Surface Properties

DOI: 10.1002/anie.200700439

Enthalpy-Driven Three-State Switching of a Superhydrophilic/Superhydrophobic Surface**

Shutao Wang, Huajie Liu, Dongsheng Liu, Xinyong Ma, Xiaohong Fang, and Lei Jiang**

The control of surface properties, such as wettability, has long been an interesting topic in materials science because of the widely practical applications.[1–7] Inspired by nature, we recently reported intelligent surfaces that are switchable between superhydrophilicity and superhydrophobicity in response to external stimuli such as heat[8] and light[9] through the introduction of surface roughness.[2–4] However, nearly all of these switches of surface wettability have so far been limited to entropy-driven processes; enthalpy-driven switchable surfaces are not well explored, although various important life phenomena and molecular recognition behaviors are often dominated by enthalpy-driven processes.[10,11] Herein we present a responsive surface that can switch between stable superhydrophilic, metastable superhydrophobic, and stable superhydrophobic states by an enthalpy-driven process. This macroscopic surface phenomenon originates from the collective motion of DNA nanodevices. Its switching behavior could provide a model to understand biological behavior, such as short- and long-term memory, as well as help in the design of intelligent surfaces.

Traditional responsive polymers usually involve an entropy-driven transformation from one disordered state into another disordered state in response to an external stimulus; however, biomolecules most probably undergo an enthalpy-driven transformation from an ordered state into another ordered state to perform various intelligent behaviors, such as gene expression. Owing to the advantages of site-to-site molecular recognition, DNA molecules have been extensively investigated in the field of smart nucleic acid nanodevices.[12–18] Herein, we modified DNA with a fluoride-containing hydrophobic group and immobilized it onto a gold surface through a gold–thoil bond to create an intelligent switching surface (Figure 1). It was envisaged that the DNA could conceal and expose the fluoride-containing hydrophobic group by virtue of a stimulus-responsive conformational change of the i-motif structure into an extended structure: either a stretched single-stranded structure or a double-stranded structure.[19–20] To obtain good switching performance, DNA strand **X** was prefolded in phosphate-buffered saline (PBS) at pH 4.5[19] and then immobilized onto the Au surface to form a self-assembled monolayer of the i-motif DNA. Under basic conditions (pH 8.5), the i-motif structure of DNA molecules on the surface (state **I**) converts into the stretched single-stranded structure (state **II**). In the presence of complementary stands (**Y**), the duplex structure (state **III**) will form. The original state of the DNA could be recovered by adding acid. The conversion from state **I** to **II** is entropy-driven, but the other transformations are enthalpy-driven processes. Thus, enthalpy-driven switching could be manipulated among three states.

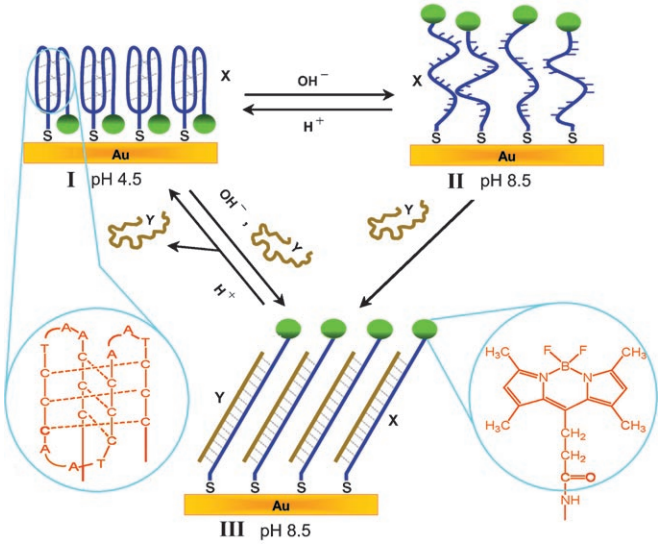

Figure 1. Intelligent reversibly switchable surface driven by DNA nanodevices. Oligonucleotide **X** is the thiolated strand 5′(SH)-TTTTTC-CCTAACCCTAACCCTAACCC-(Bodipy493/503)-3′; the hydrophobic group Bodipy493/503 (green circle) acts as the functional part and the i-motif structure functions as a nanodevice. The complementary strand **Y** (5′-GTTAGTGTTAGTGTTAG-3′) is a nonthiolated strand for forming duplex structures. At low pH, the DNA adopts an i-motif conformation (state **I**). Raising the pH destabilizes the i-motif to produce a stretched single-stranded state (state **II**) or a duplex structure (state **III**, when a complementary strand is present). Lowering the pH induces a reverse conversion process from state **II** or **III** to state **I**.

[*] Dr. S. Wang, Dr. X. Ma, Prof. X. Fang, Prof. L. Jiang
Center of Molecular Sciences, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100080 (P.R. China)
Fax: (+86) 10-8262-7566
E-mail: jianglei@iccas.ac.cn
H. Liu, Prof. D. Liu
National Center for NanoScience and Technology
No. 2 North Street, Zhongguancun, Beijing 100080 (P.R. China)
Fax: (+86) 10-6265-2116
E-mail: liuds@nanoctr.cn
Dr. S. Wang, H. Liu, Dr. X. Ma
Graduate School of Chinese Academic of Sciences
Beijing 100864 (P.R. China)

[**] The authors thank the State Key Project Fundamental Research (G1999064504), the Special Research Foundation of the National Natural Science Foundation of China (29992530, 20125102, 20573027), the Science 100 Program of CAS, and the MOST 973 project (grant No. 2005CB724701) for financial support. Moreover, the authors thank Prof. Zhenghe Tong and Prof. Qi Wu for their inspired discussions and constructive suggestions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

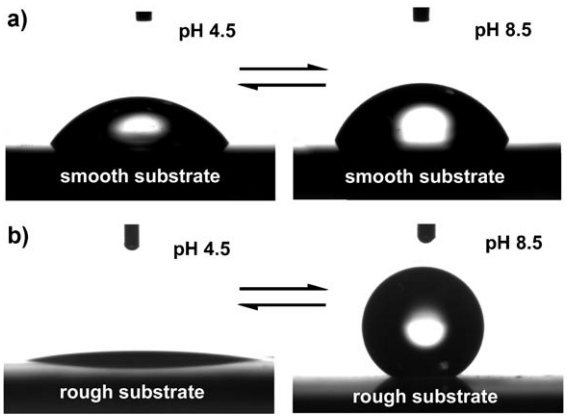

Figure 2. Profiles of a water droplet at pH 4.5 and 8.5 on a smooth (a) and on a rough substrate (b) showing the different wettability of states **I** and **II**.

The wettability on the as-prepared surface was determined by contact-angle (CA) measurements. Figure 2a shows the profiles of a water droplet on a smooth substrate in states **I** and **II**. The CA of a water drop placed on a freshly prepared surface in state **I** is $55.8 \pm 3.7°$. After pH 4.5 PBS is replaced by pH 8.5 PBS, the CA increases to $68.2 \pm 2.4°$ after 1 h (a distinct change of about 12°). These results indicate that the motion of the DNA "motors" at the nanometer scale could lead to a macroscopic change in CA. As illustrated in Figure 1, at low pH, the DNA motors adopt the i-motif structure (state **I**). Unlike the case of a random dispersion in solution, the terminal hydrophobic groups are concealed in the SAM of DNA motors on the surface, and the hydrophilic backbones of the DNA strands are exposed on the surface. Thus the surface is hydrophilic and the CA is low. At high pH, the deformation of nonclassic intramolecular base pairs between C and protonated C residues converts the DNA motors from folded i-motif structures into stretched single-stranded structures. Correspondingly, the surface changes from the closely ordered state **I** into the loosely disordered state **II**. In the process, the hydrophobic groups of DNA motors rise to the top of the surface, which was confirmed by the fluorescence microscopy observations (Figure S1 in the Supporting Information). As a result, the surface becomes hydrophobic and the CA increases. Inversely, when the pH value changes from high to low, the enthalpy-driven reverse process takes place. Thus, the reversible motion of DNA motors that lift up and lower the hydrophobic groups induces a conversion in surface wettability and switching between superhydrophilicity and superhydrophobicity.

It has been demonstrated that surface microstructures can remarkably enhance surface wettability, either hydrophilicity or hydrophobicity.[4] We selected regular, square Au-coated silicon column arrays (20 μm high, 10 μm long, and with a spacing of 15 μm between neighboring silicon columns; see the Supporting Information) as the rough substrates. Figure 2b also gives the profiles of water droplets on a rough surface at different pH values. In comparison with smooth substrates, a drastically amplified effect of CA on rough surfaces is observed. At pH 4.5, the CA is $8.8 \pm 3.4°$ (a superhydrophilic surface). At pH 8.5, the CA is $148.3 \pm 2.6°$, which indicates a superhydrophobic surface.

To verify that the switch in wettability originates from the conformational change of the DNA, the influence of pH value on the apparent CA was examined in more detail. As shown in Figure S3a (in the Supporting Information), there is a sharp increase in CA at around pH 6.5 from highly hydrophobic to highly hydrophilic on rough substrates, which is consistent with a conformational change of the DNA motors. Moreover, this switching behavior can be cycled many times and shows a good reversibility (Figure S3b). Thus, the combination of DNA motors and surface microstructures provides novel reversibly between superhydrophilicity and superhydrophobicity originating from the amplified effect of surface microstructures on the CA (see the Supporting Information).[21]

However, we found that the water droplet suffers from a dynamic spreading process to a certain extent after a period of time (210–300 s) in contact with the surface in state **II** (Figure 3) to give a metastable superhydrophobic state. This interesting phenomenon arises from the entropy-driven molecular rearrangement of DNA motors at interface because of the relatively loose arrangement of flexible single-strand DNA and the hydrophobic and hydrophilic interactions among water molecules, hydrophilic DNA skeletons, and the tailored hydrophobic groups. It is believed that two processes occur on the surface in state **II** in contact with water. Parts of the hydrophobic groups of the DNA with stretched single-stranded conformation might escape from the interface between water and the DNA-modified surface and parts of hydrophilic skeletons rise up to the interface. The other process is that some hydrophobic groups might close together to form aggregate-like structures on the surface, thus leading to some hydrophilic skeletons exposed to the water. According to this hypothesis, if complementary DNA strands are added, the rigid duplex structure of DNA will form to produce a closely packed arrangement of double-stranded DNA on the surface (state **III** in Figure 1) and the spreading phenomenon should thus be avoided. Therefore, we observed the wetting behavior of the water droplet on the surface in state **III**. As illustrated in Figure 3, no spreading was observed, which suggests a stable superhydrophobic state and that no molecular rearrangement occurred. Moreover, by

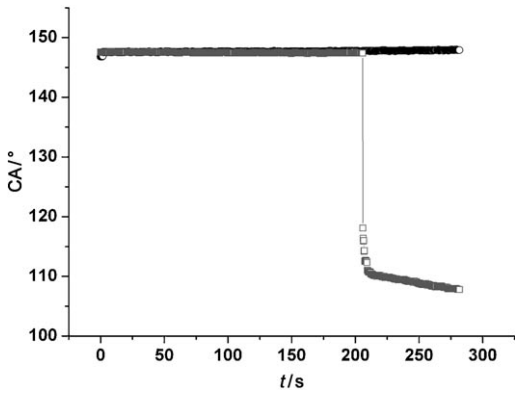

Figure 3. The wetting behavior of water droplets on surfaces in states **II** (squares) and **III** (circles). The influence of water evaporation on the CA was deducted (see the Supporting Information).

lowering the pH, the stable superhydrophobic state could also be turned into a superhydrophilic state by a relatively slow DNA dehybridization and refolding process (Figure 1).[21] Thus, we have realized a three-state switching system among a stable superhydrophilic state (**I**), a metastable superhydrophobic state (**II**), and a stable superhydrophobic state (**III**) through the reversible enthalpy-driven conformational conversion of different DNA states.

In summary, our observations demonstrate that a reversible switchable surface may provide a way of manipulating the macroscopic surface wettability by combining the coordinative effect of the collective nanoscale motion of DNA nanodevices and surface microstructure. Such enthalpy-driven switchable surfaces may bring out various unexpected opportunities in surface and biological science.

Experimental Section

Materials: Oligonucleotides were synthesized by TaKaRa Biotech (Dalian, China). 2-Mercaptoethanol (99%), HPLC-grade ethanol, and other reagents were purchased from Sigma–Aldrich and used as received unless otherwise stated. PBS solutions (100 mM sodium phosphate, 0.5 M NaCl, pH 4.5 or 8.5) were prepared with ultrapure MilliQ water (resistivity > 18 MΩ cm).

Preparation of rough Au-coated surfaces: Contact lithographic masks were constructed by Microelectronics R&D Center, the Chinese Academy of Sciences. A KARL SUSS MA6 (Germany) instrument was used to transfer the patterns of masks onto silicon wafers by a photolithographic method. A deep-etching process was conducted on an STS ICP ASE (UK) instrument. Thus, rough surfaces of a flat silicon wafer were prepared on which geometrical structures of patterned square pillars (22 μm high, 10 μm long, and with a controllable spacing of 5, 10, 15, or 20 μm between the silicon pillars) were introduced. A 100-nm-thick layer of Au with a titanium adhesion layer was then deposited onto the rough silicon surface.

SAM of DNA motors: The motor DNA was immobilized on the bare Au surface through gold–thiol self-assembly by immersing Au surfaces into a solution of the motor DNA (1 μM) in pH 4.5 PBS for 12 h. A low-pH buffer was used to ensure the DNA motors were immobilized in their folded i-motif states, which allowed sufficient surface space for the immobilized motor DNA to switch its conformation freely and reversibly. The surface was then treated with 2-mercaptoethanol (1 mM in PBS) for 1 h to remove nonspecifically adsorbed DNA[20] and then thoroughly rinsed with pH 4.5 PBS.

Characterization: A HITACHI S-3000F scanning electron microscope was used to determine the morphology of smooth and rough Au surfaces. CAs were measured on a dataphysics Germany OCA20 contact-angle system. The samples were first placed in PBS (pH 4.5) for about 1 h, than removed from the solution, and finally blow-dried with N_2. Deionized water droplets (about 2 μL) were dropped carefully onto the DNA-modified surface. An average CA value was obtained by measuring the same sample at five different positions. The samples were then placed in PBS (at various pH values) and then after 1 h the CAs were tested again. Fluorescence images were recorded on a Fluorolog 3-21 spectrofluorometer (Jobin Yvon, Inc., Edison, NJ) in air. The samples were the DNA-modified surface on flat, thin, transparent gold-coated glass coverslips (5-nm thick) with a regular strip pattern prepared by the same procedures mentioned above. The fluorescence intensity was monitored by exciting the sample at 488 nm and measuring the emission at 510 nm.

Received: January 31, 2007
Published online: April 17, 2007

Keywords: DNA structures · superhydrophilicity · superhydrophobicity · surface chemistry

[1] a) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature* **1997**, *388*, 431–432; b) K. Ichimura, S. Oh, M. Nakagawa, *Science* **2000**, *288*, 1624–1626; c) J. Lahann, S. Mitragotri, T. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, R. Langer, *Science* **2003**, *299*, 371–374; d) R. Blossey, *Nat. Mater.* **2003**, *2*, 301–306.

[2] T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125–2127.

[3] W. Chen, A. Y. Fadeev, M. C. Heieh, D. Öner, J. Youngblood, T. J. McCarthy, *Langmuir* **1999**, *15*, 3395–3399.

[4] a) T. Sun, L. Feng, X. Gao, L. Jiang, *Acc. Chem. Res.* **2005**, *38*, 644–652; b) S. Wang, H. Liu, L. Jiang, *Annu. Rev. Nano Res.* **2006**, *1*, 573–628.

[5] X. Gao, L. Jiang, *Nature* **2004**, *432*, 36.

[6] a) S. Wang, X. Feng, J. Yao, L. Jiang, *Angew. Chem.* **2006**, *118*, 1286–1289; *Angew. Chem. Int. Ed.* **2006**, *45*, 1264–1267; b) S. Wang, L. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 767–770.

[7] a) N. J. Shirtcliffe, G. McHale, M. I. Newton, G. Chabrol, C. C. Perry, *Adv. Mater.* **2004**, *16*, 1929; b) X. Zhang, F. Shi, X. Yu, H. Liu, Y. Fu, Z. Wang, L. Jiang, X. Li, *J. Am. Chem. Soc.* **2004**, *126*, 3064–3065; c) Q. Xie, J. Xu, L. Feng, L. Jiang, W. Tang, X. Luo, C. Han, *Adv. Mater.* **2004**, *16*, 302–306; d) L. Zhai, F. C. Cebeci, R. E. Cohen, M. F. Rubner, *Nano Lett.* **2004**, *4*, 1349–1353.

[8] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angew. Chem.* **2004**, *116*, 361–364; *Angew. Chem. Int. Ed.* **2004**, *43*, 357–360.

[9] X. Feng, L. Feng, M. Jin, J. Zhai, L. Jiang, D. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 62–63.

[10] L. A. Marky, K. J. Breslauer, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 4359–4363.

[11] F. Avbelj, P. Luo, R. L. Baldwin, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 10786–10791.

[12] P. Yin, H. Yan, X. G. Daniell, A. J. Turberfield, J. H. Reif, *Angew. Chem.* **2004**, *116*, 5014–5019; *Angew. Chem. Int. Ed.* **2004**, *43*, 4906–4911.

[13] J. Bath, S. J. Green, A. J. Turberfield, *Angew. Chem.* **2005**, *117*, 4432–4435; *Angew. Chem. Int. Ed.* **2005**, *44*, 4358–4361.

[14] T. Liedl, M. Olapinski, F. C. Simmel, *Angew. Chem.* **2006**, *118*, 5129–5132; *Angew. Chem. Int. Ed.* **2006**, *45*, 5007–5010.

[15] Y. Chen, M. Wang, C. Mao, *Angew. Chem.* **2004**, *116*, 5449–5452; *Angew. Chem. Int. Ed.* **2004**, *43*, 3554–3557.

[16] B. Yurke, A. J. Turberfield, A. P. Mills, Jr., F. C. Simmel, J. L. Neumann, *Nature* **2000**, *406*, 605–608.

[17] H. Yan, X. Zhang, Z. Shen, N. C. Seeman, *Nature* **2002**, *415*, 62–65.

[18] M. N. Stojanovic, D. Stefanovic, *Nat. Biotechnol.* **2003**, *21*, 1069–1074.

[19] M. Guéron, J. L. Leroy, *Curr. Opin. Struct. Biol.* **2000**, *10*, 326–331.

[20] a) D. S. Liu, S. Balasubramanian, *Angew. Chem.* **2003**, *115*, 4912–4914; *Angew. Chem. Int. Ed.* **2003**, *42*, 5734–5736; b) W. M. Shu, D. S. Liu, M. Watari, C. K. Riener, T. Strunz, M. E. Welland, S. Balasubramanian, R. A. McKendry, *J. Am. Chem. Soc.* **2005**, *127*, 17054–17060; c) D. Liu, A. Bruckbauer, C. Abell, S. Balasubramanian, D. Kang, D. Klenerman, D. Zhou, *J. Am. Chem. Soc.* **2006**, *128*, 2067–2071.

[21] a) R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988–994; b) A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944**, *40*, 546–551.

