though functional, yielded lower currents (for similar device geometry) than the mixed-metal contacts, and therefore inferior device characteristics.

Characterization: Thermogravimetric analysis (TGA) scans were performed using a TA Instruments TGA-2950. The TGA was run using a $2\,^{\circ}\mathrm{C\,min^{-1}}$ ramp rate and a flowing nitrogen atmosphere. Powder X-ray diffraction was performed using a Siemens D5000 diffractometer. MEIS analysis was performed with 200 keV protons using an electrostatic energy analyzer at a scattering angle of 120°. The large scattering angle was chosen to minimize overlap between the In and Se peaks. The system was calibrated to better than 5 % accuracy using a SiO_2 film of known thickness. TFT devices were tested using a Hewlett–Packard 4145B semiconductor analyzer, employing a medium integration time (16.7 ms) during the measurement. Devices exhibited substantial sensitivity to air exposure after fabrication, with the mobility and current being substantially reduced upon extensive exposure to the ambient atmosphere (whether or not the device was being operated). Consequently, devices were maintained and measurements were performed in a nitrogen-filled dry box.

Received: September 3, 2004
Final version: December 28, 2004

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Reversible pH-Responsive Surface: From Superhydrophobicity to Superhydrophilicity**

By *Xi Yu*, *Zhiqiang Wang*,* *Yugui Jiang*, *Feng Shi*, and *Xi Zhang**

The wetting property of a solid surface is one of the most important aspects in both theoretical research and industrial applications. Two extreme cases, namely superhydrophobic surfaces with a contact angle (CA) larger than 150° and superhydrophilic surfaces with a CA lower than 10°, have attracted extensive interest considering their intriguing promise in self-cleaning materials.[1,2] In general, superhydrophobic surfaces can be obtained by controlling the roughness and topography of hydrophobic surfaces,[3] while superhydrophilic surfaces can be achieved by utilizing a capillary effect[4] on hydrophilic surfaces. Stimuli-responsive surfaces,[5] the wettability of which can be reversibly controlled, have been realized by various stimulus methods including light irradiation,[6] electric field,[7] thermal treatment,[8] and so on. Recently, by introducing stimuli-responsive materials into special rough surface structures, Jiang and co-workers have successfully demonstrated reversible switching between superhydrophobic and superhydrophilic surface properties triggered by temperature or UV irradiation.[9] Surface materials with wetting properties responding to certain conditions of water, such as pH value, electrolyte, and so on, are very important in controlled microfluidic switches, controllable separation systems, etc. For example, Whitesides and co-workers have demonstrated a pH-

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[**] Financial support from the Major State Basic Research Development Program (Grant. No. G2000078102), 863 High-tech R&D Program (2003AA302140), the National Natural Science Foundation of China (20334010, 20473045), and the Ministry of Education is gratefully acknowledged.

DOI: 10.1002/adma.200401646

responsive behavior on a smooth surface due to the deprotonation of the surface carboxylic acid groups.[10] The fabrication of a surface that can be both superhydrophobic or superhydrophilic in response to the conditions of water, however, remains an intriguing issue. Herein, a pH-responsive surface that can be superhydrophobic in an acidic and even neutral aqueous environment, but superhydrophilic under basic conditions, is reported.

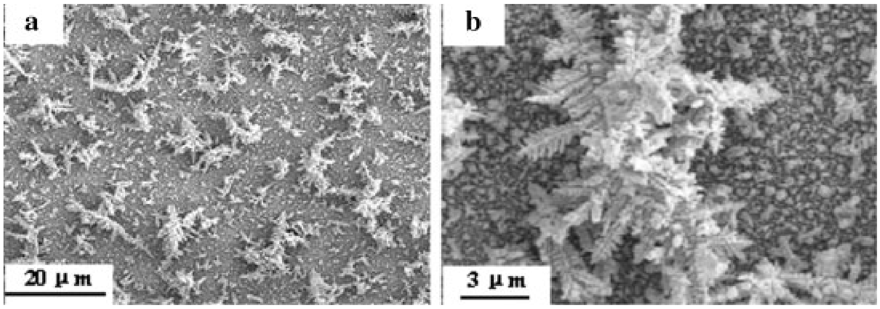


Figure 1. SEM images of deposited gold structures: a) microscale gold structures distributed on the surface; b) magnified image of the gold clusters; nanostructures on and between the clusters can be observed.

To achieve a superhydrophobic or superhydrophilic surface, a rough substrate is prerequisite, as the wetting property can be amplified by the roughness.[1,9] Herein, gold electrodeposition is employed on a 'full-of-defect' matrix of a dendritic thiol self-assembled monolayer to obtain a rough gold surface, which exhibits micro- and nanoscale roughness.[11] First, a flat gold substrate was modified with a dendron thiol molecule, and gold electrodepostion was performed on the modified substrate at –200 mV (vs. Ag/AgCl) in a $HAuCl_4/H_2SO_4$ mixed electrolyte solution for 40 min. In this way, a rough gold surface can be obtained. The substrate was then immersed in a piranha solution ($H_2O_2/H_2SO_4 = 3:7$) to give a fresh gold surface. Figure 1 shows scanning electron microscopy (SEM) images of the deposited gold structures. As shown in the picture, the structure of the gold deposited is fractal-like with a dimension between two and three to obtain a large surface area, which is believed to benefit the realization of a superhydrophobic surface.[15,3d]

In order to obtain pH-responsive surface properties, the above rough gold substrate was then immersed in a mixed solution of $HS(CH_2)_9CH_3$ and $HS(CH_2)_{10}COOH$ (the total thiol concentration of the solution was 1 mmol L^{-1} in ethanol) overnight. In this way, a mixed monolayer containing both alkyl and carboxylic acid groups can form on the surface of the gold and the composition of the mixed monolayer can be tuned by the composition of the modifying solution.[12] Moreover, substrates modified with this kind of monolayer exhibit a pH-responsive wetting behavior due to the deprotonation of the surface carboxylic acid groups.[10] It is expected that on a rough surface, this effect can be amplified.[9] The surface composition is determined by X-ray photoelectron spectroscopy (XPS) by comparing the C 1s peak intensity of the carboxylic acid groups with that of the alkyl carbons on the surface. XPS results indicate that the composition of the monolayer on both the flat and rough gold surface is comparable.

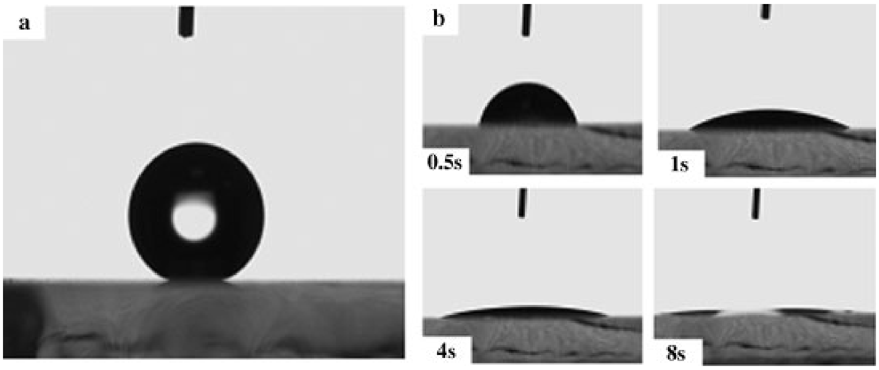


Figure 2. Photographs of a) acid and b) base droplet applied on the surface. The CA of the acid droplet is 154° and the basic droplet will spread out on the surface gradually, the CA is 77.6° (0.5 s); 26.9° (1 s); 12.0° (4 s), <10° (8 s). The volume of the droplet is 4 µL.

The wetting properties of the substrate are examined by means of contact angle measurements. We observe that the substrates modified with a solution containing 40 % $HS(CH_2)_{10}COOH$ (molar fraction) exhibit a pH-responsive wetting property. Figure 2a shows an acid droplet (pH 1) on such a surface. It forms a sphere with a CA of about 154°, which means that a superhydrophobic surface for acid has been achieved. However, when applying a base water droplet (pH 13) on the surface, it gradually spreads out in less than 10 s, as shown in Figure 2b. At the beginning, the droplet spreads on the surface very quickly, reaching a CA of lower than 90° in less than 0.5 s and 26.9° in 1 s, respectively. At 4 s it is 12°. Finally, the droplet spreads out completely. Within such a short time, the contact angle can decrease to zero and this indicates that the surface is superhydrophilic for a base droplet.[2,4]

After being rinsed with distilled water and dried with an N_2 stream, the base-exposed surface can recover its pH-responsive property, thus suggesting that the pH surface sensitivity is preserved, as shown in Figure 3. The reversible cycle can be repeated many times without any change in responsive property. The surface is mechanically and chemically stable, as its responsive property does not change, even over one month without any special protection.

In addition to the reversible switching of surface properties between superhydrophobic and superhydrophilic, more detailed studies about the pH–CA relationship have been per-

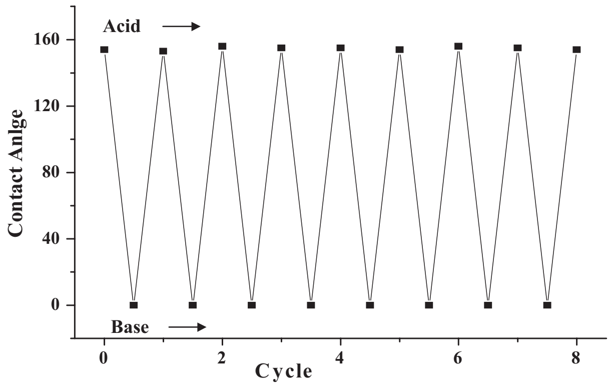


Figure 3. Reversible superhydrophobicity–superhydrophilicity for acid (pH 1) and base (pH 13) on the surface modified with a solution containing 40 % $HS(CH_2)_{10}COOH$ and 60 % $HS(CH_2)_9CH_3$. The base-contaminated surface was rinsed with distilled water and dried with an N_2 stream.

formed. It is observed that the surface is superhydrophobic for both acid and neutral water, as shown in Figure 4a. For the probe liquid with a pH value between 7 and 13, the CA will decrease dramatically. When the pH value is above 13, it is superhydrophilic. This characteristic is comparable with that on a flat surface, though there is an amplified effect on the rough surface.

The wetting characteristic of the mixed monolayer, which results from different compositions of the thiol coating, is critical for this responsive wettability. The substrate modified with the solution containing 40 % $HS(CH_2)_{10}COOH$ ($\chi_{COOH} = 0.4$) exhibits the pH-responsive superhydrophobic–superhydrophilic property. When $\chi_{COOH} = 0.3$, the surface will be superhydrophobic for acid, while for base the CA can only drop to about 40°, as shown in Figure 5. When $\chi_{COOH} = 0.5$ the surface will be superhydrophilic for base, while for an acid droplet the CA can only reach about 130°. Substrates modified with solutions of $\chi_{COOH} = 0.2$ or 0.6 will give a similar wetting property for acid or base, either only superhydrophobic or only superhydrophilic.

To characterize the wetting property of the mixed monolayer, the relationship between the contact angle of the flat Au substrates modified with mixed monolayers of different composition and the pH value of the droplet were examined (as shown in Fig. 5). It was observed that the CA does not change with the pH value when the surface was modified with pure *n*-decanethiol. As the proportion of the $HS(CH_2)_{10}COOH$ increases, the surface becomes more hydrophilic, and the difference of the CA between the acid and base increases. In other words, the surface becomes more hydrophilic for bases than for acids. For surfaces modified with a solution of $\chi_{COOH} = 0.4$, the CA changes between about 82° and 65°. This phenomenon is attributed to the better hydrophilicity of the deprotonated carboxylic acid groups compared with the protonated carboxylic acid groups. Moreover, because of the reaction of the base in the droplets with surface acid groups, such droplets tends to increase their contact area with the surface, and consequently the CA decreases.[10] The contact angle on the flat surface as a function of the pH value of the probe liquid is shown in Figure 4b. The CA characteristic is the same as that on rough surfaces, which is that the contact angle changes very little before pH 7, and decreases dramatically thereafter. This means that the acidity of the carboxylic acid on the surface (indicated by a CA titration curve) is lower than that in the solution. It is believed that two factors may contribute to this decrease. First is that the existence of methyl groups decrease the local dielectric constant of the environment around the carboxylic acid groups on the surface. The second is the hindrance effect on the formation of hydrogen bonds between the carboxylic acid and the water resulting from the steric bulk of adjacent chains at the surface of the monolayer.[10b]

Taking the contact angle on the flat gold as reference, the pH-responsive superhydrophobicity and superhydrophilicity was modeled using the Wenzel or Cassie equation.[13,14] As the intrinsic contact angle of the mixed monolayer on a flat substrate is smaller than 90°, about 82° even for acid droplet in our experiments, Wenzel's equation is usually used to describe the contact angle on the rough surface in this situation, e.g., $\cos\theta_r = r\cos\theta$. However, according to this equation, the substrate should be hydrophilic even in acid conditions. It was assumed that it should be in the Cassie state under acid condi-

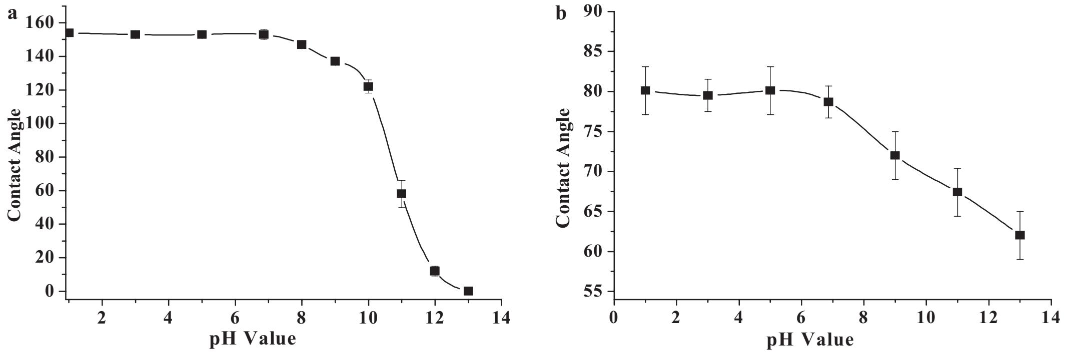


Figure 4. Contact angle as a function of pH value on a rough (a) and flat (b) gold surface modified with a solution containing 40 % $HS(CH_2)_{10}COOH$ and 60 % $HS(CH_2)_9CH_3$. The probe liquid is a buffered aqueous solution.

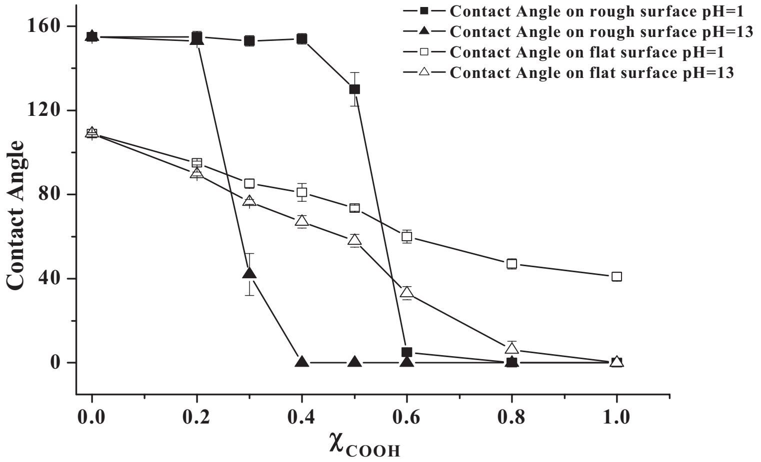


Figure 5. Contact angle as a function of χ_{COOH} (mole fraction of $HS(CH_2)_{10}COOH$ in the solution used for the modification of the substrate).

tions, and the acid liquid may be suspended on the top of the gold clusters with air trapped beneath the droplet. In this case, the Cassie–Baxter equation, $\cos\theta_{CB} = f_1\cos\theta - f_2$, is used to described the contact angle, in which θ is the contact angle on a flat surface, θ_{CB} is the contact angle on a rough surface, f_1 and f_2 are the fractions of solid surface and air in contact with the liquid, respectively (i.e., $f_1 + f_2 = 1$). It indicates that air trapped beneath the water can dramatically intensify the hydrophobicity. Using $\theta = 82°$ and $\theta_{CB} = 154°$ in the Cassie equation, values of $f_1 = 0.09$ and $f_2 = 0.91$ are determined. This means that a large fraction of air is trapped beneath the water. This assumption is also supported by the small contact angle hysteresis of about 3°.[1] Herminghaus has indicated that a superhydrophobic property can be achieved even from a material with a contact angle smaller than 90° as long as the liquid can suspend on the rough structure. The fractal-like surface structure reported here is believed to be well suited to trapping air, which then is responsible for the superhydrophobic wetting effect.

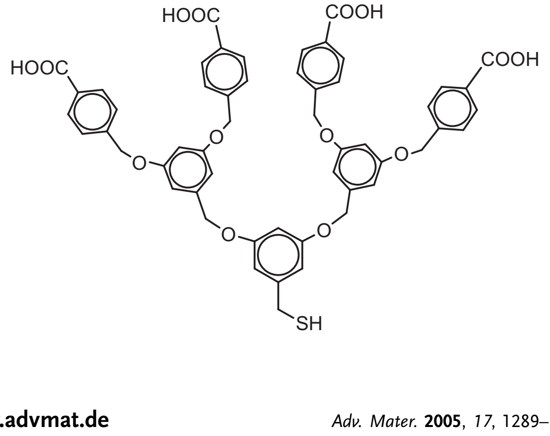
In addition, when applying a base droplet on the surface, it will react with the acid groups and make the surface more hydrophilic, so the base liquid can enter more easily into the cavities of the gold substrate. In this case, surface roughness will enhance the hydrophilicity as described by Wenzel's equation.[13] On the electrodeposited gold surface, as mentioned before, the fractal-like structure with a dimension between two and three makes the surface bear a large surface area and increases the roughness, such that the imbibition of water will occur on the rough surface as a result of a three-dimensional capillary effect,[4] and the surface exhibits superhydrophilicity.

We emphasize that the superhydrophobic–superhydrophilic property is a coordinated result of the proper composition of the mixed monolayer and the rough gold surface. A solution of $\chi_{COOH} = 0.4$ provides a proper wettability for the gold surface. In this case, the surface exhibits hydrophobic properties for acids and hydrophilic properties for bases. In contrast to this extreme change of the surface properties for different pH values, solutions of $\chi_{COOH} = 0.2$, or $\chi_{COOH} = 0.6$ render the surface either too hydrophobic or too hydrophilic, thus the surfaces only exhibit a similar wettability for acids and bases. The roughness and the fractal-like topology of the substrate also plays a critical role. In our experiments we found that as the deposition time increases, the difference of CA between acid and base droplets increases accordingly. Only when the deposition time is beyond 40 min will the surface be superhydrophobic for acid and superhydrophilic for base. Phase segregation of the mixed monolayer is not considered as it is believed that this kind of monolayer does not phase-segregate into single-component domains large enough to influence the contact angle.[12c]

In conclusion, an acid–base sensitive surface, which can be superhydrophobic for acid and superhydrophilic for base, was constructed by a simple method of combining a fractal-like gold surface and a mixed thiol self-assembled monolayer. For an acid droplet (pH 1) the contact angle can reach as high as154°, while a base droplet (pH 13) will spread out on this surface. We find that both the composition of the mixed monolayer and the rough gold structure are critical for this responsive property. We also expect that by using mercaptocarboxylic acids with a different pK_a, it is possible to shift the switching point between superhydrophobicity and superhydrophilicity. Furthermore, the combination of rough gold structures and thiol monolayer assembly provides an ideal system for exploring the relationship between wettability and surface chemical properties in more detail and should allow a correlation of the wetting properties with the surface structure.

Experimental

The flat gold substrate was prepared by thermal evaporation of gold on polished glass wafers with an adhesion promoter layer of chromium. Before further modification was carried out, the substrate was immersed in piranha solution ($H_2O_2/H_2SO_4 = 3{:}7$) for 1 h and then rinsed thoroughly with distilled water, and finally sonicated in pure ethanol for 1 h. A dendron thiol molecule for modifying the gold substrate was synthesized in our lab, the structure of the molecule is shown below.



The pretreated gold substrate was immersed in the 1 mmol L^{-1} dendritic thiol–ethanol solution overnight, and then rinsed with ethanol and dried in an N_2 stream. The monolayer-modified substrate was immersed in a mixed aqueous solution of H_2SO_4 (0.5 mol L^{-1}) and $HAuCl_4$ (1 mg mL^{-1}), and the electrochemical deposition was performed at –200 mV in the single potential time base mode, using a platinum electrode as the counter electrode and Ag/AgCl as the reference electrode [11]. The substrate was immersed in the piranha solution for 20 s, rinsed with distilled water and ethanol thoroughly, dried in the N_2 stream, and then immersed in the mixed thiol solution overnight. The mole fractions of the mixed solution of $HS(CH_2)_9CH_3$ and $HS(CH_2)_{10}COOH$ were varied while keeping the total concentration of thiol in the solutions constant at 1 mmol L^{-1} in the ethanol solution.

Scanning electron microscopy images were obtained on a Sirion 200 scanning electron microscope at 10.0 kV. X-ray photoelectron spectra (XPS) were obtained on a PHI-5300/XPS spectrometer with an Al Kα monochromatic X-ray source. Contact angle measurements were conducted with a dataphysics OCA20 contact angle system at ambient temperature. The average CA value was obtained by measuring the same sample at five different positions. Buffered solutions of different pH values were used to investigate the pH dependence of the wettability properties of the different substrates: pH 1, 0.1 mol L^{-1} HCl; pH 3 and 5, potassium hydrogen phthalate; pH 7 and 8, mixed phosphate; pH 9, 10, and 11, sodium tetraborate; pH 12, 0.01 mol L^{-1} NaOH; pH 13, 0.1 mol L^{-1} NaOH.

Received: October 16, 2004
Final version: January 7, 2005

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Direct Nanoimprinting of Si Single Crystals Using SiC Molds for Ordered Anodic Tunnel Etching

By *Kazuyuki Nishio*, *Kenji Yasui*, *Futoshi Matsumoto*, *Kenji Kanezawa*, and *Hideki Masuda**

The processes for the preparation of ordered structures on a nanometer scale are important for the development of various types of functional nanodevices. Among these, the nanoimprinting process, in which nanometer-scale fine patterns are formed using a master mold, is one candidate for a high-throughput technique for the preparation of fine patterns.[1–3] In previous work, we reported the direct imprinting of several types of semiconductor single crystals, such as InP or TiO_2, using an SiC mold, and the subsequent fabrication of ordered structures by chemical or electrochemical etching.[4,5] In this process, an ordered array of concaves is formed on the surface of a semiconductor by direct imprinting at room temperature, using the master mold made of SiC, which has the highest grade of hardness among applicable materials. Furthermore, ordered periodic structures of nanometer scale can be fabricated by subsequent chemical or electrochemical etching, in which the concaves on the surface can initiate the selective etching of the semiconductors, which results in ordered arrays of uniform-sized holes or pillars. This process is simple and has the advantage of high throughput for the preparation of ordered periodic semiconductor structures on a nanometer scale. In the present report, the application of direct imprinting using an SiC mold on a single crystal of Si followed by electrochemical etching in hydrofluoric acid solution, whereby the array of concaves can act as starting points for the development of uniform-sized straight holes with high

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DOI: 10.1002/adma.200401879