Control Over the Responsive Wettability of Poly(*N*-isopropylacrylamide) film in a Lagre Extent by Introducing An Irresponsive Molecule

Taolei Sun,[a] Wenlong Song,[b,c] Lei Jiang*[a,b]*

[a] *National Center for Nanoscience and Technology, Beijing 100080, P. R. China; E-mail: suntaolei@iccas.ac.cn.*
[b] *Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China; E-mail: jianglei@iccas.ac.cn.*
[c] *Department of Chemistry, Jilin University, Changchun 130023, P. R. China.*

Supporting Information

I. Experimental Details:

HTMS (Degussa), ATMS (97%, Fluka), BIB (97%, Fluka) and pentamethyl diethylene triamine (PMDETA, 99 %, Aldrich), toluene, methanol, dichloromethane, and pyridine were used as received. *N*-isopropylacrylamide (99%, Acros) was purified by recrystalization in hexane for at least three times and Cu(I)Br was purified by recrystalization in concentrated HBr before being used.

Cleaned silicon wafer was firstly immersed in 0.1N KOH for 2 minutes and subsequently in 0.1N HNO_3 for 10 minutes to generate surface hydroxyl. Then it was refluxed in 10 ml mixed solution of HTMS and ATMS in dried toluene with a total concentration of 2 vol% for about 6 hours. Subsequently it was rinsed with excessive toluene and dichloromethane to remove unreacted ATMS and after dried with nitrogen gas, it was immersed in dried dichloromethane containing 2 wt% pyridine. Initiator bromoisobutyryl bromide was added dropwise into the solution. The reaction was carried out under ice/water bath for 1 hour and then at room temperature for 12 hours. The silicon substrate was then cleaned with acetone and toluene and subsequently dried under nitrogen flow. Polymerization of PNIPAAm was achieved by immersing the silicon substrate with initiators grafted on surface in a 5 mL degassed 25 wt% solution of *N*-isopropylacrylamide in 1:1

(v:v) mixture of H_2O and MeOH containing 0.032 g CuBr and 0.14 mL PMDETA for different period of time. In this paper, polymerisation times were all 100 minutes for all substrates and the reaction temperature was maintained at 30 ^oC.

X-ray photoelectron spectroscopic (XPS) data on mixed self-assembled film of HTMS and ATMS were collected on an ESCA Lab 220i-XL (VG Sci., UK), using a monochromatic Al Kα X-ray source. The elemental compositions were determined from the peak area of the XPS spectra.

The surface morphology and phase image for the PNIPAAm / HTMS composite film were investigated by scanning probe microscopy (SPI3800N, Seiko Instruments Inc.) in tapping mode with a micro-fabricated cantilever with spring constant of 1.8 N/m and resonance frequency of 25 k Hz.

The water CA was measured by SCA20 system (Dataphysics). The measurement was conducted under saturated humidity.

II. XPS Results of Self-Assembled Film of HTMS and ATMS.

Table S1. XPS results for mixed self-assembled films of HTMS and ATMS

HTMS/ATMS in solution (v:v in 10 mL Toluene)	Atom Ratio				
	F / atom%	N / atom%	Si / atom%	C / atom%	O / atom%
0:200	0	5.1	33.5	32.1	29.3
50:150	11.0	3.7	34.9	24.1	26.3
175:25	24.3	2.2	28.9	23.8	20.8
190:10	23.3	1.8	31.5	21.2	22.1
198:2	38.3	1.6	13.9	30.9	14.7
199:1	36.4	1.3	18.6	30.3	13.4

II. Relationship between Contact Angle on the Self-Assembled Film of HTMS and ATMS, and the Dosage Ratio in Solution.

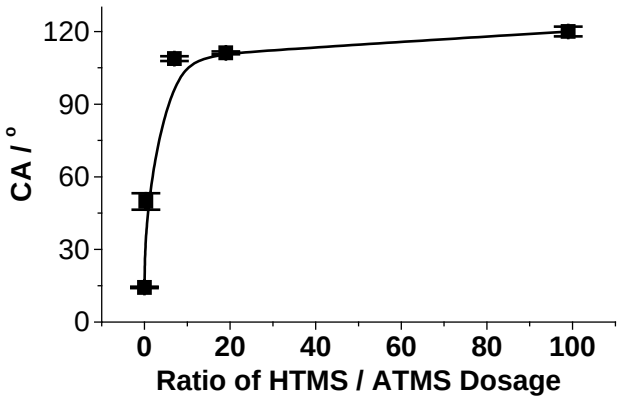
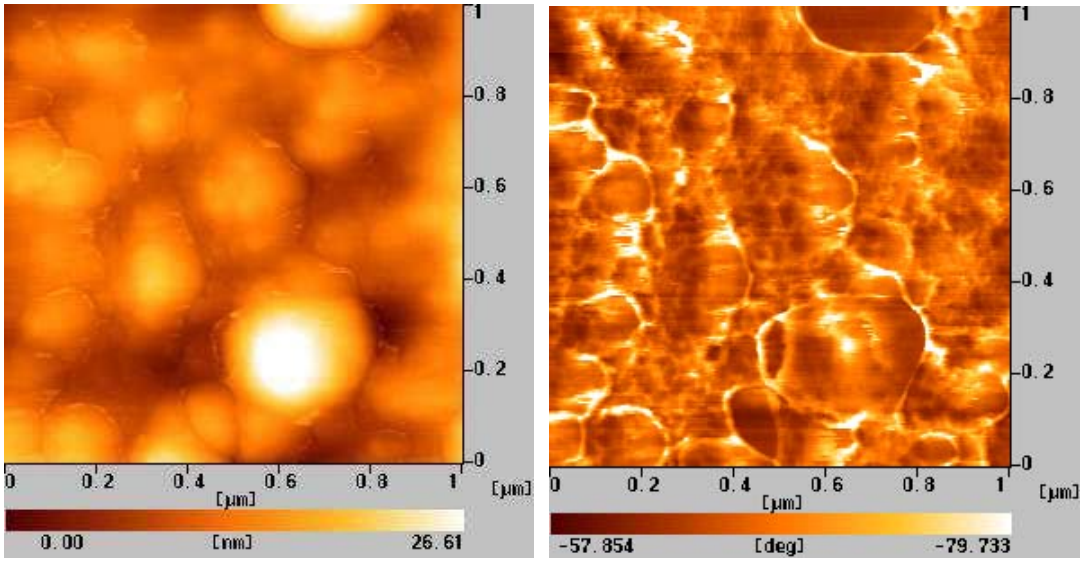
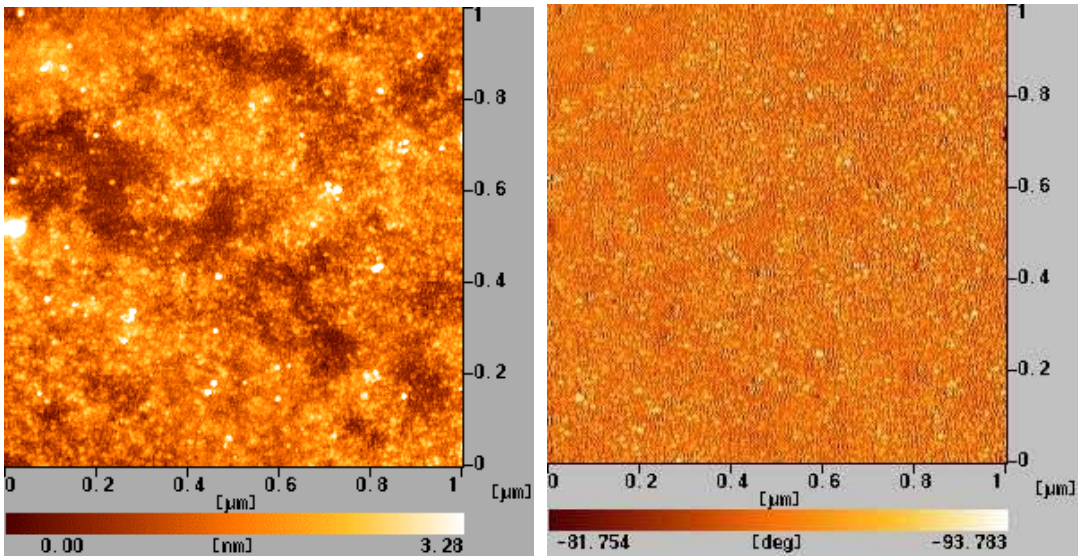


Figure S1. Relationship between the water CA on the mixed self-assembled film of HTMS and ATMS, and the dosage ratio of them in solution.

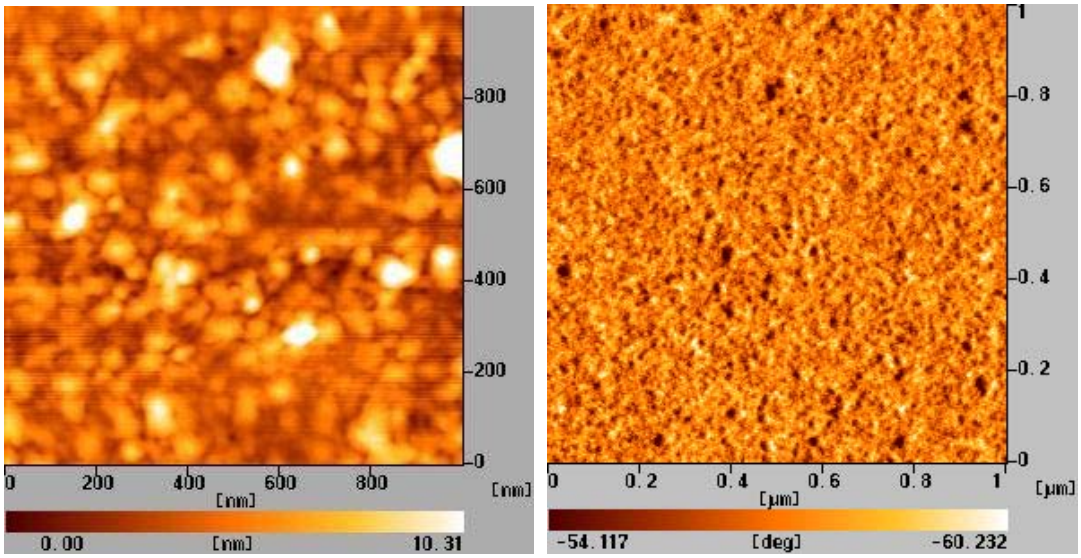
III. AFM images for composite films of PNIPAAm and fluoroalkylsilane from a relatively low dosage ratios of HTMS and ATMS.



(a) **(b)**



(c) (d)



(e) (f)

Figure S2. AFM images for composite films of PNIPAAm and fluoroalkylsilane from a relatively low dosage ratios of HTMS and ATMS. Dosage ratio: (a, b) 0:1 (pure PNIPAAm film); (c, d) 3.1:1; (e, f) 8.4:1. (a, c, e) Morphological images; (b, d, f) Corresponding phase images.