhEtMA exhibits lower critical solution temperature (LCST) behavior in [EMIm][NTf₂], that is, PPhEtMA is soluble at 20°C and phase-separated at 100°C, and this behavior is reversible (Figure S7c).



Figure S7. Optical images of 0.5 wt% PMMA, PSt and PPhEtMA in [EMIm][NTf₂] at 20°C and 100°C, respectively. PMMA is soluble (a) and PSt is insoluble (b) in [EMIm][NTf₂] independent on temperature, while PPhEtMA exhibits reversible LCST behavior in [EMIm][NTf₂] (c).

5. Synthesis of a series of silicon substrates modified with different silane coupling agents: Silicon nanowire arrays (SiNWA) (Figure S8) were fabricated using a wet etching chemical method.⁵ The smooth silicon wafers and SiNWA were treated with Piranha solution as described above. For blank surfaces (i.e., –OH terminated surfaces), cleaned silicon wafers were directly treated with oxygen plasma (200 W for 300 s). The smooth silicon wafers and SiNWA modified with different silane coupling agents were prepared through vapor phase deposition. Specifically, the silicon wafers were placed in a vacuum chamber with silane coupling agent on the bottom of vacuum chamber, then applied a vacuum to the chamber, and kept the vacuum chamber at 150°C for 2 h. Different silane coupling agents-modified silicon wafers can be obtained when the temperature down to room temperature.⁶

6. Determination of the intrinsic wetting threshold of [EMIm][NTf₂]: Intrinsic wetting threshold (θ^*)—the limitation between lyophilicity and lyophobicity—is very important for various liquid droplets. When the contact angles (CAs) of liquid droplets on the surface are between two sides of θ^* , surface roughness can enhance the difference of wettability greatly. In this study, we explore the θ^* of [EMIm][NTf₂] using the method as previously reported.⁶ A series of silanes with different surface tension are chosen to modify smooth and SiNWA. We test [EMIm][NTf₂] CAs on both sets of silicon substrates. For smooth silicon wafers, CAs on the substrates increase with decrease of surface tension of silanes. For SiNWA, abrupt change of CAs from ILphilicity to ILphobicity appears between C3F3 and C6 modified substrates. The intrinsic wetting threshold θ^* of ionic liquid [EMIm][NTf₂] is thus obtained in the range of 43.0-55.8° (Figure S8).



Figure S8. The intrinsic wetting threshold θ^* of [EMIm][NTf₂] is in the range of 43.0-55.8°. The SEM images show the morphology of the smooth silicon wafer and SiNWA, and the scale bar is 20 µm. The length of the SiNWA is about 10µm.



Figure S9. QCM results show that about 6.7 μ g cm⁻² [EMIm][NTf₂] is absorbed on PPhEtMAmodified Q sensors at 20°C, indicating strong cation- π interaction between PPhEtMA and [EMIm][NTf₂]. With increasing temperature, the absorbed [EMIm][NTf₂] decreases because lower temperature is benefit for the cation- π interaction.

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