Control over the responsive wettability of poly(*N*-isopropylacrylamide) film in a large extent by introducing an irresponsive molecule†

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An irresponsive but very hydrophobic molecule—fluoroalkylsilane—can be used to cooperate with PNIPAAm to obtain tunable and enhancedly responsive wettability, and thus largely extend the application scope of PNIPAAm film.

Wettability can be enhanced or adjusted by surface topographic structure[1] and the chemical composition.[2] It has been reported that special surface structure may lead to special wettability, such as superhydrophobicity and superhydrophilicity. For example, we have demonstrated in a previous paper[3] the responsive switching between superhydrophilicity and superhydrophobicity on a rough poly(*N*-isopropylacrylamide) (PNIPAAm)[4,5] modified surface, although the responsive wettability on the corresponding flat surface is very limited. However, in some applications, especially those in micro-scales, such as microfluidic channel, it is difficult to create roughness on the surface. Therefore, it is desirable to obtain the adjustable responsive wettability on flat substrate by controlling the surface chemical composition. Here we report that the irresponsive but very hydrophobic molecule—fluoroalkylsilane—can be used to form composite film[6] with PNIPAAm to realize tunable responsive wettability. By this method, the responsive wettability of PNIPAAm film can be switched to not only a more hydrophobic, but also a much more hydrophilic range, and as a result, for a certain kind of the composite films, an enhancement of the responsive wettability to the both sides can be obtained, which is unexpected according to Cassie's equation[7] that describes the contact angle (CA) on heterogeneous surfaces.

Surface-initiated atom transfer radical polymerization (SI-ATRP)[8] was used to fabricate composite film of PNIPAAm and fluoroalkylsilane on silicon wafer, in which three steps were included (for more details, see ESI†): (1) a mixed self-assembled layer of heptadecafluorodecyltrimethoxy-silane (HTMS) and (3-aminopropyl)-trimethoxysilane (ATMS) was firstly generated on silicon wafer by refluxing in a mixed toluene solution of them; (2) initiator molecules were grafted onto the NH_2– groups of ATMS through the reaction between the acyl bromide and NH_2– groups; (3) polymerization of PNIPAAm (100 minutes, 30 °C).

In the first step, the dosage ratio for HTMS and ATMS can vary with a total amount of 200 μL in 10 mL toluene, and five ratios were selected in this work, which were 0 : 1 (pure polymer film), 3.1 : 1, 8.4 : 1, 43.7 : 1, and 87.7 : 1 (mol : mol), respectively. X-ray photoelectron spectrum results show that the surface concentration on silicon wafer of N atoms decreases and that of F atoms increases with the increase of the dosage ratio. Because the polymer chains can only grow from the initiator molecules that grafted onto NH_2– groups, it can be inferred that after the third procedure, the surface density of PNIPAAm may also decrease.

For the dosage ratios of 3.1 : 1 and 8.4 : 1, the as-prepared composite films of PNIPAAm and HTMS are rather homogeneous, as shown by the AFM images in supporting information, indicating that the PNIPAAm chains did not grow uprightly from the initiators but spread to the surrounding area and had covered the areas of the HTMS modified surface. It can be inferred from this fact that the polymer chains may be much looser in the composite film than in the pure film. However, when the dosage ratio for HTMS and ATMS increases further, the surface density of PNIPAAm chains may become very low because of the sparse surface anchored initiators, and insufficient to cover the whole surface that a portion of fluoroalkylsilane modified surface may be exposed. Fig. 1(a) and (b) show the morphology image and the corresponding phase image for the composite film with dosage ratio of 43.7 : 1, in which obvious heterogenity can be observed. The points A and B represent the polymer particles and the surrounding areas which are considered to be the HTMS coated surface. The morphology image indicates a height difference of about 6.2 nm, while the phase image shows a phase difference of about 26.0° between them.

The temperature dependent curve for water CA on pure and the composite films [Fig. 2(a)] indicates that all these films exhibit remarkable temperature responsive wettability and the water CA increases with the increase of temperature, and more interestingly, when the composite film forms, the responsive wettability can be switched to not only a more hydrophobic but also a much more hydrophilic range, depending on the dosage ratio for HTMS and ATMS. Fig. 2(b) shows the dependence of the CAs of pure and composite PNIPAAm films on the applied dosage ratio of HTMS and ATMS under temperatures of 20 °C and 50 °C. For pure polymer film, the CA can change from 60.1 ± 2.5 to 93.2 ± 2.0°. While for the composite films, both the CAs at 20 and 50 °C change a lot and exist a maximum point at hydrophilicity before the further increase of hydrophobicity when the dosage ratio increases. For the ratios of 3.1 : 1, 8.4 : 1, 43.7 : 1, and 87.7 : 1, the CAs at 20 °C changes from 60.1 ± 2.5 to 41.1 ± 2.1, 26.7 ± 2.6, 48.2 ± 1.5, and 75.9 ± 1.5°, while that at 50 °C it changes from 93.2 ± 2.0 to 82.9 ± 2.0, 88.6 ± 1.4, 98.0 ± 2.1, and 113.0 ± 0.8°. Furthermore, it can also be noticed that for the composite film with ratio of 8.4 : 1, the water CA can vary from 48.2 ± 1.5 to

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† Electronic supplementary information (ESI) available: Experimental details; relationship between contact angle on the self-assembled film of HTMS and ATMS, and the dosage ratio in solution; AFM images for composite films of PNIPAAm and fluoroalkylsilane from a relatively low dosage ratios of HTMS and ATMS. See http://www.rsc.org/suppdata/cc/b4/b417670g/

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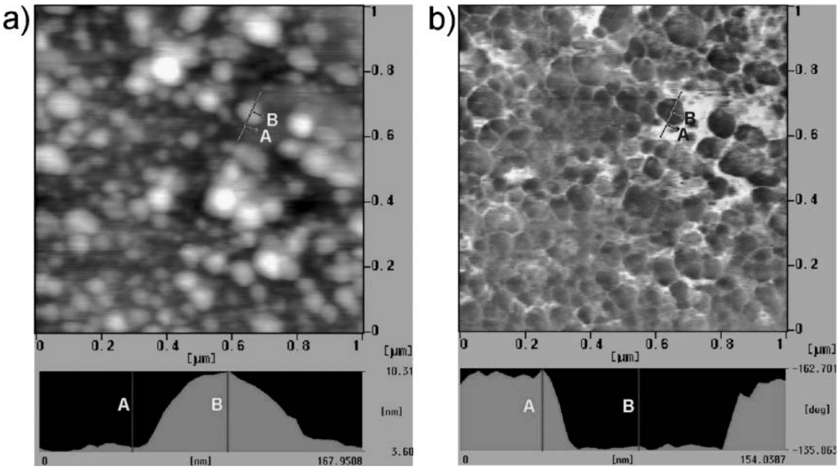

Fig. 1 Heterogenity of PNIPAAm/fluoroalkylsilane composite film when the dosage ratio for HTMS and ATMS is relatively high. (a) Typical AFM image (tapping mode) for film with dosage ratio of 43.7 : 1. (b) Corresponding phase image.

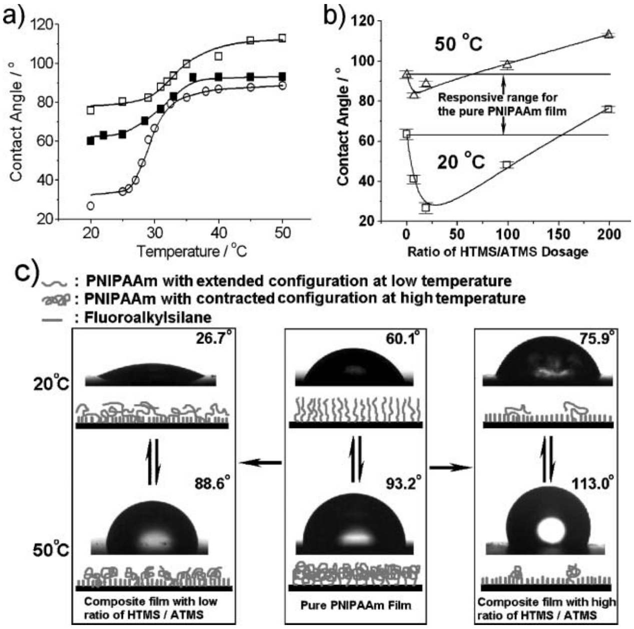

Fig. 2 (a) Temperature dependence for water CA on pure PNIPAAm film (■) and composite films with dosage ratio of ○: 8.4 : 1, and □: 87.7 : 1. (b) Relationship between CA and the dosage ratio under low (□) and high (Δ) temperatures. (c) Schematic diagram of the relationship between PNIPAAm configurations and the responsive wettability. When composite film forms, the PNIPAAm chains may become looser but still cover the whole surface if the dosage ratio is relatively low (left), while the surface is heterogeneous when it is high enough (right).

98.0 ± 2.1° with the elevation of temperature, indicating an enlarged responsive wettability comparing with the pure film. The responsive wettability on all films exhibit good reversibility in the temperature cycling experiments. It indicates that we can control over the responsive wettability in a much broader range of water CA from less than 30 to higher than 110°.

The fluoroalkane-modified surface is reported[9] to possess the lowest surface free energy and the largest CA on flat surface. Therefore, the increase of the hydrophilicity is abnormal from the view of Cassie's equation, because as it anticipated that forming composite film with a more hydrophobic molecule can only give rise to the increase of the hydrophobicity. And on the other hand, the contaminations, for example, dissociative HTMS molecules, on air/water interface, which would lead to the reduction of the surface tension of water drop and thus the decrease of CA, could be excluded from the view of experiments. Thus, we consider that this effect is due to the much looser configuration of PNIPAAm chains in the composite films, which makes it easier for the hydrophilic groups, such as N–H and C=O, to contact with water (as shown in the left higher part of Fig. 2(c) for the situation when the dosage ratio is relatively low). Under high temperatures, the PNIPAAm chains may exhibit a contracted configuration compared with the extended one under low temperatures because of the competition between the intermolecular and intramolecular hydrogen bonding.[3,10] Therefore the above mentioned effect may be much weaker under high temperatures [left lower part of Fig. 2(c)].

However, when the dosage ratio increases further, the surface density of PNIPAAm chains may be insufficient to cover the whole surface and part of the HTMS-modified surface may be exposed, and the upper surface of the composite film is heterogeneous. As anticipated by Cassie's equation, the CA will increase with the increase of the surface fraction of HTMS. Thus, an increase of hydrophobicity under both low and high temperatures is observed (Fig. 2(b) and the right part of Fig. 2(c)).

In conclusion, the cooperation between PNIPAAm and an irresponsive but very hydrophobic molecule—fluoroalkylsilane—can lead to tunable and enhanced responsive wettability and thus largely extend the application scope of PNIPAAm film. In the one hand, it may enhance the hydrophobicity of the film, as normally anticipated by Cassie's equation. While more interestingly, in the other hand, it can also bring about an increase of hydrophilicity, which is abnormal and unexpected by Cassie's equation, but can be explained by a looser configuration of PNIPAAm chains. This effect is not only important to the application of responsive wettability, but also give an interesting insight from a view of experiment into the traditional wettability concepts.

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