
Supporting Information for

Tuning Surface Wettability through Supramolecular Interactions

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1. Materials

N-Isopropylacrylamide (NIPAAm, Fluka, Switzerland) was recrystallized in n-hexane. Hydrochloric acid, nitric acid, methanol, sodium hydroxide, sodium bicarbonate, anhydrous magnesium sulfate, tetrahydrofuran (THF), pyridine, α-bromoisobutyryl bromide (Fluka, Switzerland), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, Aldrich, Germany), aminopropyl trimethoxysilane (ATMS, Fluka, Switzerland), *β*-CD (Sigma–Aldrich) and 1-adamantylamine (Zhejiang Yasuhiro pharmaceutical Co. Ltd.) were used as received. CuBr was recrystallized before use. Toluene and dichloromethane were dried by molecular sieves for 24 h before use. Acryloyl chloride (Sinopharm Chemical Reagent Co.) was distilled prior to use. Dichloromethane (CH_2Cl_2) and triethylamine were dried over CaH_2 and distilled just prior to use. All the water used was purified through an inverse osmosis filtration (Millipore, Cat. No. ZMQS50001) satisfying the resistivity being 18.2 MΩ•cm at 25 °C.

2. Synthesis of 1-Adamantylacrylamide (ADAAm)

A solution of 1-adamantylamine (14.8 g, 0.066 mol), triethylamine (16 mL, 0.079

mol), and 4-dimethylaminopyridine (10 mg) in CH_2Cl_2 (200 mL) was heated to 42 °C under nitrogen. Subsequently a solution of acryloyl chloride (9 mL, 0.073 mol) in CH_2Cl_2 (10 mL) was added dropwise within 70 min. After complete addition the reaction mixture was stirred for 2.5 h and then cooled to room temperature. It was washed with aqueous HCl (100mM), aqueous sodium bicarbonate, and MilliQ water for three times. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The obtained crude product was recrystallized from acetone. ^{1}H-NMR spectra were recorded with a Bruker AV 300 NMR spectrometer.

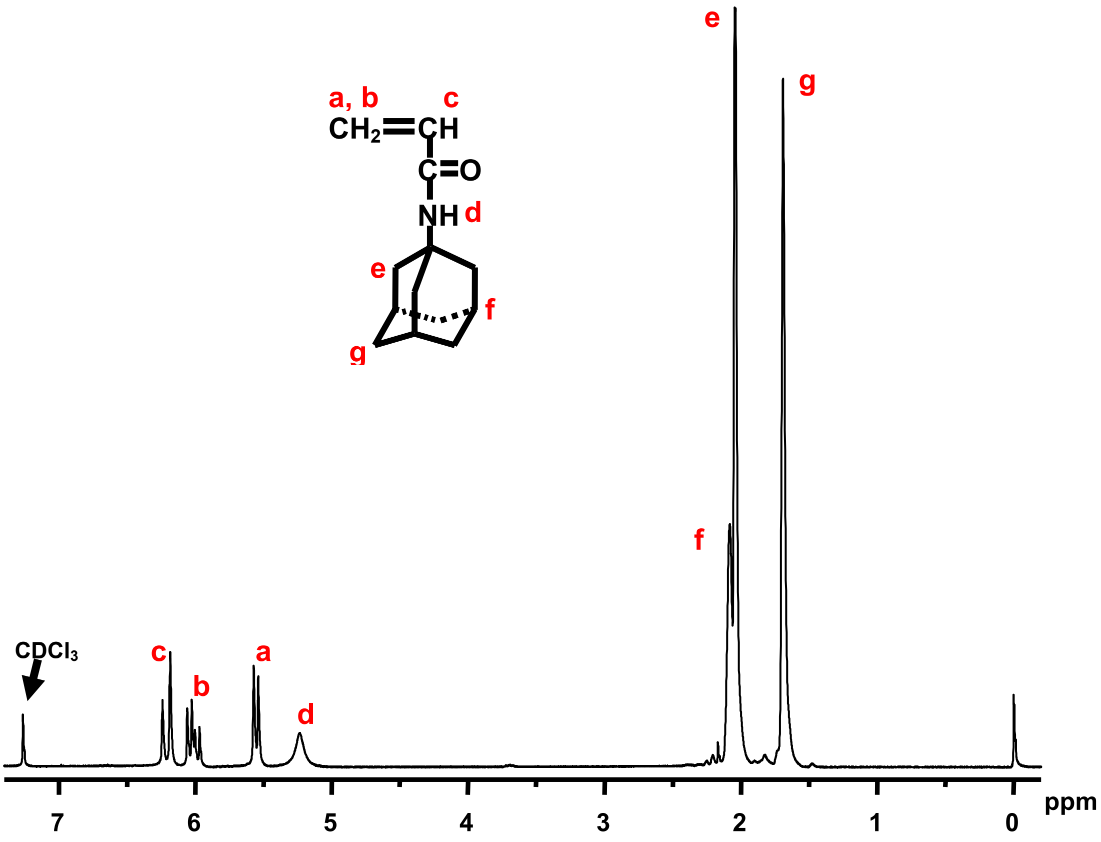

Fig. S1 ^{1}H-NMR spectra of the monomer ADAAm.

3. Surface Modifications and polymerization grafting from silicon substrate by

surface-initiated atom transfer radical polymerization.

Microgrooves on silicon wafers were generated by KARL SUSS MA6 (Germany) instrument through a photolithographic method, the scale of the microgrooves for rough silicon substrates is length = 12 μm, depth = 30 μm and space = 6 μm. A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 5 min, and subsequently in HNO_3 (0.1 M) for 10 min to generate surface hydroxyl groups. After the substrate had been washed with an excess of water and dried under a flow of nitrogen, it was immersed in methanol containing 5 wt% ATMS for at least 10 h to obtain chemically bonded –NH_2 groups on the surface. The surface was rinsed with methanol and dichloromethane to remove the remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry CH_2Cl_2 that contained pyridine (2% v/v). The polymerization initiator α-bromoisobutyryl bromide was added dropwise into the solvent containing the silicon substrate at 0 ºC, and the mixture was left at this temperature for 1 h, and then at room temperature for 12 h. The silicon substrate was cleaned with CH_2Cl_2, and dried under a nitrogen flow. Polymerization of NIPAAm-co-ADAAm was achieved by immersing the silicon substrate with the initiator grafted onto the surface in a degassed solution of NIPAAm (0.5 g) and ADAAm (0.05 g) in THF (5 mL) containing CuBr (0.016 g, 0.115 mmol) and PMDETA 0.07 mL for the substrates, for 6 h at 60 ºC.

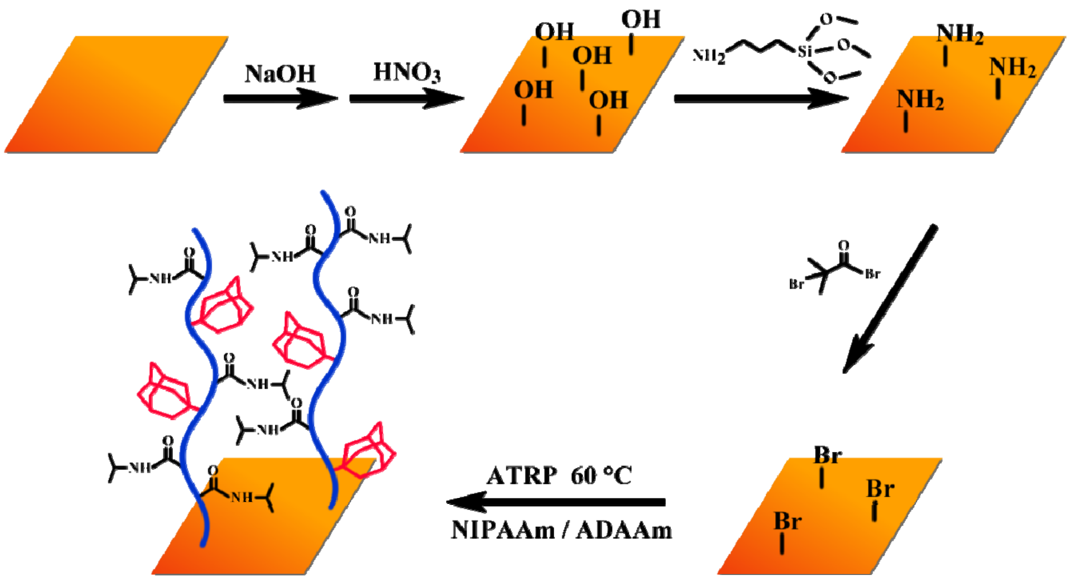

Fig. S2 Pretreatment for the Si surfaces.

Contact angle (CA) measurement at different temperatures was conducted after each immersion in certain β-CD concentration. CAs on both flat and rough substrates before immersing in β-CD (β-CD concentration = 0 M) was shown in Figure S3. As shown in Figure S4 CAs on flat surfaces are almost the same change from around 40° to 80° when the β-CD concentration from 10^{-6} M to 10^{-1} M.

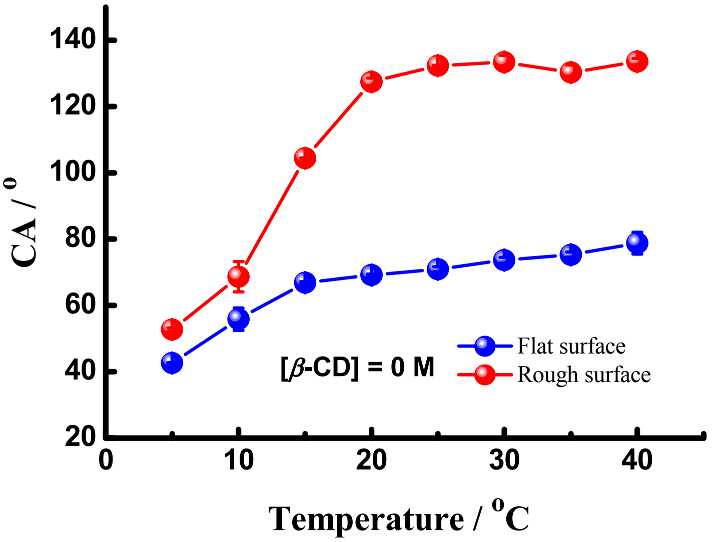

Fig. S3 CAs on both flat and rough surfaces changes with temperature when the concentration of *β*-CD is 0 M.

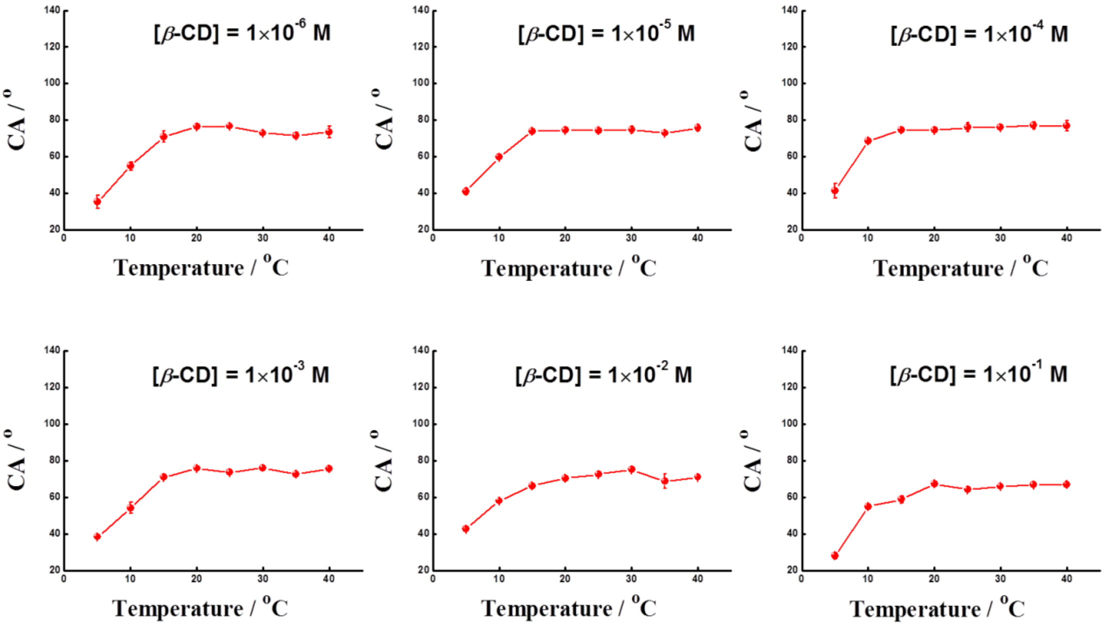

Fig. S4 The CAs on flat surfaces changes with temperature when the concentration of *β*-CDs is fixed.