ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Smart Anisotropic Wetting Surfaces with Reversed pH-Responsive Wetting Directions

Peng Ge, Jianglei Zhang, Yongshun Liu, Shuli Wang, Wendong Liu, Nianzuo Yu, Yuxin Wu, Junhu Zhang, and Bai Yang*

Smart pH-responsive surfaces that could autonomously induce unidirectional wetting of acid and base with reversed directions are fabricated. The smart surfaces, consisting of chemistry-asymmetric "Janus" silicon cylinder arrays (Si-CAs), are prepared by precise modification of functional groups on each cylinder unit. Herein, amino and carboxyl groups are chosen as typical pH-responsive groups, owing to their protonation/deprotonation effect in response to pH of the contacted aqueous solution. One side of the Si-CAs is modified by poly(2-(dimethylamino)ethyl methacrylate), while the other side is modified by mixed self-assembled monolayers of 1-dodecanethiol and 11-mercaptoundecanoic acid. On such surfaces, it is observed that acid and base wet in a unidirectional manner toward corresponding directions that are modified by amino or carboxyl groups, which is caused by asynchronous change of wetting property on two sides of the asymmetric structures. The as-prepared Janus surfaces could regulate the wetting behavior of acid and base and could direct unidirectional wetting of water with reversed directions when the surfaces are treated by strong acid or base. Due to the excellent response capability, the smart surfaces are potential candidates to be applied in sensors, microfluidics, oil/water separation, and smart interfacial design.

1. Introduction

Stimuli-responsive surface wettability is of significant interest in both fundamental research and industry,[1–3] owing to their applications in separators,[4] sensors,[5,6] chemical valves,[7] drug delivery systems,[8,9] and microfluidic devices.[10,11] Essentially, the ability to switch between hydrophilicity and hydrophobicity is a crucial condition for the preparation of stimuli-responsive wetting surfaces. With this aim, a variety of stimuli, including temperature,[12–14] light,[15–18] counterions,[2,19,20] solvent/solute,[19,21] electric potential,[22–24] and pH have been explored.[25–29] Stimuli-sensitive polymers are particularly promising candidates to meet the demands above. Physical and chemical properties of these polymers are able to undergo abrupt and large changes in response to the environmental stimuli.[30] For instance, through combining poly(N-isopropylacrylamide) and poly(2-vinylpyridine) with special rough surfaces, reversible switch of wetting property between superhydrophobicity and superhydrophilicity has been obtained by the variation of temperature and pH values.[12,31]

Actually, in majority of current studies, stimuli-responsive wetting surfaces switched between hydrophobicity (superhydrophobicity) and hydrophilicity (superhydrophilicity) with isotropic wetting states as mentioned above. Considering the future application prospect, it would be multifunctional if anisotropic wettability was introduced to smart wetting surfaces during the transformation process. Anisotropic wetting surfaces have attracted enormous attentions because of the effective applications in liquid transportation,[32,33] water-directional collection,[34,35] drag reduction,[36] and microfluidics.[37] When stimuli-responsive and anisotropic wetting properties are combined, performance of anisotropic wetting surfaces would be controllable by external stimuli, and the range of applications would be enlarged. For example, thermal-responsive anisotropic wetting surfaces could serve as smart microvalves, which were benefited from the conversion between isotropic and anisotropic wetting.[38] Literature reports mainly focused on responsive anisotropic wetting surfaces that switched between anisotropic and isotropic wetting.[38,39] Smart wetting surfaces that convert between two kinds of anisotropic wetting with reversed wetting directions are inspiring, and it would provide more extensive applications.

Generally, anisotropic wetting surfaces are fabricated through the introduction of groove structures,[40,41] asymmetric morphology,[42,43] or chemical heterogeneity.[44,45] Recently,

Dr. P. Ge, J. Zhang, S. Wang, N. Yu, Y. Wu, Prof. J. Zhang, Prof. B. Yang
State Key Laboratory of Supramolecular Structure and Materials
College of Chemistry
Jilin University
Changchun 130012, P. R. China
E-mail: zjh@jlu.edu.cn
Dr. Y. Liu
State Key Laboratory of Applied Optics
Changchun Institute of Optics
Fine Mechanics and Physics (CIOMP)
Chinese Academy of Sciences
Changchun 130033, P. R. China
Dr. W. Liu
Max Planck Institute for Polymer Research
Ackermannweg 10, D-55128 Mainz, Germany
The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201802001.

DOI: 10.1002/adfm.201802001

we have reported a new strategy to control anisotropic wetting of liquids under various media, which are realized through introducing "Janus" silicon cylinder arrays (Si-CAs) and modifying functional groups selectively.[46–48] Herein, we demonstrate the fabrication of smart pH-responsive anisotropic wetting surfaces by combining the Janus system with typical pH-responsive groups (amino and carboxyl groups). In this case, one side of the Si-CAs is modified by poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), and the other side is decorated by mixed self-assembled monolayers (SAMs) of 1-dodecanethiol (DDT) and 11-mercaptoundecanoic acid (MUA). Among them, amino groups are provided by PDMAEMA, while carboxyl groups are provided by the mixed SAMs.[25,49] We found that on the surface of Janus Si-CAs, acid solution is autonomously directed to PDMAEMA-modified direction, while base solution is directed to mixed SAM-modified direction. In addition to acid and base, when the surfaces are treated with strong acid or base, the Janus surfaces could direct unidirectional wetting of water toward PDMAEMA- or mixed SAM-modified directions. The smart phenomena are caused by asynchronous protonation/deprotonation behavior on two sides of the asymmetric structures. Under acidic conditions, the amino groups could be positively charged because of the protonation effect, which could attract hydrate shells, resulting in the hydrophilicity of the PDMAEMA-modified area. On the contrary, the hydrate layers formed because of the deprotonated and negatively charged carboxylic groups. Therefore, the asynchronous protonation/deprotonation behavior causes differences of contact angle (CA) value between two sides of the asymmetric Si-CAs either under acidic or basic conditions, leading to the smart wetting behavior. Moreover, from the perspective of anisotropic wetting, anisotropic wetting surfaces in literatures mainly focus on water, oil, and liquids with surface tension between water and oil in air, water and oil media.[40–46] Our "Janus" surface is a first study to investigate the anisotropic wetting behavior of acid and base, and it is a new smart pH-responsive anisotropic wetting surface that utilizes typical pH-responsive molecules to achieve pH-tunable unidirectional liquid spreading. The wetting direction could be tuned through changing the pH of the contacted liquids.

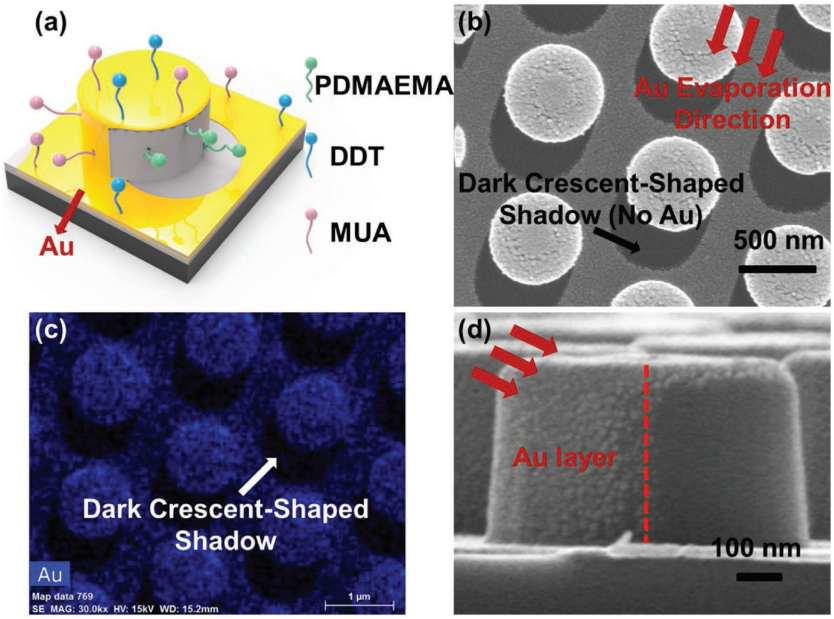

Figure 1. a) The schematic diagram of the Janus PDMAEMA-SAMs (DDT and MUA) Si-CAs. SEM image show the b) top and d) side view of the asymmetric surface. c) Corresponding EDX mapping of Au.

2. Results and Discussion

2.1. Smart Anisotropic Wetting Surfaces

In order to prepare smart surfaces that could autonomously direct unidirectional wetting of acid and base with reversed directions, we designed Janus PDMAEMA-SAMs (DDT and MUA) Si-CAs, which were prepared through colloidal lithography and asymmetric modification.[46–48] As shown in the schematic diagram of the surfaces (**Figure 1**a), one side of the Si-CAs is modified by PDMAEMA, while the other side is modified by mixed SAMs of DDT and MUA on Au. The average height of the Si-CAs was about 390 nm and the diameter was about 710 nm (Figure S1a, Supporting Information). The red arrows in scanning electron microscopy (SEM) image of Janus PDMAEMA-SAMs Si-CAs represent the direction of Au deposition (Figure 1b,d). The dark crescent-shaped shadows in top-view SEM image of the Janus surface could indicate the asymmetric structures (Figure 1b).[46–48] The shadows are generated by oblique 45° thermal evaporation, which is similar to projection effect, therefore, there is no Au in the area of shadows and one side of the Si-CAs that is opposite to the evaporation source. Au was only deposited on one side of the Si-CAs that is oriented to the evaporation source. Moreover, distribution of Au in the corresponding energy-dispersive X-ray (EDX) mapping clearly shows the asymmetric structure (Figure 1c). Cross-sectional SEM image of the Janus Si-CAs exhibits the asymmetric nature more distinctly (Figure 1d), which shows that Au was deposited on one side (detailed characterization of the Janus surfaces is shown in Figure S1, Supporting Information). We measured the wetting behavior of liquids (8 μL) with different pH values (pH = 0.98, 1.99, 3.99, 7.04, 9.99, 12.00, and 13.05 were selected as examples) on Janus PDMAEMA-SAMs Si-CAs (polymer thickness = 20.8 nm; DDT/MUA = 0.45/0.55), and time-lapse photographs are shown in **Figure 2**a–g. The moving distances of liquids with different pH values along two directions of the asymmetric surfaces are shown in Figure 2h, and the distances were measured 8 s after the initial spreading of the drops. Encouraging phenomena were found that acid (pH = 0.98) shows unidirectional wetting behavior on Janus Si-CAs toward the PDMAEMA-modified direction with advancing CA

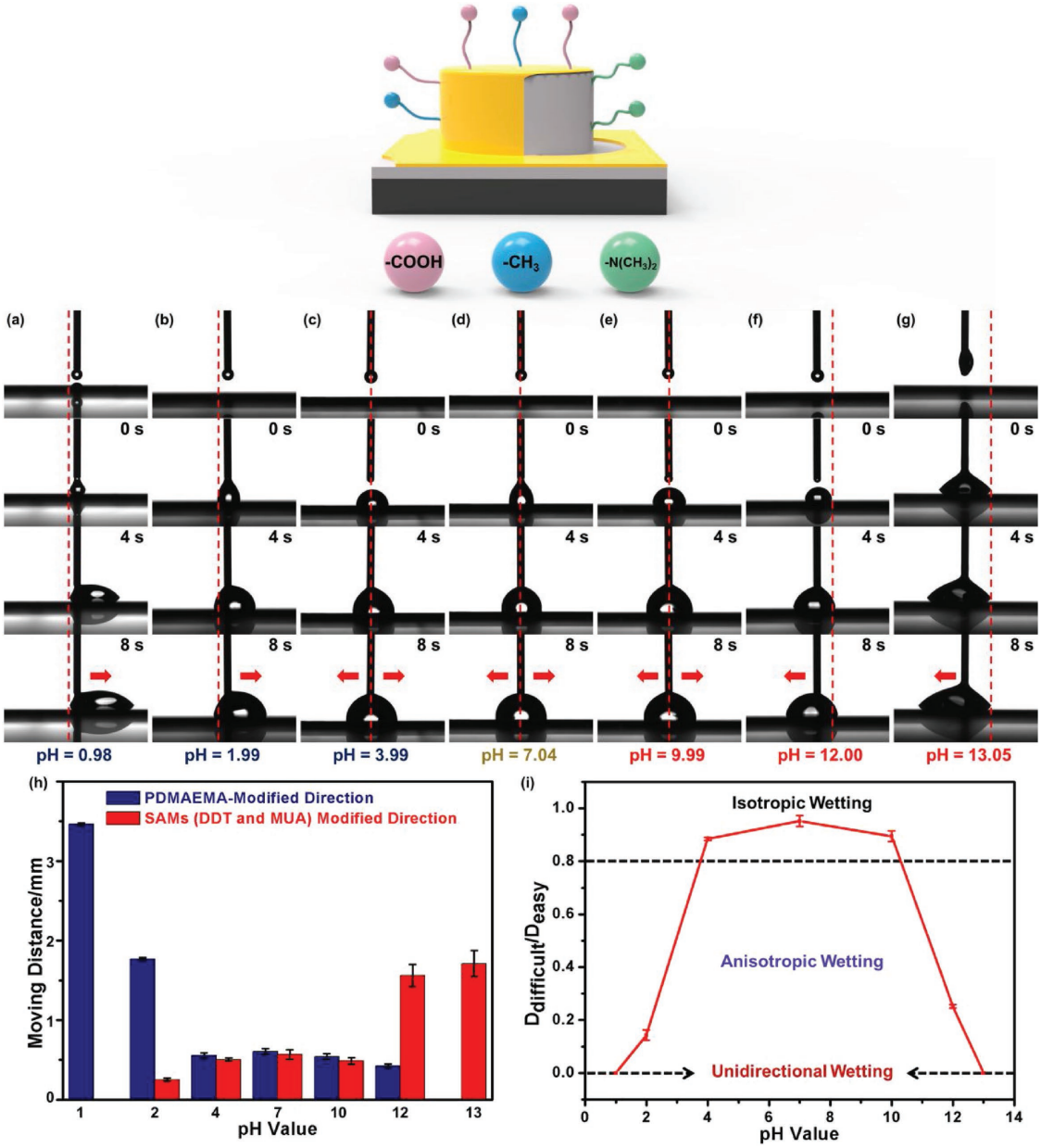

Figure 2. a–g) Time-lapse photographs of wetting behavior of 8 µL liquids with different pH values on Janus PDMAEMA-SAMs (DDT and MUA) modified Si-CAs (polymer thickness = 20.8 nm; $X_{DDT} = 0.45$). The pH values are 0.98, 1.99, 3.99, 7.04, 9.99, 12.00, and 13.05, respectively. The red arrows indicate the moving direction of liquids. The red dotted lines represent center axis of the syringe needle (c–e), left (a, b), and right (f, g) positions of the droplets when they contacted the asymmetric surface. The PDMAEMA-modified direction was placed on the right side when taking photographs. The injection velocity is 1 µL s^{-1}. h) Moving distances of liquids with different pH values along two directions of the Janus PDMAEMA-SAMs (DDT and MUA) modified Si-CAs. The moving distances of liquids were measured 8 s after the initial spreading of the drops. i) Plots of ratio ($D_{difficult}/D_{easy}$) as a function of pH. $D_{difficult}$ and D_{easy} represent the moving distances of liquids along two directions of the asymmetric surface. Herein, we define $D_{difficult}$ is less than D_{easy}.

45.2°, while pins along the mixed SAM-modified direction with static CA 60.3° (Figure 2a,h). Simultaneously, asymmetric surfaces autonomously induce unidirectional wetting of base (pH = 13.05) toward the mixed SAM-modified direction with advancing CA 45.5°, and the static CA along the PDMAEMA-modified direction is 48.2° (Figure 2g,h). When decreasing acidity or basicity of the solution, it was observed that the anisotropic wetting behavior is weakened. Liquids with pH values of 1.99 and 12.00 were basically directed to the corresponding directions that are modified by amino or carboxyl groups, meanwhile, a little amount of the solutions moved along reversed directions, which indicate anisotropic wetting of the liquids on the Janus surfaces (Figure 2b,f,h). With further decreasing in the acidity or basicity of the liquids, the liquids with moderate pH values (pH = 3.99, 7.04, and 9.99) moved freely toward the two directions with approximately equal

moving distances (Figure 2c–e,h). In other words, the liquids nearly show isotropic wetting behavior on the asymmetric surfaces. The response speed of the Janus Si-CAs is immediate. When liquids with different pH values were dropped onto the asymmetric surface, responsive wetting behavior occurs immediately. The corresponding video that records the entire wetting behavior of liquids with different pH values on the Janus Si-CAs is shown in Video S1 (Supporting Information). As long as the liquid droplets were injected onto the surface, a sustained liquids transport is observed (Video S1, Supporting Information). In addition, Video S2 (Supporting Information) shows the high-magnification video of wetting behavior of strong acid and base on the Janus Si-CAs (Supporting Information). From Video S2 (Supporting Information), we could conclude that the wetting behavior of acid (pH = 0.98) and base (pH = 13.05) on the Janus Si-CAs is unidirectional with reversed directions.[43] Moreover, the ratio of $D_{difficult}/D_{easy}$ is plotted as a function of pH (Figure 2i). $D_{difficult}$ and D_{easy} represent the moving distances of liquids along two directions of the asymmetric surfaces. Herein, we define $D_{difficult}$ is less than D_{easy}, and $D_{difficult}/D_{easy} > 0.8$ indicates isotropic wetting behavior, while $D_{difficult}/D_{easy} < 0.8$ represents anisotropic wetting behavior. From the function, we could understand the capacity of the Janus surfaces for regulating the wetting behavior of liquids with various pH values. The Janus surfaces could roughly regulate the ratio from 0 (strong acid and base) to 1 (liquids with moderate pH values). Strong acid and base result in a small $D_{difficult}/D_{easy}$. In order to explore the repeatability of the Janus Si-CAs, we reprepared the Janus PDMAEMA-SAMs Si-CAs (polymer thickness = 20.8 nm; DDT/MUA = 0.45/0.55), and measured the wetting property of it. For liquids with different pH values, we measured ten times. Results show that the repeatability is excellent (Figure S2, Supporting Information). More intuitive observations could be realized in Video S3 (Supporting Information). Strong acid and base wet in a unidirectional manner with reversed directions, and make pH paper red and blue. The above results show that smart pH-responsive anisotropic wetting surfaces were prepared, which autonomously induce acid (pH = 0.98) and base (pH = 13.05) unidirectional wetting with reversed directions and show high sensitivity to strong acid and base.

2.2. pH-Responsive Asymmetric Surfaces

Si-CAs modified asymmetrically by hydrophilic and hydrophobic molecules could induce unidirectional wetting of water, because of the large difference in wettability of water between two sides of the cylinders.[46,48] Similarly, large difference in wettability between two sides of the Si-CAs is essential to operate the smart surfaces when acidic and basic conditions are given. Therefore, CA values of acid and base on either side of the Janus Si-CAs are both important factors. We believe that the thickness of the polymer (PDMAEMA) and the mixture ratio of the mixed SAMs (DDT and MUA) would influence the wetting property of acid and base. Thus, in the following sections, these two factors are explored to search for the best operating condition of the smart asymmetric surfaces.

2.2.1. PDMAEMA-Modified Si-CAs

Surface-initiated atom transfer radical polymerization (SI-ATRP) method allows us to finely modulate the thickness of the obtained PDMAEMA films and thus investigate the relationship between the wetting property and the film thickness. We modified the surfaces of Si-CAs by PDMAEMA of different thickness (**Figure 3**a). A linear increase of the polymer thickness with polymerization time could be observed (Figure S3, Table S1, Supporting Information). CA measurements were then employed to characterize the wetting behavior of acid (pH = 0.98) and base (pH = 13.05) on PDMAEMA-modified Si-CA (different polymer thickness, Figure 3b). The surfaces exhibit CA of about 80° with basic droplets, while when acidic droplets were applied, the droplets gradually spread on PDMAEMA-modified Si-CAs, and the PDMAEMA-modified Si-CAs with polymer thickness larger than 13.2 nm show superhydrophilicity (includes 13.2 nm). We ascribe the phenomena to protonation/deprotonation effect of PDMAEMA molecule in response to different pH. As illustrated in Figure 3a, under acidic conditions, the amino groups of the PDMAEMA molecule could be mostly protonated and positively charged, which could attract hydrate shells, resulting in the hydrophilicity of the entire surface.[50] Correspondingly, the deprotonation of amino groups could be accomplished under basic conditions, which would decrease the hydrophilicity of the surface, leading to a less hydrophilic state. Note that the hydrophilicity evidently decreased with the polymer thickness of 5.7 and 8.8 nm (Figure 3b). Along with the polymer thickness reduced, the lengths of the two kinds of PDMAEMA brushes are too short to build superhydrophilic surfaces. Meanwhile, initiators occupy a leading role, resulting in a relatively less hydrophilic state (Figure S4, Supporting Information). Actually, although the final state of acidic droplets on PDMAEMA-modified Si-CAs with polymer thickness larger than 13.2 nm is basically consistent (superhydrophilic state), the spreading speed is different. It is observed that the thin polymer thickness of PDMAEMA-modified Si-CAs undergoes high spreading speed of acidic droplets (Figure 3c, Figures S5 and S7a, Supporting Information).

Then, the wetting behavior of liquids with other pH values (pH = 3.99, 7.04, and 9.99) on PDMAEMA-modified Si-CAs was studied (polymer thicknesses = 13.2, 20.8, and 45.0 nm were selected). We noticed the thickness of the PDMAEMA film hardly affected the wetting behavior of liquids with different pH values (Figure 3d), because these three curves are basically coincident. The only difference is the wetting speed of acidic droplets on these three kinds of PDMAEMA-modified Si-CAs. Similar to the previous results, PDMAEMA-modified Si-CAs with polymer thickness of 13.2 nm possess the highest wetting speed for acid. To investigate the details of the transition process, wetting behavior of liquids with pH values from 1 to 13 on PDMAEMA-modified Si-CAs was measured (polymer thickness = 13.2 nm, Figure 3e). The surfaces maintained hydrophilic with increasing pH values from 1 to 3, became less hydrophilic when the pH value reached 4, and maintained a less hydrophilic state between pH values of 4 and 13. It is obvious that with liquids at pH values below 4, the CA of liquids increased with the increase of pH values. The phenomenon

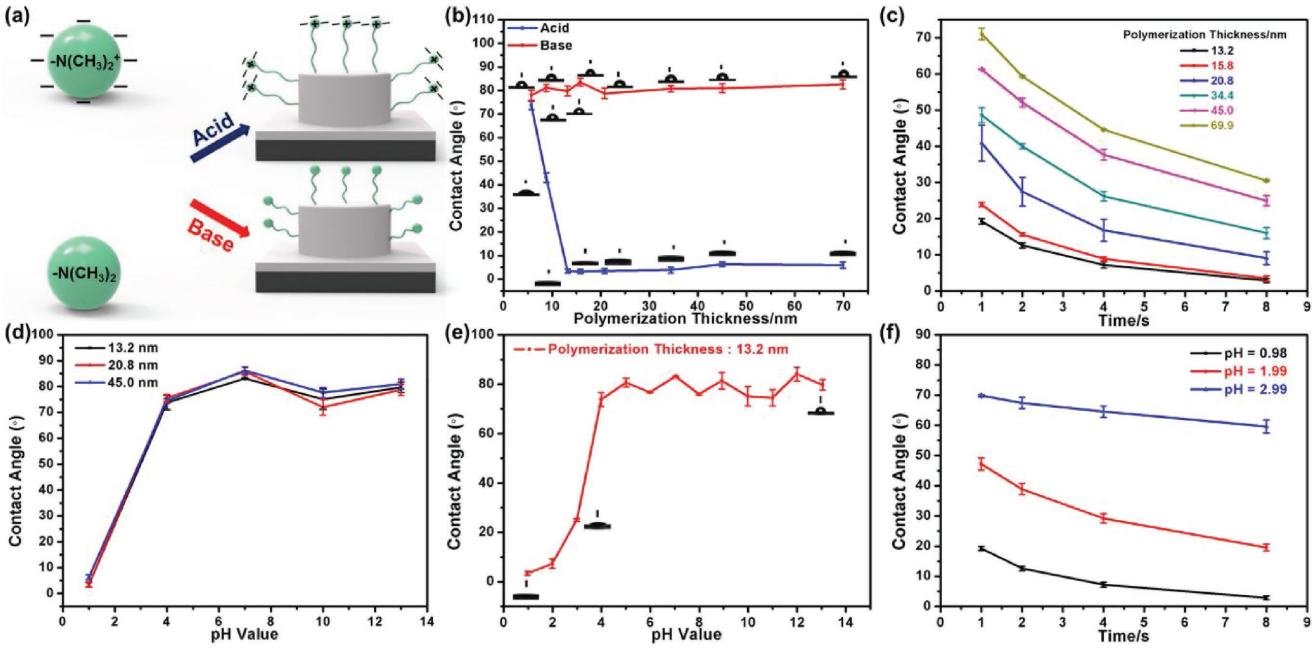

Figure 3. a) Illustration of the transformation of the properties of Si-CAs in response to different pH after modification by PDMAEMA. b) Plots of CA values as a function of the polymer thickness for strong acid (blue) and base (red) on PDMAEMA-modified Si-CA. c) Plots of CA values as a function of time for acid (pH = 0.98) on PDMAEMA-modified Si-CAs (different polymer thickness). d) Plots of CA values as a function of pH on PDMAEMA-modified Si-CAs (polymer thicknesses = 13.2, 20.8, and 45.0 nm). e) Plots of CA values as a function of pH on PDMAEMA-modified Si-CAs (polymer thicknesses = 13.2 nm). f) Plots of CA values as a function of time for liquids with different pH on PDMAEMA-modified Si-CAs (polymer thickness = 13.2 nm).

could be ascribed to the concentration of hydrogen ions. With the increase of the pH value, the low hydrogen ion concentration of liquids becomes hard to protonate the PDMAEMA molecule, resulting in the decrease of hydrophilicity. Moreover, the wetting speed of liquids with different pH values on PDMAEMA-modified Si-CAs is also different. Acid solutions at low pH values possess high spreading speed (Figure 3f and Figure S7b, Supporting Information). In a word, PDMAEMA-modified Si-CAs show intensive sensitivity to liquids with high hydrogen ion concentration, and could transform from less hydrophilicity to superhydrophilicity.

2.2.2. Mixed SAM-Modified Si-CAs

Mixed SAM-modified Si-CAs were prepared through a surface modification process (self-assembly).[25,49] To further explore the effect of the ratio of methyl/carboxyl groups in the SAMs, Si-CAs were modified with various DDT/MUA mole ratios, which were 0.35/0.65, 0.4/0.6, 0.45/0.55, 0.50/0.50, 0.55/0.45, 0.60/0.40, and 0.65/0.35 (**Figure 4**a). Then, the wetting behavior of acid (pH = 0.98) and base (pH = 13.05) on each surface was measured. It is found that at all these mole ratios, the surfaces exhibit a pH-responsive transformation (Figure 4b). CA values of acid are always larger than that of base. For example, when X_{DDT} (mole fraction of DDT in the mixed thiol solution) is adjusted to 0.45, the surfaces were hydrophilic (25.5°, Table S2, Supporting Information) for basic droplets and less hydrophilic for acidic droplets (85.2°). When X_{DDT} is changed to 0.35, compared with 0.45, the hydrophilicity for both basic (2.8°) and acidic droplets (69.3°) was amplified. Moreover, note that for the value of X_{DDT} = 0.55, the surfaces show less hydrophilic for basic droplets (75.0°). Therefore, appropriate ratio of DDT/MUA results in pH-responsive surfaces from hydrophilic to less hydrophilic state. We ascribe the phenomena to protonation/deprotonation effect of MUA molecule in response to pH. Figure 4a shows the illustration of the transformation of surface properties in response to different pH values after modification with mixed SAMs of MUA and DDT. Under basic conditions, the hydrate layers formed, because of the deprotonated and negatively charged carboxylic acid groups, which contribute to the hydrophilicity of the entire surface.[25] But under acidic conditions, there is no change on DDT and MUA, causing relatively less hydrophilic surface.

Then, wetting properties of the mixed SAM-modified Si-CAs (DDT/MUA = 0.45/0.55 and 0.20/0.80) were studied with droplets of various pH. As for the ratio of 0.45/0.55, acidic droplet shows hydrophobic state on them, while the surfaces only show hydrophilic states at strong base area (Figure 4c, pH = 12.00 and 13.05). To improve the hydrophilicity for basic droplets with relatively low pH values, we increased the ratio of MUA (blue curve, 0.2/0.8). The results show that the scope of hydrophilicity for basic droplets is increased (Figure 4c, pH = 11.00, 12.00, and 13.05), however, the hydrophilicity for acid is also increased simultaneously (from about 90° to 60°). Based on the above results, we conclude that as for the appropriate ratio of DDT/MUA, the surfaces exhibit pH-responsive wetting properties, which show high sensitivity to strong acid and base.

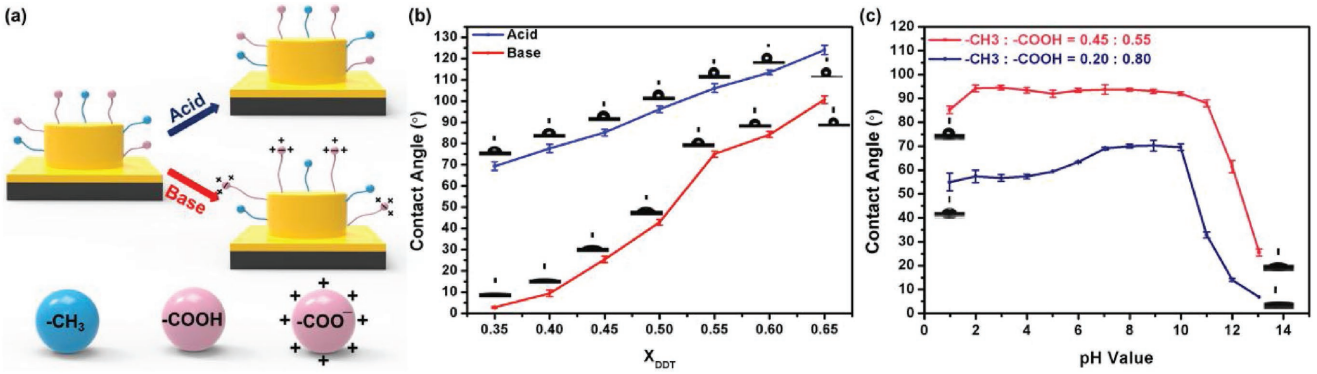

Figure 4. a) Illustration of the transformation of the properties of Si-CAs in response to different pH after modification by mixed SAMs (DDT and MUA). b) Plots of CA values as a function of X_{DDT} (mole fraction of DDT in the mixed thiol solution) for strong acid (blue) and base (red) on mixed SAM-modified Si-CAs. The total thiol concentration is 1×10^{-3} M in ethanol. c) Plots of CA values as a function of pH on mixed SAMs (DDT and MUA) modified Si-CAs (X_{DDT} = 0.20 and 0.45).

2.3. Mechanism and Operating Condition of the Asymmetric Surfaces

Through polymerizing PDMAEMA with appropriate thickness and selecting DDT/MUA with appropriate ratio, the Janus PDMAEMA-SAMs Si-CAs could operate with pH-responsive anisotropic wetting property. As illustrated in **Figure 5**a, under acidic conditions, the amino groups of PDMAEMA molecules could be mostly protonated and positively charged, which could attract hydrate shells, resulting in the hydrophilicity of the PDMAEMA-modified area. Meanwhile, the other side of the Si-CAs could not be changed, causing a relatively less hydrophilic state. Correspondingly, deprotonation of amino groups could be accomplished under basic conditions, which decrease the hydrophilicity of the PDMAEMA-modified area, leading to a less hydrophilic property. Simultaneously, the hydrate layers formed because of the deprotonated and negatively charged carboxylic acid groups, which contributed to the hydrophilicity of the mixed SAM-modified area. Essentially, the asynchronous protonation/deprotonation behavior caused asymmetric changes in surface tension of the Janus Si-CAs.[51] Therefore, either under acidic or basic conditions, there are always differences of CA value between two sides of the asymmetric Si-CAs. In order to better understand the wetting behavior of liquids with different pH values on the Janus PDMAEMA-SAMs Si-CAs (Figure 2), we calculated the differences between CA values (ΔCA) of liquids with different pH values on PDMAEMA-modified Si-CAs (polymer thickness = 20.8 nm) and mixed SAM-modified Si-CAs (X_{DDT} = 0.45), results are shown in **Table 1** and Figure 5b. For strong acid and base (pH = 0.98 and 13.05), the large ΔCA values cause unidirectional wetting of them with reversed wetting directions. When decreasing acidity or basicity of the solution, although the ΔCA is large enough, liquid droplets (pH = 1.99) show anisotropic wetting behavior on the asymmetric surfaces. The phenomenon ascribes to the relatively low spreading speed of the droplets (pH = 1.99) compared to the droplets (pH = 0.98) as mentioned before. Once the droplets (pH = 1.99) were dropped onto the asymmetric surfaces, owing to the relatively low spreading speed, a little amount of the droplets would move along SAM-modified direction till ΔCA is large enough to direct directional wetting of the droplets toward PDMAEMA-modified direction. For liquid droplets with pH value of 12.00, the diminished ΔCA between two sides of the asymmetric surfaces results in

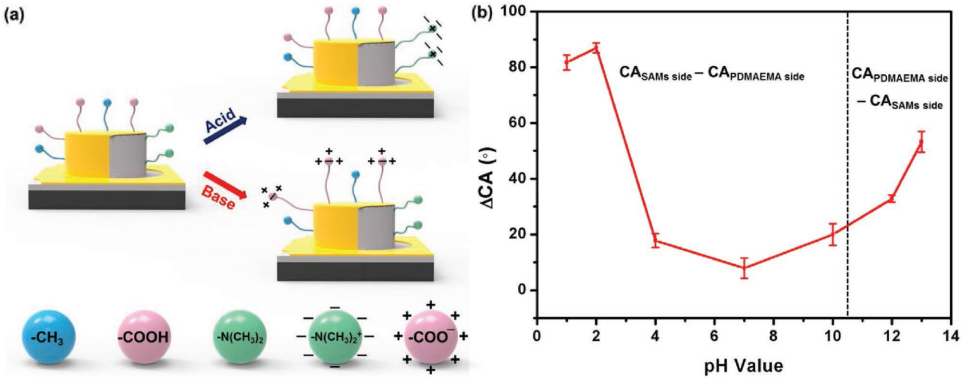

Figure 5. a) Illustration of the transformation of the properties of the asymmetric surface in response to different pH. b) Plots of ΔCA as a function of pH. ΔCA: Differences between CA values of liquids with different pH on PDMAEMA-modified Si-CAs (polymer thickness = 20.8 nm) and mixed SAMs (DDT and MUA, X_{DDT} = 0.45) modified Si-CAs. When pH < 11, ΔCA means $CA_{SAMs\ side} - CA_{PDMAEMA\ side}$, which indicate liquids were directed to PDMAEMA-modified direction. For strong base (pH = 12.00 and 13.05), ΔCA means $CA_{PDMAEMA\ side} - CA_{SAMs\ side}$ that demonstrates liquids were induced to SAM-modified direction.

Table 1. CA values of liquids with different pH on PDMAEMA-modified Si-CAs (film thickness = 13.2 nm) and mixed SAMs (DDT and MUA, X_{DDT} = 0.45) modified Si-CAs. The differences between CA values of liquids with different pH on PDMAEMA-modified Si-CAs (polymer thickness = 20.8 nm) and mixed SAMs (DDT and MUA, X_{DDT} = 0.45) modified Si-CAs.

	PDMAEMA-modified Si-CAs (film thickness = 20.8 nm)	Mixed SAMs (DDT and MUA) modified Si-CAs (X_{DDT} = 0.45)	
pH value	ΔCA [°]	ΔCA [°]	ΔCA [°]
0.98	3.5 ± 1.0	85.2 ± 1.6	81.7 ± 2.6
1.99	7.3 ± 0.4	94.2 ± 1.4	86.9 ± 1.8
3.99	75.6 ± 1.3	93.5 ± 1.2	17.9 ± 2.5
7.04	85.8 ± 1.6	93.7 ± 2.1	7.9 ± 3.7
9.99	72.1 ± 3.1	92.1 ± 0.8	20.0 ± 3.9
12.00	84.1 ± 0.2	51.2 ± 1.1	32.9 ± 1.3
13.05	78.8 ± 2.2	25.5 ± 1.5	53.3 ± 3.7

anisotropic wetting of the droplets on the Janus surfaces. With further decrease in the acidity or basicity of the liquids, as for droplets with moderate pH values (pH = 3.99, 7.04, and 9.99), the minimal ΔCA between two sides of the asymmetric surfaces hardly affects the wetting behavior of the liquids. Therefore, liquids nearly show isotropic wetting manner on the surfaces.

Due to the excellent response capability for strong acid and base, herein, we would search for the operating condition of the smart asymmetric surfaces. As mentioned before, the working precondition of the pH-responsive asymmetric surfaces is the relatively large differences of CA value between two sides of the Si-CAs when acidic and basic conditions are employed. We calculated the differences between CA values of strong acid and base on PDMAEMA-modified Si-CAs (different polymer thickness) and mixed SAMs (DDT and MUA) modified Si-CAs (different mixture ratios). As shown in **Table 2**, when DDT/MUA are 0.35/0.65, 0.4/0.6, and 0.45/0.55, meanwhile, the polymer thickness is larger than 13.2 nm (includes 13.2 nm), the differences between CA values of acid and base on the two kinds of the surfaces are both relatively large (Table 2 red area, greater than 50.0°). In addition, in consideration of the relatively high wetting speed of acid on PDMAEMA-modified surfaces with thin film thickness, polymer thickness less than 34.4 nm is selected. Therefore, the operating condition of the Janus PDMAEMA-SAMs (DDT and MUA) Si-CAs is established. One side of the Si-CAs is modified by PDMAEMA with polymer thickness from 13.2 to 20.8 nm, and the other side is modified by mixed SAMs with X_{DDT} from 0.35 to 0.45.

2.4. Direction-Controllable Anisotropic Wetting Surfaces for Water

As we know, anisotropic wetting of water has attracted enormous attention owing to their various applications from fundamental to practical aspects. The as-prepared Janus PDMAEMA-SAMs Si-CAs not only could regulate the wetting behavior of acid and base but also could direct unidirectional wetting of water toward PDMAEMA- or mixed SAM-modified directions when the surfaces are treated with strong acid or base (**Figure 6**). For injecting water onto Janus Si-CAs (polymer thickness = 20.8 nm; DDT/MUA = 0.45/0.55) without acid and base treatment, water moved freely toward the two directions with approximately equal moving distances (Figure 6b). When immersing the surfaces into acid (pH = 0.98) for 2 s, washing with ethanol to remove the redundant acid, and drying at a nitrogen atmosphere, the Janus Si-CAs induce unidirectional wetting of water along PDMAEMA-modified direction (Figure 6a). While replacing the acid with base (pH = 13.05), water could wet in a unidirectional wetting manner toward mixed SAM-modified direction (Figure 6c). The phenomena were also attributed to asynchronous protonation/deprotonation behavior on two sides of the asymmetric structures shown in Figure 5a. Satisfactorily, reversible transformation of wetting

Table 2. The differences between CA values of strong acid and base on PDMAEMA-modified Si-CAs (different polymer thickness) and mixed SAMs (DDT and MUA) modified Si-CAs (different mixture ratios).

Film Thickness (nm) / X_{DDT} / ΔACA, ΔBCA (°)	5.7	8.8	13.2	15.8	20.8	34.4	45.0	69.9
0.35	-4.3, 75.2	26.2, 78.3	**65.9, 76.9**	**66.0, 80.7**	**65.8, 76.0**	65.4, 77.3	63.0, 77.3	63.4, 79.8
0.40	4.1, 68.5	34.6, 71.6	**74.3, 70.2**	**74.4, 74.0**	**74.2, 69.3**	73.8, 70.6	71.4, 70.6	71.8, 73.1
0.45	11.6, 52.5	42.1, 55.6	**81.8, 54.2**	**81.9, 58.0**	**81.7, 53.3**	81.3, 54.6	78.9, 54.6	79.3, 57.1
0.50	22.5, 35.1	53.0, 38.2	92.7, 36.8	92.8, 40.6	92.6, 35.9	92.2, 37.2	89.8, 37.2	90.2, 39.7
0.55	32.5, 3.0	63.0, 6.1	102.7, 4.7	102.8, 8.5	102.6, 3.8	102.2, 5.1	99.8, 5.1	100.2, 7.6
0.60	39.9, -6.2	70.4, -3.1	110.1, -4.5	110.2, -0.7	110.0, -5.4	109.6, -4.1	107.2, -4.1	107.6, -1.6
0.65	50.5, -22.6	81.0, -19.5	120.7, -20.9	120.8, -17.1	120.6, -21.8	120.2, -20.5	117.8, -20.5	118.2, -18.0

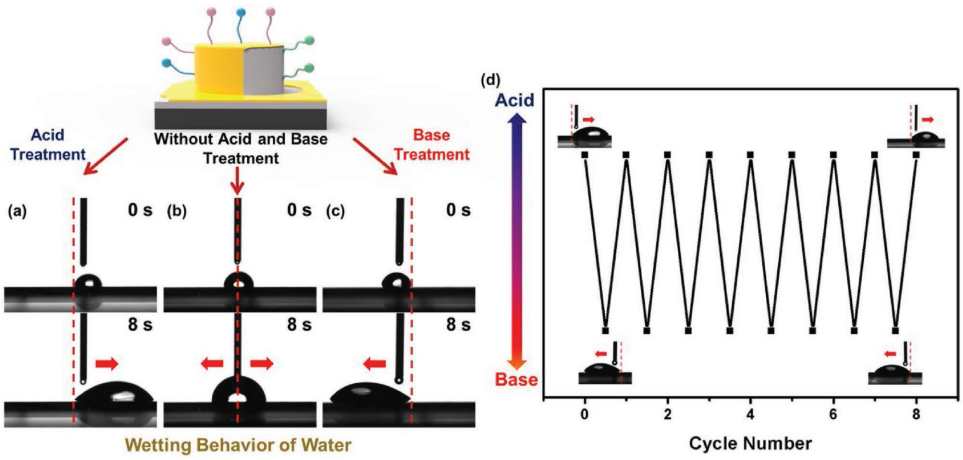

Figure 6. Time-lapse photographs of wetting behavior of 8 µL deionized water on Janus PDMAEMA-SAMs (DDT and MUA) modified Si-CAs (polymer thickness = 20.8 nm; $X_{DDT} = 0.45$). The Janus surfaces were treated by acid a, pH = 0.98 and base c, pH = 13.05. b) The Janus surfaces were measured with water without acid and base treatment. The red arrows indicate the moving direction of liquids. The red dotted lines represent center axis of the syringe needle (b), left (a), and right (c) positions of the water droplets when they contacted the asymmetric surface. The PDMAEMA-modified direction was placed on the right side when taking photographs. The injection velocity is 1 µL s^{-1}. d) Reversible transformation of wetting behavior of water is observed with alternately treated by acid (pH = 0.98) and base (pH = 13.05) of Janus PDMAEMA-SAMs (DDT and MUA) Si-CAs (polymer thickness = 20.8 nm; $X_{DDT} = 0.45$).

behavior of water is observed with alternate treatment by acid and base of the Janus Si-CAs (Figure 6d).

3. Conclusion

In summary, utilizing protonation/deprotonation effect, we fabricated smart surfaces possessing extraordinary property to manipulate the wetting behavior of acid and base by combining "Janus" system with typical pH-responsive groups (amino and carboxyl groups). After asymmetric modification of the pH-responsive groups onto Si-CAs, the as-prepared Janus PDMAEMA-SAMs (DDT and MUA) Si-CAs direct unidirectional wetting of strong acid and base toward corresponding directions that are modified by amino or carboxyl groups. Through investigating the wetting behavior of liquids with other pH values, it was found that the molecules we selected show high sensitivity to strong acid and base. The smart phenomena are caused by asynchronous protonation/deprotonation behavior on two sides of the asymmetric surfaces. We proposed the precondition of the smart asymmetric surfaces for simultaneously regulating the wetting behavior of acid and base, which are relatively large differences of CA value between two sides of the Si-CAs when acidic and basic conditions are given. Following the principle, the operating condition of the Janus Si-CAs is identified. In addition to acid and base, the Janus surfaces could direct unidirectional wetting of water toward PDMAEMA- or mixed SAM-modified directions when the surfaces are treated by strong acid or base. Furthermore, owing to the remarkable responsive behavior, such smart surfaces are great tools to be applied in microfluidics for fluid control, sensors, and oil/water separation. The surfaces would show a broad range of applications in the future stimuli-responsive materials and interfacial chemistry fields.

4. Experimental Section

Materials: Silicon wafers (100) were cut into the size of 2.0 cm × 2.0 cm and soaked in piranha solution (3:7 30% H_2O_2/concentrated H_2SO_4) for 1 h at 110 °C to create hydrophilic surfaces and then rinsed with ethanol and Milli-Q water (18.2 MΩ cm^{-1}) repeatedly. Before use, the substrates were dried in a nitrogen flow. Polystyrene (PS) microspheres (1 µm in diameter), copper (I) chloride (CuCl), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), 2-bromoisobutyrylbromide, 3-aminopropyltrimethoxysilane (APTMS), DDT, and MUA were all purchased from Aldrich. 2-(Dimethylamino) ethyl methacrylate was purchased from TCI. $CuBr_2$ was provided by Alfa. Sulfuric acid, hydrogen peroxide, absolute ethanol, toluene, dichloromethane, methanol, hydrochloric acid, sodium hydroxide, and triethylamine were used as received. Water used in the experiments was deionized.

Functionalization of the Si-CAs with PDMAEMA-SAMs (DDT and MUA) via Asymmetric Modification: Si-CAs were fabricated by the combination of interfacial self-assembly and colloidal lithography (Process 1, Supporting Information).[52] To prepare the smart surfaces, the Si-CAs were first modified by PDMAEMA through SI-ATRP with polymerization time of 10 min (Process 2, Supporting Information),[53] and then one side of the cylinders was deposited by Cr (3 nm in thickness, to improve the adhesion between Au and the substrates) and Au (20 nm in thickness) successively through oblique 45° thermal evaporation.[46–48] Finally, through immersing the as-prepared substrates into a mixed ethanol solution of DDT (0.045×10^{-3} M) and MUA (0.055×10^{-3} M) for 8 h, PDMAEMA-SAM-modified Janus Si-CAs were obtained.

Functionalization of the Si-CAs with PDMAEMA via SI-ATRP: Si-CAs were modified by PDMAEMA with polymerization time of 0.5, 1, 2.5, 5, 10, 20, 30, and 40 min through SI-ATRP.

Functionalization of the Si-CAs with DDT and MUA via Thermal Evaporation and Self-Assembly: Si-CAs were first deposited with 3 nm Cr and 20 nm Au through vertical thermal evaporation. Then, through immersing the as-prepared substrates into a mixed ethanol solution of DDT and MUA for 8 h, Si-CAs modified by DDT and MUA were performed. The total thiol concentration was 0.1×10^{-3} M in ethanol. The mixture ratios of the two kinds of thiol were adjusted to 0.2 (DDT)/0.8 (MUA), 0.35/0.65, 0.4/0.6, 0.45/0.55, 0.50/0.50, 0.55/0.45, 0.60/0.40, and 0.65/0.35.

Characterization: SEM images were taken by a JEOL FESEM 6700F electron microscope with primary electron energy of 3 kV, and the surfaces were sputter-coated with 2 nm Pt before testing. Thickness of the PDMAEMA brushes was measured by atomic force microscopy. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was applied to explore the chemical compositions of the Janus arrays. Wetting behavior of liquids on the prepared surfaces was measured using "sessile drop" mode of DataPhysics OCA20. Liquids with various pH values were prepared with aqueous solutions of HCl (1 M) and NaOH (1 M). The surfaces were washed with copious water followed by ethanol and dried in nitrogen flow between each CA measurement with droplets of different pH values, to ensure the substrates were clean before CA testing at another pH value.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 21774043, 21474037, and 51505456) and Jilin Province Development and Reform Commission (2015Y028). This project was also supported by the State Key Laboratory of applied optics.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

anisotropic wetting, asymmetric structures, pH-responsive materials, protonation/deprotonation effects

Received: March 21, 2018
Published online:

[1] F. Xia, Y. Zhu, L. Feng, L. Jiang, *Soft Matter* **2009**, *5*, 275.
[2] B. Xin, J. Hao, *Chem. Soc. Rev.* **2010**, *39*, 769.
[3] X. Liu, Y. Liang, F. Zhou, W. Liu, *Soft Matter* **2012**, *8*, 2070.
[4] M. Cheng, Y. Gao, X. Guo, Z. Shi, J.-f. Chen, F. Shi, *Langmuir* **2011**, *27*, 7371.
[5] S. J. D. Jeyaprakash, P. Ruther, H.-P. Frerichs, M. Lehmann, O. Paul, J. Ruhe, *Sens. Actuators, B* **2005**, *110*, 218.
[6] J. Chapman, F. Regan, *Adv. Eng. Mater.* **2012**, *14*, B175.
[7] F. Rios, S. N. Smirnov, *Chem. Mater.* **2011**, *23*, 3601.
[8] P. Gupta, K. Vermani, S. Garg, *Drug Discovery Today* **2002**, *7*, 569.
[9] M. Kurisawa, N. Yui, *J. Controlled Release* **1998**, *54*, 191.
[10] D. J. Beebe, J. S. Moore, Q. Yu, R. H. Liu, M. L. Kraft, B.-H. Jo, C. Devadoss, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 13488.
[11] K. M. Grant, J. W. Hemmert, H. S. White, *J. Am. Chem. Soc.* **2002**, *124*, 462.
[12] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angew. Chem., Int. Ed.* **2004**, *116*, 361.
[13] J. Gao, Y. Liu, H. Xu, Z. Wang, X. Zhang, *Langmuir* **2010**, *26*, 9673.
[14] F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang, L. Jiang, *Adv. Mater.* **2006**, *18*, 432.
[15] K. Ichimura, S.-K. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624.
[16] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 62.
[17] G. Caputo, B. Cortese, C. Nobile, M. Salerno, R. Cingolani, G. Gigli, P. D. Cozzoli, A. Athanassiou, *Adv. Funct. Mater.* **2009**, *19*, 1149.
[18] T. Kamegawa, Y. Shimizu, H. Yamashita, *Adv. Mater.* **2012**, *24*, 3697.
[19] B. S. Lee, Y. S. Chi, J. K. Lee, I. S. Choi, C. E. Song, S. K. Namgoong, S.-G. Lee, *J. Am. Chem. Soc.* **2004**, *126*, 480.
[20] F. Zhou, H. Hu, B. Yu, V. L. Osborne, W. T. S. Huck, W. Liu, *Anal. Chem.* **2007**, *79*, 176.
[21] O. Azzaroni, A. A. Brown, W. T. S. Huck, *Adv. Mater.* **2007**, *19*, 151.
[22] J. Lahann, S. Mitragotri, T.-N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, R. Langer, *Science* **2003**, *299*, 371.
[23] T. N. Krupenkin, J. A. Taylor, E. N. Wang, P. Kolodner, M. Hodes, T. R. Salamon, *Langmuir* **2007**, *23*, 9128.
[24] L. Xu, W. Chen, A. Mulchandani, Y. Yan, *Angew. Chem., Int. Ed.* **2005**, *44*, 6009.
[25] X. Yu, Z. Wang, Y. Jiang, F. Shi, X. Zhang, *Adv. Mater.* **2005**, *17*, 1289.
[26] P. Wan, Y. Wang, Y. Jiang, H. Xu, X. Zhang, *Adv. Mater.* **2009**, *21*, 4362.
[27] S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke, M. Stamm, *J. Am. Chem. Soc.* **2003**, *125*, 3896.
[28] S. Wang, H. Liu, D. Liu, X. Ma, X. Fang, L. Jiang, *Angew. Chem., Int. Ed.* **2007**, *46*, 3915.
[29] J. Wang, J. Hu, Y. Wen, Y. Song, L. Jiang, *Chem. Mater.* **2006**, *18*, 4984.
[30] J. M. Swann, A. J. Ryan, *Polym. Int.* **2009**, *58*, 285.
[31] L. Zhang, Z. Zhang, P. Wang, *NPG Asia Mater.* **2012**, *4*, e8.
[32] X. Yao, Y. Song, L. Jiang, *Adv. Mater.* **2011**, *23*, 719.
[33] B. Zhao, J. S. Moore, D. J. Beebe, *Science* **2001**, *291*, 1023.
[34] J. Ju, H. Bai, Y. Zheng, T. Zhao, R. Fang, L. Jiang, *Nat. Commun.* **2012**, *3*, 1247.
[35] Y. Zheng, H. Bai, Z. Huang, X. Tian, F.-Q. Nie, Y. Zhao, J. Zhai, L. Jiang, *Nature* **2010**, *463*, 640.
[36] B. Bhushan, Y. C. Jung, *Prog. Mater Sci.* **2011**, *56*, 1.
[37] L. Ionov, N. Houbenov, A. Sidorenko, M. Stamm, S. Minko, *Adv. Funct. Mater.* **2006**, *16*, 1153.
[38] T. Wang, H. Chen, K. Liu, S. Wang, P. Xue, Y. Yu, P. Ge, J. Zhang, B. Yang, *Appl. Mater. Interfaces* **2015**, *7*, 376.
[39] J. Isaksson, C. Tengstedt, M. Fahlman, N. Robinson, M. Berggren, *Adv. Mater.* **2004**, *16*, 316.
[40] D. Xia, L. M. Johnson, G. P. Lopez, *Adv. Mater.* **2012**, *24*, 1287.
[41] D. Xia, S. R. J. Brueck, *Nano Lett.* **2008**, *8*, 2819.
[42] W. Wu, L. Cheng, S. Bai, Z. L. Wang, Y. Qin, *Adv. Mater.* **2012**, *24*, 817.
[43] K.-H. Chu, R. Xiao, E. N. Wang, *Nat. Mater.* **2010**, *9*, 413.
[44] F. D. Dos Santos, T. Ondarçuhu, *Phys. Rev. Lett.* **1995**, *75*, 2972.
[45] C. D. Bain, G. D. Burnett-Hall, R. R. Montgomerie, *Nature* **1994**, *372*, 414.
[46] P. Ge, S. Wang, W. Liu, T. Wang, N. Yu, S. Ye, H. Shen, Y. Wu, J. Zhang, B. Yang, *Langmuir* **2017**, *33*, 2177.
[47] P. Ge, S. Wang, Y. Liu, W. Liu, N. Yu, J. Zhang, H. Shen, J. Zhang, B. Yang, *Langmuir* **2017**, *33*, 7248.
[48] P. Ge, S. Wang, W. Liu, T. Wang, N. Yu, P. Xue, H. Chen, H. Shen, J. Zhang, B. Yang, *Adv. Mater. Interfaces* **2017**, *4*, 1700034.
[49] G. Ju, M. Cheng, F. Shi, *NPG Asia Mater.* **2014**, *6*, e111.
[50] X. Chen, R. Ferrigno, J. Yang, G. M. Whitesides, *Langmuir* **2002**, *18*, 7009.
[51] M. Cheng, Q. Liu, G. Ju, Y. Zhang, L. Jiang, F. Shi, *Adv. Mater.* **2014**, *26*, 306.
[52] J. Zhang, Y. Li, X. Zhang, B. Yang, *Adv. Mater.* **2010**, *22*, 4249.
[53] L. Fang, Y. Li, Z. Chen, W. Liu, J. Zhang, S. Xiang, H. Shen, Z. Li, B. Yang, *ACS Appl. Mater. Interfaces* **2014**, *6*, 19951.