

Switchable Surfaces; Superhydrophilic to Superhydrophobic

Jeremy Hatch

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A superhydrophilic surface is one in which the contact angle of water on the surface is less than 5° and a superhydrophobic surface is one where the contact angle is greater than 150° (see Figure 1). The hydrophilic or hydrophobic quality of a surface arises from its chemical make-up. These qualities are enhanced by the roughness of the surface; due to the trapping of air in the cavities between a drop and a rough superhydrophobic surface, and by capillary wicking on a superhydrophilic surface.¹ These surfaces have many properties that are useful, including the ability to be self cleaning, anti-bacterial, anti-reflecting, and anti-fogging.² A switchable surface combines the attributes of both superhydrophilic and superhydrophobic surfaces and can potentially be used in a variety of applications including microfluidic pumps, drug delivery systems, separations, and protein concentrators.³ In order to be switchable, there must be a way to reversibly change a surface's chemical make-up. This may be done in several ways including temperature,⁴⁻⁶ pH,^{3,5,7,8} solvent,⁹ electric potential,¹⁰⁻¹² light,¹³ and mechanical stress¹⁴.



Figure 1: a) Contact angle measurement. b) Generic example of switching between superhydrophilic and superhydrophobic.⁴

One way to approach the switching of a surface based on temperature is to use a thermo-sensitive polymer. These polymers undergo a phase transition at a temperature known as the lower critical solution temperature (LCST) where their behavior switches between hydrophobic and hydrophilic. Sun and coworkers⁴ put poly(*N*-isopropylacrylamide), commonly referred to as poly(NIPAAm), on roughened silicon to make the surface temperature responsive. The LCST of poly(NIPAAm) is about 32° - 33°C and it changes its conformation from hydrogen bonding with the solvent at low temperatures to internal hydrogen bonding above the LCST. The combination of the rough silicon and poly(NIPAAm) give the surface the ability to switch reversibly between superhydrophilicity (at $\sim 25^\circ\text{C}$) and superhydrophobicity (at $\sim 40^\circ\text{C}$).

The construction of a rough surface functionalized with carboxylic acid groups is capable of switching between superhydrophilic and superhydrophobic in response to pH. Wang and coworkers⁷ produced a pH responsive surface from self assembled layers of polystyrene-poly(methyl methacrylate)/poly(acrylic acid) core-shell beads. The beads form the rough surface that is needed to obtain the extreme contact angles. Sodium dodecyl-benzenesulfonate (SDBS) was added as an emulsifier but is also part of the key to switching the behavior of the surface. The SO_3^- group of the SDBS hydrogen bonds with the COOH groups on the bead, creating a hydrophobic surface state. When the acid groups are deprotonated the COO^- and the SO_3^- repel each other and provide a hydrophilic surface state.

In 2003, Lahann demonstrated that sparsely distributed charged thiols on a gold surface could switch via the potential applied to the gold surface (see Figure 2).¹² When the charged end of the thiol is attracted to the surface, the hydrophobic chain is exposed. Likewise, when the potential is reversed the charged end is exposed and the surface becomes hydrophilic. Xu and coworkers¹⁰ created a rough, porous polypyrrole (ppy) film that would exhibit switching behavior based on the oxidation and reduction of the film. It has the advantage of being able to be transferred to other surfaces by simply peeling the film off of the first and reapplying it to a second.

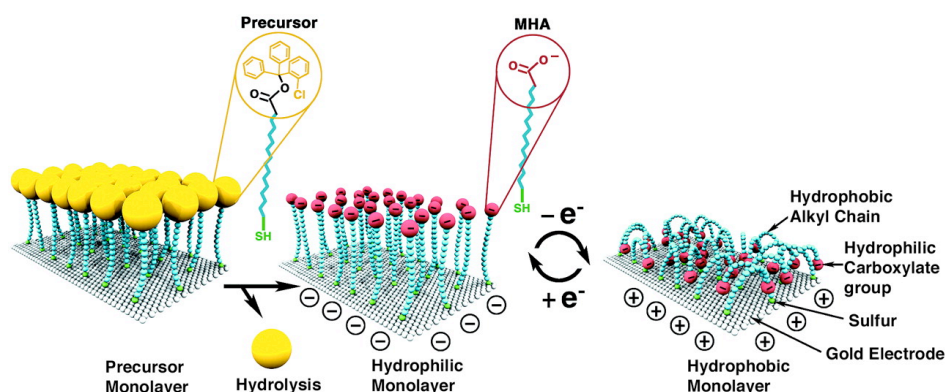


Figure 2: The charged ends of the thiol chains are attracted or repelled by the potential applied to the gold surface.¹²

References

1. (a) Wenzel, R. N. Surface roughness and contact angle. *Journal of Physical and Colloid Chemistry* **1949**, *53*, 1466-1467 (b) Cassie, A. B. D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546-551 (c) Wenzel, R. N. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.* **1936**, *28*, 988-994.
2. (a) Cebeci, F. C.; Wu, Z.; Zhai, L.; Cohen, R. E. Rubner, M. F. Nanoporosity-Driven Superhydrophilicity: A Means to Create Multifunctional Antifogging

- Coatings. *Langmuir* **2006**, *22*, 2856-2862 (b) Sun, T.; Feng, L.; Gao, X. Jiang, L. Bioinspired Surfaces with Special Wettability. *Acc. Chem. Res.* **2005**, *38*, 644-652.
3. Yu, X.; Wang, Z.; Jiang, Y.; Shi, F. Zhang, X. Reversible pH-responsive surface: From superhydrophobicity to superhydrophilicity. *Adv. Mater.* **2005**, *17*, 1289-1293.
 4. Sun, T.; Wang, G.; Feng, L.; Liu, B.; Ma, Y.; Jiang, L. Zhu, D. Reversible switching between superhydrophilicity and superhydrophobicity. *Angew. Chem. Int. Ed.* **2004**, *43*, 357-360.
 5. Xia, F.; Feng, L.; Wang, S.; Sun, T.; Song, W.; Jiang, W. Jiang, L. Dual-responsive surfaces that switch between superhydrophilicity and superhydrophobicity. *Adv. Mater.* **2006**, *18*, 432-436.
 6. Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C. Roach, P. Porous materials show superhydrophobic to superhydrophilic switching. *Chem. Comm.* **2005**, 3135-3137.
 7. Wang, J.; Hu, J.; Wen, Y.; Song, Y. Jiang, L. Hydrogen-Bonding-Driven Wettability Change of Colloidal Crystal Films: From Superhydrophobicity to Superhydrophilicity. *Chem. Mater.* **2006**, *18*, 4984-4986.
 8. Jiang, Y.; Wang, Z.; Yu, X.; Shi, F.; Xu, H.; Zhang, X.; Smet, M. Dehaen, W. Self-Assembled Monolayers of Dendron Thiols for Electrodeposition of Gold Nanostructures: Toward Fabrication of Superhydrophobic/Superhydrophilic Surfaces and pH-Responsive Surfaces. *Langmuir* **2005**, *21*, 1986-1990.
 9. (a) Motornov, M.; Minko, S.; Eichhorn, K.-J.; Nitschke, M.; Simon, F. Stamm, M. Reversible Tuning of Wetting Behavior of Polymer Surface with Responsive Polymer Brushes. *Langmuir* **2003**, *19*, 8077-8085 (b) Uhlmann, P.; Ionov, L.; Houbenov, N.; Nitschke, M.; Grundke, K.; Motornov, M.; Minko, S. Stamm, M. Surface functionalization by smart coatings: Stimuli-responsive binary polymer brushes. *Progress in Organic Coatings* **2006**, *55*, 168-174.
 10. Xu, L.; Chen, W.; Mulchandani, A. Yan, Y. Reversible conversion of conducting polymer films from superhydrophobic to superhydrophilic. *Angew. Chem. Int. Ed.* **2005**, *44*, 6009-6012.
 11. Joerg Lahann, S. M., Thanh-Nga Tran, Hiroki Kaido, Jagannathan Sundaram, Insung S. Choi, Saskia Hoffer, Gabor A. Somorjai, Robert Langer A Reversibly Switching Surface. *Science* **2003**, *299*, 371-374.
 12. Lahann, J.; Mitragotri, S.; Tran, T.-N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A. Langer, R. A Reversibly Switching Surface. *Science* **2003**, *299*, 371-374.
 13. (a) Wang, R.; Hashimoto, K.; Fujishima, A.; Chikuni, M.; Kojima, E.; Kitamura, A.; Shimohigoshi, M. Watanabe, T. Light-induced amphiphilic surfaces. *Nature* **1997**, *388*, 431-432 (b) Lim, H. S.; Han, J.; Kwak, D.; Jin, M. Cho, K. Photoreversibility Switchable Superhydrophobic Surfaces with Erasable and Rewritable Pattern. *J. Am. Chem. Soc.* **2006**, *xxx*, xxxx.
 14. (a) Zhang, J.; Lu, X.; Huang, W. Han, Y. Reversible Superhydrophobicity to Superhydrophilicity Transition by Extending and Unloading an Elastic Polyamide Film. *Macromol. Rapid Commun.* **2005**, *26*, 477-480 (b) Hemmerle, J.; Roucoules, V.; Fleith, G.; Nardin, M.; Ball, V.; Lavalle, P.; Marie, P.; Voegel, J.-C. Schaaf, P. Mechanically Responsive Films of Variable Hydrophobicity Made of Polyelectrolyte Multilayers. *Langmuir* **2005**, *21*, 10328-10331.