Wettability switching between high hydrophilicity at low pH and high hydrophobicity at high pH on surface based on pH-responsive polymer†

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Surfaces obtained by modifying poly(*N*,*N*′-dimethylaminoethyl methacrylate) (PDMAEMA) on rough silicon substrates are highly hydrophilic at low pH and highly hydrophobic at high pH; such surfaces effectively supplement the research on the wettability of solid surfaces based on the pH-responsive polymers.

Wettability is a very important property of solid surfaces and can be enhanced by both the surface geometry and the chemical composition.[1–3] In recent years, stimuli-responsive surfaces with tunable wettability have gained much attention because of their usefulness in fundamental research and industrial applications such as controllable separation systems, micro-fluidic devices, *etc*.[4,5] These smart surfaces can reversibly switch their physicochemical characteristics (*e.g.* wettability) in response to external stimuli, alone or in combination, including pH,[6] temperature,[7] light,[3,8] electrical field,[9] chemical substances,[10] and so on.

As is well known, pH-responsive polymers have been applied in many fields, such as drug delivery systems,[11] enzyme immobilization,[12] separation,[13] chemo-mechanical systems,[14] chemical valves,[15] sensors,[16] and so forth. In addition, the design and artificially control of environmental pH stimuli have been acheived in some cases. All of these facts show that surfaces based on pH-responsive polymers are of practical importance. There has been a little research on the wettability of solid surfaces based on pH-responsive polymers which are hydrophobic at low pH and hydrophilic at high pH. However, such surfaces have some limitations in applications. For example, they are limited in drug delivery systems because they cannot interact with DNA, enzymes, and polyanion drugs because of electrostatic repulsion at low pH. Therefore, research on the wettability of solid surfaces based on pH-responsive polymers which are hydrophilic at low pH is imperative.

Herein, a novel pH-responsive surface with tunable wettability, reversible switching between high hydrophilicity at low pH and high hydrophobicity at high pH, is reported. Such surfaces are achieved by fabricating a poly(*N*,*N*′-dimethylaminoethyl methacrylate) (PDMAEMA) thin film on roughly etched silicon substrates. PDMAEMA homopolymer is a weak polybase, which undergoes a phase transition owing to protonation at low pH and deprotonation at high pH of tertiary amine groups, and can interact with anionic substances by electrostatic attraction at low pH. Reversible switching between high hydrophilicity at pH = 2 and high hydrophobicity at pH = 9 can be well realized. This property is a result of the combined effect of the chemical variation of the surface and the surface roughness.

The PDMAEMA thin films are prepared on both flat and rough silicon substrates *via* a typical surface-initiated atom transfer radical polymerization (SI-ATRP),[17] which has proven to be effective and versatile among various methods for creating "smart" surfaces. The results of scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) provided the morphology of the silicon substrate and the chemical composition of the treated surface (see ESI†).

Contact angle (CA) measurements have been carried out to characterize the wetting property of the film. On the flat silicon substrate, the water CAs (neutral deionized water droplets) increased from 78.9 ± 0.4° (Fig. 1A (a) to 83.8 ± 1.3° (Fig. 1A (b) when the pH value changed from 2 to 9, and the

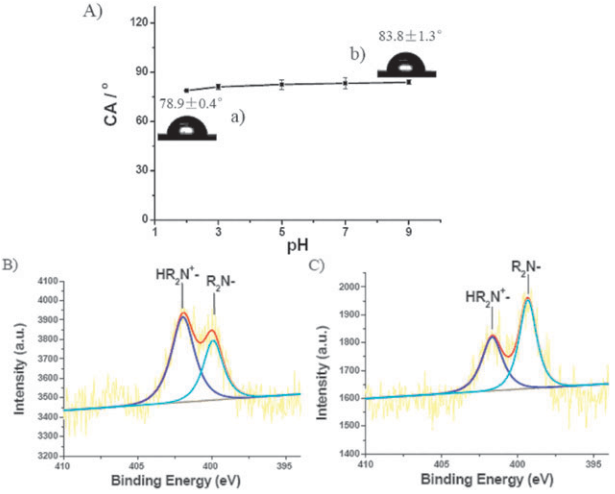

Fig. 1 (a) pH dependence of water CAs (neutral deionized water droplets) for PDMAEMA thin films on a flat substrate. Inset: photographs of the CAs on a flat surface which has been treated with solution (pH = 2), (a) and solution (pH = 9), (b). XPS spectra of N1s signals of the PDMAEMA film that has been treated with solution (pH = 2) (b) and solution (pH = 9) (c).

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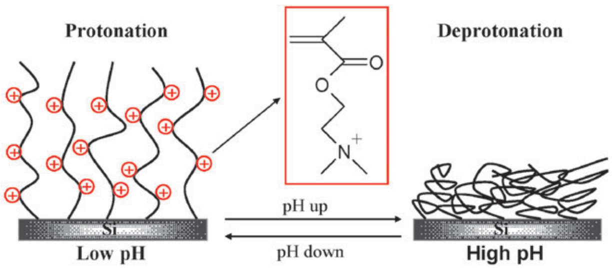
phenomenon is reversible. The small reversible change of CAs (about 5°) on the flat surfaces indicates the PDMAEMA thin film exhibits reversible pH-responsive wettability.

The phenomenon can be explained by the reversible phase transition of the PDMAEMA surface, or rather, by the result of the competition between protonation at low pH and deprotonation at high pH.[18] The PDMAEMA consists of ionizable pendants (tertiary amine groups) which can accept and donate protons in response to the environmental change in pH value. As the pH changes, the degree of ionization in the polymer bearing weakly ionizable groups is dramatically altered. This rapid change in net charge of pendant group causes an alteration of the hydrodynamic volume of the polymer chain.[19–21] The details of the mechanism are described as follows. PDMAEMA has a sensitive balance between charged repulsion and hydrophobic interactions. At low pH, tertiary amine groups are protonated and electrostatic repulsion force dominates, rendering an expanded state of the polymer chains (Scheme 1 left) that causes a smaller water CA. At high pH, hydrophobic interactions become dominant because the ionizable groups are deprotonated. That introduces a larger water CA and causes aggregation of the polymer chains (Scheme 1 right).

XPS (measured at 90°) analysis is used to clarify the change of chemical component distribution of the surface which has been immersed in aqueous solutions of different pH values to further prove the above-mentioned academic description. Reversibly changing the pH of the film between 2 and 9 (Fig. 1B and 1C), the N1s core-level spectra is curve-fitted with two species that are HR_2N^+– and R_2N– whose binding energies are at about 401.8 and 399.5 eV, respectively. The intensity of the HR_2N^+– peak is larger than the intensity of R_2N– peak at pH = 2 because tertiary amine groups are protonated, and the inverse phenomenon occurs at pH = 9 owing to the deprotonation of ionizable groups. The results effectively illuminate that tertiary amine groups are protonated at low pH in accord with the academic rationale.

Importantly, an interesting phenomenon happened on the rough surface. An extremely great change of CAs (neural deionized water droplets, about 110°) is induced on the rough surface compared with the flat surface (about 5°). At pH = 2, the water CAs decreased from 78.9 ± 0.4° for a flat substrate (Fig. 1A (a) to 9.5 ± 3.5° for a rough surface (Fig. 2A (a), because the water CA is smaller and water enters the microgrooves beneath the water droplet as described by Wenzel's equation.[22] In this situation, the surface roughness becomes the dominant factor that intensifies the hydrophilicity. At pH = 9, the water CA is larger and the rough surface enhances the hydrophobicity by increasing the air–water interface.[23] Thus, the CA increased from 83.8 ± 1.3° (flat substrate, Fig. 1A (b)) to 119 ± 4.1° (rough surface, Fig. 2A (b)). This interesting phenomenon is a result of the combined effect of the chemical variation of the surface and the surface roughness. And this process has been repeated several times, and good reversibility of the surface wettability observed (shown in Fig. 2B). To determine the effect of pH value on the CAs for the rough substrate, further detailed study has been conducted and is summarized in Fig. 2A.



Scheme 1 Reversible conformation changes of PDMAEMA at different pH. At low pH, tertiary amine groups are protonated and the polymer chains are extended (left) because of the electrostatic repulsion force, introducing a smaller water CA. At high pH, the ionizable groups are deprotonated and the electrostatic repulsion force disappears within the polymer chains. That causes aggregation of the polymer chains (right) that introduces a larger water CA.

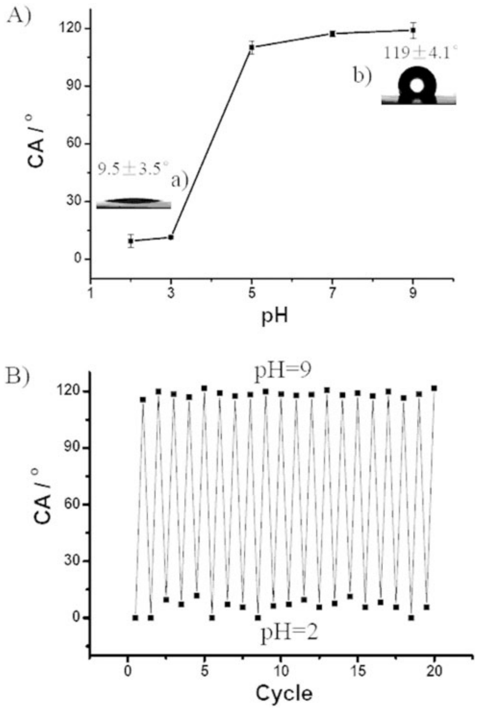


Fig. 2 (a) pH dependence of water CAs (neutral deionized water droplets) for PDMAEMA thin films on a rough substrate. Inset: photographs of the CAs on the rough surface which has been treated with solution (pH = 2), (a) and solution (pH = 9), (b). (b) Water CAs (neutral deionized water droplets) at two different pH values for a PDMAEMA-modified rough substrate. Half cycle: pH = 2 and integral cycles: pH = 9.

In summary, a novel pH-responsive surface has been fabricated by modification with PDMAEMA. Wettability study shows that the PDMAEMA film is highly hydrophilic at low pH and highly hydrophobic at high pH. That is the result of the combined effect of the competition between protonation and deprotonation of tertiary amine groups of PDMAEMA and the surface roughness. And the results from XPS further indicate the mechanism of pH-responsive switching. Additionally, the pH-responsiveness of the PDMAEMA thin films is reversible and stable. Such a surface that is highly hydrophilic at low pH and highly hydrophobic at high pH effectively supplements research on the wettability of solid surfaces based on pH-responsive polymers, and will have applications in microfluidic devices, controllable separation systems, biotechnology, and other biomaterial applications.

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