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Photoreversibly Switchable Superhydrophobic Surface with Erasable and Rewritable Pattern

Ho Sun Lim, Joong Tark Han, Donghoon Kwak, Meihua Jin, and Kilwon Cho*

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

Received August 2, 2006; E-mail: kwcho@postech.ac.kr

Smart surfaces with reversibly switchable wettability have aroused great interest because of their myriad applications as biosensors, microfluidic devices, intelligent membranes, and so on.[1] This reversible switching can be achieved through an externally applied stimulus such as light irradiation,[2] electrical potential,[3] temperature,[4] solvent,[5] and pH.[6] Among these external stimuli-responsive materials, azobenzene and its derivatives are known to exhibit large changes in both geometry and dipole moments as a result of UV/visible irradiation because of reversible photoisomerization between the cis and trans conformations, which means that the wettability of azobenzene-modified surfaces can be altered with UV/visible irradiation. However, most azobenzene-modified surfaces prepared on flat substrates exhibit only minor changes in the water contact angle (CA), that is, less than 10°, as a result of UV light illumination.[7] No organic surface that can be switched between superhydrophobicity and superhydrophilicity with UV irradiation has yet been reported.

Herein, we report the facile fabrication of a photoswitchable nanoporous multilayer film with wettability that can be reversibly switched between superhydrophobicity and superhydrophilicity with UV/visible irradiation. To produce this surface, we used a method that combines facile surface roughness control with an electrostatic self-assembly process[8] and photoresponsive molecular switching of fluorinated azobenzene molecules (Scheme 1). Furthermore, we demonstrate that this approach can be used to fabricate substrates with erasable and rewritable patterns of extreme wetting properties as a result of selective UV irradiation.

To fabricate porous organic−inorganic hybrid multilayer films with hierarchical structures on negatively charged Si wafers, we used the layer-by-layer (LBL) technique with the polyelectrolyte, poly(allylamine hydrochloride) (PAH, $M_w \approx 70\,000$), and SiO_2 nanoparticles ($d \approx 11$ nm) as the polycation and polyanion, respectively. After completion of deposition, these films were modified with 3-(aminopropyl)triethoxysilane, which provides the binding sites for introducing the photoswitchable moieties, and then treated with photoswitchable agent, 7-[(trifluoromethoxyphenylazo)phenoxy]pentanoic acid (CF3AZO), which was synthesized as previously reported (see Supporting Information).[9]

In our method, the surface roughness and nanoporosity of the films gradually intensify with increases in the number of PAH/SiO_2 bilayers (see Supporting Information). Figure 1a shows a scanning electron microscopy (SEM) image of an azobenzene-modified $(SiO_2/PAH)_9$ polyelectrolyte multilayer. The use of nine deposition cycles was found to be sufficient to significantly increase the nanoporosity and surface roughness, that is, a substrate with enhanced surface roughness. By increasing bilayers from three to nine, the peak−peak height (height difference between highest and lowest pixel) increased from 100 ± 14 to 241 ± 15 nm from atomic force microscopy (AFM) images. Moreover, from three bilayers, nanopores of several tens nm were formed, and porous domains finally create a combination of submicro- (200∼300 nm) and nanopores with increasing PAH/SiO_2 bilayers. Figure 1b shows a highly magnified image of the $(PAH/SiO_2)_9$ film, with its multilevel structures created hierarchically on the substrate. The cross-sectional view shows that the inner structure of the rough substrate contains many pores because of its complex network of silica nanoparticles (Figure 1c).

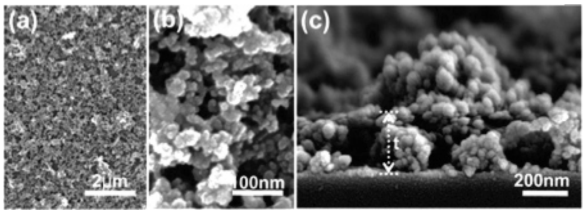
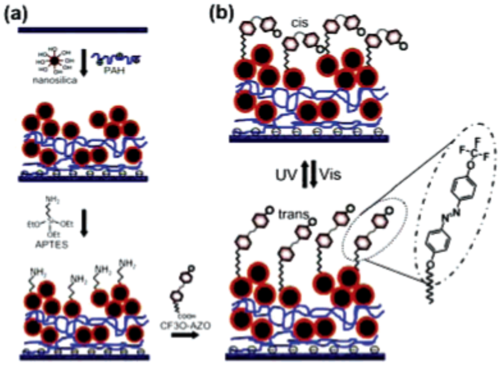


Figure 1. (a) SEM images of a substrate formed after nine deposition cycles; (b) magnified image; (c) cross-sectional view. The dotted arrow indicates the film thickness, which is approximately 250 nm.

Scheme 1. (a) Fabrication and (b) Reversible Photoisomerization of a Roughness-Enhanced Photoswitchable Surface



The reversible wettability of the fluorinated azobenzene-modified substrates was studied by measuring the CA. On a flat substrate, after exposure to UV light (365 nm) for 10 min, the CA change was found to be about 5 ± 1°, that is, it was decreased from 76 ± 1° to 71 ± 1°. Further, when the surface was irradiated with visible light (440 nm) for a certain time, the CA was restored to its initial state, as shown in Figure 2a. This phenomenon is due to the change in the dipole moment of the azobenzene molecules upon trans to cis photoisomerization via UV/vis irradiation (Scheme 1b).[7] In the trans state, the azobenzene molecules on the substrate self-assemble in a monolayer array as a result of the van der Waals forces between the alkyl chains and the π-stacking forces between the aromatic rings, so in this state the substrate has a small dipole moment, a low surface energy, and a higher CA because of the fluorine atoms of the chain tails. The trans-to-cis transformation of azobenzene induced by UV light irradiation leads to a large increase in the dipole moment of these molecules, and the chain ordering in the azobenzene monolayers is demolished.[10] Thus, the cis substrate has a lower CA.

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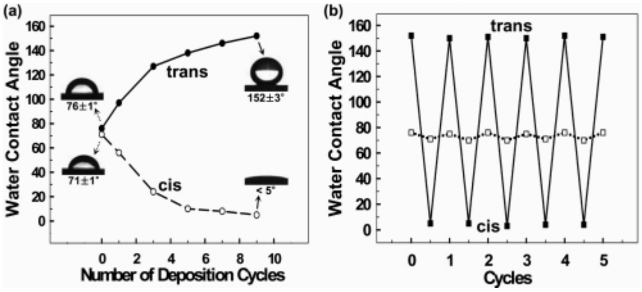

Figure 2. (a) The relationships between the number of deposition cycles and the water contact angles: water droplet profiles on the smooth substrate (dotted arrows) and on the $(PAH/SiO_2)_9$ multilayer film (solid arrows) after UV/visible irradiation. (b) Reversible wettability transitions of a smooth substrate (□) and a $(PAH/SiO_2)_9$ multilayer film (■).

Surprisingly, in contrast to the flat surface, the wettability of the nanostructured multilayer film modified with CF3AZO was found to change from superhydrophobic to superhydrophilic as a result of UV/vis irradiation. Figure 2a shows the relationship between the CA and the number of deposition cycles. The CAs of CF3AZO modified multilayer films gradually increase from 76 ± 1° for a flat substrate to 97 ± 2° ($n = 1$), 127 ± 3° ($n = 3$), 138 ± 2° ($n = 5$), 146 ± 1° ($n = 7$), and 152 ± 3° ($n = 9$), where n is the number of PAH/SiO_2 bilayers. These results clearly show that the CA increases as the substrate roughness increases. The porous structures of the rough substrates ensure that the surface contact area available to water is very low. The large fraction of air trapped in the substrates forms a cushion at the film-water interface that prevents the penetration of the water droplets into the inner pores, and thus the substrates support the water droplets.[11]

When the samples are irradiated with UV light, the CA slowly decreases from 71 ± 1° (flat, $n = 0$) to 56 ± 2° ($n = 1$), 24 ± 1° ($n = 3$), 10 ± 3° ($n = 5$), 8 ± 3° ($n = 7$), and <5 ± 1° ($n = 9$). In particular, the CA of the $(PAH/SiO_2)_9$ film was found to be dramatically reduced from superhydrophobic to superhydrophilic by UV irradiation. The enhanced hydrophilicity is strongly dependent on the surface roughness. Since azobenzene molecules have a cis form on the porous substrates, the imbibition of water into the inner pores occurs, and water will fill the inner pores below the droplets owing to the 3D capillary effect.[12] Figure 2a shows photographs of the water drop profile after UV/visible irradiation. These results indicate that switching the wettability from superhydrophobic to superhydrophilic can easily be achieved by using photoresponsive azobenzene molecules on a nanostructured surface fabricated with simple LBL assembly and just nine cycles of deposition of PAH and SiO_2 nanoparticles.

We repeatedly irradiated a $(PAH/SiO_2)_9$ multilayer film and a flat substrate with UV/visible light and measured the changes in the CA as shown in Figure 2b. These provide evidence of the reversibility achieved with this system, with little degradation occurring after many switching cycles. The surface roughness plays the most important role in intensifying hydrophobicity and hydrophilicity.[13] Therefore, these indicate that interplay between the photosensitive surface chemistry and the surface roughness can be used to greatly intensify both the hydrophobicity of a hydrophobic surface and the hydrophilicity of a hydrophilic surface as a result of UV/vis irradiation.

To clarify the nature of the photoswitchable wetting transition, we fabricated a pattern of superhydrophobic and superhydrophilic regions on a single specimen by using selective UV light irradiation through an aluminum mask (2.5 mm × 2.5 mm square patterns with a 2 mm pitch). Prior to UV irradiation the substrates are superhydrophobic all over, but after UV irradiation the selectively exposed regions become superhydrophilic and the masked areas maintain their superhydrophobic properties (Figure 3). Moreover, on visible light illumination, the patterns vanish; that is, the CA recovers to its initial state. These results indicate that by using a photosensitive surface in combination with selective irradiation erasable and rewritable patterned substrates with extreme wetting properties can easily be created.

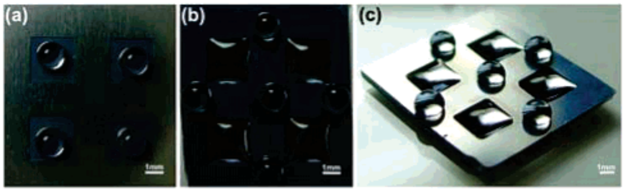

Figure 3. Photographs of substrates with patterned extreme wetting properties: (a) photomask and water droplet profiles on the as-prepared substrate; (b) top and (c) angled views of water droplet profiles on the patterned substrate as a result of selective UV irradiation.

In conclusion, we have presented a facile method for the fabrication of a wetting surface that is photoswitchable from superhydrophobicity to superhydrophilicity, which combines layer-by-layer assembly and the introduction of photoresponsive moieties onto the top surface. The proposed method is reproducible and can be applied in a wide range of fields requiring external stimuli-responsive surface.

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Supporting Information Available: Detailed information on experimental procedures and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Russell, T. P. *Science* **2002**, *279*, 964. (b) Sun, T.; Feng, L.; Gao, X.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644.
(2) (a) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145. (b) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M.; Watanabe, T. *Nature* **1997**, *388*, 431. (c) Koçer, A.; Walko, M.; Meijberg, W.; Feringa, B. L. *Science* **2005**, *309*, 755. (d) Feng, X.; Feng, L.; Jin, M.; Zhai, J.; Jiang, L.; Zhu, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 62.
(3) (a) Lahann, J.; Mitragotri, S.; Tran, T.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371. (b) Gallardo, B. S.; Gupta, V. K.; Eagerton, F. D.; Jong, L. I.; Craig, V. S.; Shah, R. R.; Abbott, N. L. *Science* **1999**, *283*, 57.
(4) (a) Crevoisier, G. B.; Fabre, P.; Corpart, J. M.; Leibler, L. *Science* **1999**, *285*, 1246. (b) Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 357. (c) Fu, Q.; Rao, G. V. R.; Basame, S. B.; Keller, D. J.; Artyushkova, K.; Fulghum, J. E.; López, G. P. *J. Am. Chem. Soc.* **2004**, *126*, 8904.
(5) Minko, S.; Muller, M.; Motornov, M.; Nitschke, M.; Grundke, K.; Stamm, M. *J. Am. Chem. Soc.* **2003**, *125*, 3896.
(6) Matthews, J. R.; Tuncel, D.; Jacobs, R. M. J.; Bain, C. D.; Anderson, H. L. *J. Am. Chem. Soc.* **2003**, *125*, 6428.
(7) (a) Ichimura, K.; Oh, S.; Nakagawa, M. *Science* **2000**, *288*, 1624. (b) Siewierski, L. M.; Brittain, W. J.; Petrash, S.; Foster, M. D. *Langmuir* **1996**, *12*, 5838. (c) Jiang, W.; Wang, G.; He, Y.; Wang, X.; An, Y.; Song, Y.; Jiang, L. *Chem. Commun.* **2005**, 3550.
(8) (a) Decher, G. *Science* **1997**, *277*, 1232. (b) Zhai, L.; Cebeci, F. Ç.; Cohen, R. E.; Rubner, M. F. *Nano Lett.* **2004**, *4*, 1349. (c) Park, J.; Fouche, L. D.; Hammond, P. T. *Adv. Mater.* **2005**, *17*, 2575. (d) Cebeci, F. Ç.; Wu, Z.; Zhai, L.; Cohen, R. E.; Rubner, M. F. *Langmuir* **2006**, *22*, 2856. (e) Xu, X.; Han, J. T.; Cho, K. *Chem. Commun.* **2003**, 966. (f) Han, J. T.; Zheng, Y.; Cho, J. H.; Xu, X.; Cho, K. *J. Phys. Chem. B* **2005**, *109*, 20773.
(9) Prescher, D.; Thiele, T.; Ruhmann, R.; Schulz, G.; *J. Fuorine Chem.* **1995**, *74*, 185.
(10) Seki, T.; Sekizawa, H.; Morino, S.; Ichimura, K. *J. Phys. Chem. B* **1998**, *102*, 5313.
(11) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
(12) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.
(13) (a) Han, J. T.; Lee, D. H.; Ryu, C. Y.; Cho, K. *J. Am. Chem. Soc.* **2004**, *126*, 4796. (b) Hikita, M.; Tanaka, K.; Nakamura, T.; Kajiyama, T.; Takahara, A. *Langmuir* **2005**, *21*, 7299.

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