Simple Fabrication of Hierarchical Structures on a Polymer Surface

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ABSTRACT

The ability to fabricate hierarchical structures has drawn significant interest as a means of achieving superhydrophobic surfaces. Water repellency has potential industrial importance, such as self-cleaning, anti-oxidation and minimization of the resistance against liquid flow in microfluidic systems. In this paper we introduce a simple and fast technique to fabricate hierarchical structures on polymer surface in order to achieve a superhydrophobic surface. In the first step microstructures were fabricated on surface of poly(methyl methacrylate) using a sand paper. In order to make nanostructures on top of microstructures O_2 reactive ion etching was employed. In the last step the surface was coated with fluorinated silane molecules to lower its surface energy. Static and dynamic contact angle measurement showed water contact angles were higher than 150° and sliding angles were 2° on the fabricated surface.

Keywords: hierarchical structures, superhydrophobic surface, self cleaning, Cassie's state, Wenzel's state.

1 INTRODUCTION

The ability to fabricate hierarchical structures has drawn significant interest as a means of achieving superhydrophobic surfaces. It is well proven that in addition to surface chemistry topography of a surface has a significant influence on the wettability. Some of the plant leaves have shown superhydrophobic properties in a way that water droplet can easily roll off and carry away the dust and debris on their surface, a mechanism which is called as self-cleaning [1]. This property has been demonstrated for lotus, rice, taro, india canna leaves and is known as lotus effect [2]. It was first believed that this behavior is because of microscale textures and chemistry of the surfaces of those leaves but further investigation of those leaves under scanning electron microscope (SEM) revealed that there are branch-like nanostructures on top of microstructures of those surfaces. For example, the surface of a lotus leaf is composed of fine, branched nanostructures (120 nm) on top of micropapilla (5-9 µm) [3]. In fact, the combination of hierarchical structures on the surface of those leaves and their chemistry is the cause of their water repellency. Water repellency has potential industrial importance, such as self cleaning, anti-oxidation, minimization of the resistance against liquid flow in microfluidic systems. Ou et al. [4, 5] fabricated a microchannel which had a superhydrophoic bottom and systematically investigated the effect of topography on drag reduction and velocity profiles using pressure drop measurements and microparticle image velocimetry. They reported a pressure drop reduction of over 40% and an apparent slip length exceeding 20 µm.

The two major models to predict water contact angles on rough surfaces are the Wenzel and Cassie models. In the Wenzel's theory a droplet deposited on a rough surface fills completely the grooves of the rough surface. The Wenzel's contact angle can be calculated using equation 1 [6].

$$\cos \theta^{*} = r \cos \theta \qquad (1)$$

where θ^* and θ are contact angles on rough and flat surfaces, respectively, and r is surface roughness. The key parameter controlling Wenzel's contact angel is the roughness defined as the ratio of true surface area to the projected area. Therefore r is always larger than 1. Based on this equation, if the contact angle on flat surface is less than 90°, the contact angel on a rough surface will be smaller than that for the corresponding flat surface while for a true contact angle higher than 90° an increase in surface roughness increases the contact angle.

In the Cassie's state air pockets are assumed to be trapped under the surface of liquid droplet. As a result the liquid doesn't wet completely the surface area under the liquid droplet and a composite surface consisting of air and substrate forms under the droplet. If we assume $Ø_s$ as the surface fraction of solid under droplet then contact angle can be calculated using equation 2 [6].

$$\cos \theta^{*} = -1 + Ø_s (\cos \theta + 1) \qquad (2)$$

The Cassie's contact angle monotonously increases as $Ø_s$ decreases, implying that $Ø_s$ should be as small as possible. But it should be noted that reducing $Ø_s$ decreases roughness as well causing to reach the critical roughness below which Wenzel's state is energetically more preferable.

There are two requirements for a surface to be superhydrophobic. The surface should have a very high contact angle, larger than 150°, and the sliding angle should be less than 10° [7]. The tilting angle at which the droplet rolls off the substrate is called as the sliding angle. In case of superhydrophobic surfaces the droplet can easily roll off by tilting the surface for a small amount. It is well known that both Cassie and Wenzel's states can make high contact angle droplets but it is only Cassie's state which can cause a low sliding angle. In Wenzel's state droplets wet the surface completely and therefore it cannot easily move on the surface. In Cassie's state the droplet is in touch with solid in less area, thus reducing the dragging force (friction) applied on the droplet. As a result, the droplet can easily move on the surface at a low sliding angle. Therefore, it can be concluded that only Cassie state can fulfill the two requirements for a superhydrophobic surface.

Various micro- and nanofabrication techniques have been employed to artificially produce superhydrophobic surfaces. Sun et al. [8] has reported creating of a superhydrophobic surface using a natural template of lotus leaf and replicating it by casting. Jeong et al. [9] have investigated the wettability of nanoengineered dual-roughness surfaces fabricated by UV-assisted capillary force lithography. Lee et al. [10] have fabricated multiscale structures on high density polyethylene (HDPE) by heat and pressure-driven imprinting methods using patterned anodized alumina as replication template.

In this paper we introduce a simple and fast technique to fabricate hierarchical structures on polymers surface in order to achieve a superhydrophobic surface. In the this technique we make a superhydrophobic surface on poly(methyl methacrylate) (PMMA) surface by scratching it by sand paper followed by reactive ion etching (RIE) and silane coating processes. Scanning electron microscope (SEM) images of surfaces fabricated using abovementioned technique proved formation of hierarchical structures on PMMA. Static and dynamic contact angle of water droplet on fabricated surfaces were measured. We also observed bouncing of water droplet on the fabricated surface.

2 EXPERIMENTAL PROCEDURES

2.1 Fabrication of superhydrophobic surface on PMMA.

Figure 1 shows schematics of the process steps to achieve a hierarchical structure with superhydrophobic property in polymer substrates. PMMA sheet with thickness of 2.9 mm were purchased from United States plastic corp. and cut in 10×30 mm^2 pieces. For comparison, four pieces of PMMA sheets which underwent different treatments were prepared. The first piece (S0) is considered as a reference sample and is used to measure contact angle on plane PMMA. A commercial sand paper with 240 grit number was used to sand surfaces of second and third PMMA pieces (S1 and S2). Then oxygen plasma etching process was done to treat surface of third and fourth sample (S2 and S3). The RIE power and oxygen pressure were set at 150 W and 150 mTorr respectively and the surface of samples S3 and S4 were treated for 20 minutes. Finally samples S1, S2 and S3 were treated for 20 minutes with a fluorinated silane molecule (heptadecafluoro-1, 1, 2, 2-tetrahydrodecyl) trichlorosilane ($C_{10}H_4Cl_3F_{17}Si$) in the vapor phase using a home built vacuum chamber in order to reduce surface energy of the samples. In table 1, the type of surface treatment on each sample is summarized.

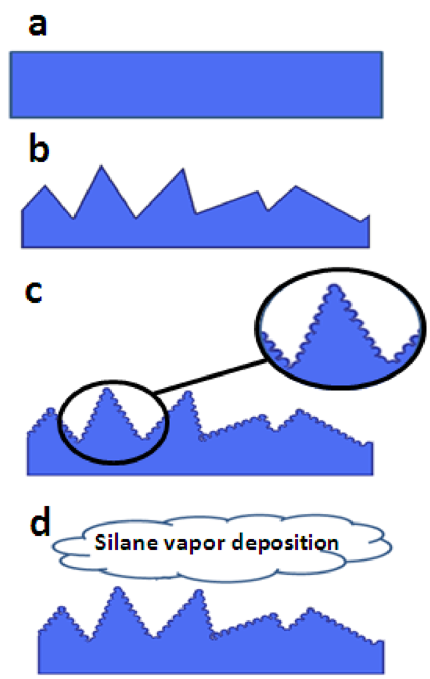

Figure 1- Schematic illustration of the process used to fabricate hierarchical structure on surface of PMMA to achieve a superhydrophobic surface. (a) Plane PMMA. (b) PMMA sanded by sand paper. (c) oxygen plasma etching of PMMA. (d) vapor deposition of silane molecules on surface.

Table 1- Type of surface treatment on different PMMA samples.

Sample	Treatment
S0	No treatment (plane PMMA)
S1	Sanded + silane coated
S2	Sanded + oxygen plasma + silane coated
S3	Oxygen plasma + silane coated

2.2 Contact angle measurements.

A contact angle analyzer (FTA 125, First Ten Ångstrom, Inc. Portsmouth, Virginia) was used to measure static contact angles of water droplets on the samples prepared in this study. The samples were placed on a stage and adjusted to an appropriate level. A droplet is dispensed on the sample by pushing a button of the pipette. The image is captured immediately after the droplet is placed on the sample for accurate measurement. The software automatically analyzes the drop shape and computes the contact angle. For each sample contact angle measurements were done 3 times with water droplets of a target volume of 5 μL. The averaged values of contact angles were used for each data point. Sliding angle measurements were done for samples which had a static contact angle higher than 150°. In order to measure sliding angle water droplet with volume of 5 µL were placed on sample with zero degree of tilting and then sample was tilted manually. The angle at which droplet slides on surface was measured using a goniometer. 3 measurements were done to define sliding angle of each sample.

2.3 Recording of bouncing droplet.

To record bouncing of water droplets on the sample S2 water droplets with volume of 8 – 10 µL were released from height of 3.4 mm to 8.4 mm respect to the sample surface. The high speed camera (Kodak Ektapro 1000HRC), which has a maximum frame rate of 1000 fr/s and minimum exposure time of 50 µs, was used to capture images during droplet impact on the surface.

3 RESULTS AND DISSCUSION

In figure 2 water droplets on the surfaces of plane PMMA (S0), PMMA sanded with sand paper and coated with silane (S1), PMMA sanded with sanded paper, etched using oxygen plasma and coated with silane (S2) and PMMA etched using oxygen plasma and coated with silane (S3) are shown.

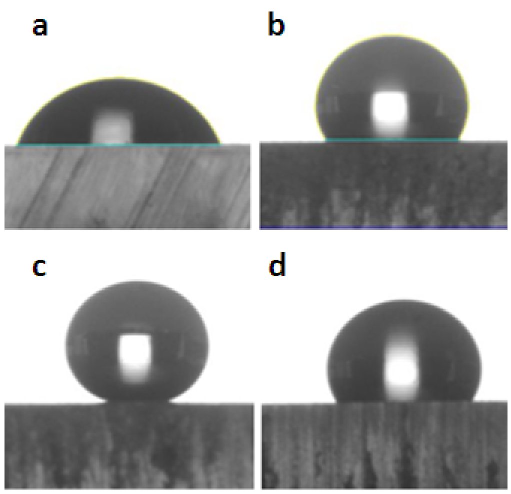

Figure 2- water droplet on surface of (a) S0, (b) S1, (c) S2 and (d) S3 samples.

Static contact angles of water droplet on samples S0, S1, S2 and S3 were measured as 70.5±1.6°, 119.1±1.9°, 165.3±3.2° and 115.7±1.0° respectively. As can be seen the contact angle for plane PMMA without any silane coating (S0) is the lowest among all samples while for the sample (S2) which has a hierarchical structure and treated with silane molecule it is the highest. Scanning electron microscope image of sample S2 is shown in figure 3. In fact sanding PMMA produces mostly microstructures on the sample surface while the subsequent O_2 plasma etching process bring about the formation of nanostructures on top of sanded microstructures. Despite the presence of hierarchical micro/nanostructures, the surface (S2) does not produce superhydrophobicity without combining a fluorinated silane coating. Coating the sample with fluorinated silane molecules further reduces their surface energy. A combination of formation hierarchical structures on surface of PMMA and silnae coating on sample surface will cause water droplets to follow the Cassie's model where it just stays on top of protrusions on sample surface. Having silane molecules on surface of sample will cause the water droplet not to fill cavities of samples and be repelled by silane molecules. In this state water is in touch with the solid substrate in much lower area compared to the case it is placed on plane PMMA. Our sliding angle measurements showed water slides on surface at 2° which is due to low friction of water droplet and the substrate. The contact angle of water droplet on sample S1 and S3 which have only microstructures and nanostructures and are silane coated are lower than sample S2. The results corroborate the fact that having hierarchical structures in combination of appropriate surface chemistry is an important means in order to minimize surface fraction of solid substrate, increase roughness and increase contact angle.

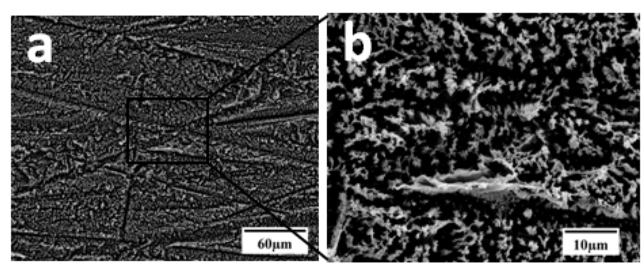

Figure 3- SEM images of sample S2 which is sanded by sanded by sand paper, etched by oxygen plasma and silane coated.

One efficient way to show water-repellency on superhydrophobic surface is the droplet impact experiment. The impact of microliter water droplets in the range of injection droplet volume of 8 – 10 µL on the superhydrophobic surface (sample S2) was investigated for different initial impact speeds (v_0: 12.4 – 33.6 cm/s), which were varied by changing the dropping needle height from 3.4 mm to 8.4 mm. The Weber number, a dimensionless number indicative of the ratio between the kinetic energy of the droplet and surface energy, were in the range of 0.28 − 2.04 depending on the needle height. Figure 4 shows image sequences for one of the examples of rebounding behavior of water droplet, which was released at 8.4 mm needle height. For all the Weber numbers, water droplets successively bounce off the surface. The restitution coefficient of droplet, *e*, gradually decreases from 0.73 to 0.28 as every rebound occurs (or the number of rebound increases), where *e* was obtained by dividing initial impact speed into take-off speed. The bouncing continues until all the energy in the droplet was dissipated by internal flow of the bouncing droplet and surface friction [11]. The impact experiments on superhydrophobic PMMA sufaces (sample S2) indicate that the surface exerts an excellent anti-sticking character with water droplets.

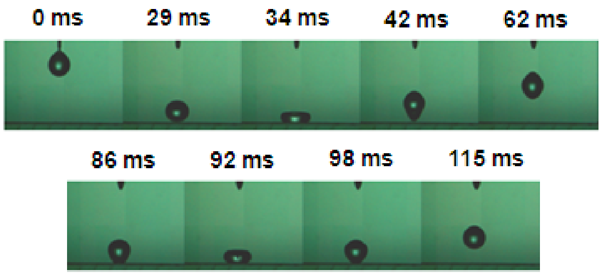

Figure 4- image sequences for rebounding water droplet (droplet volume V0: 9.3 µL) on superhydrophobic PMMA surface (sample S2, needle height: 8.4 mm, initial impact speed v0: 33.6 cm/s and We: 2.04).

4 CONCLUSIONS

In this paper we have introduced a cheap, fast and easy technique to produce hierarchical structures in order to achieve superhydrophic surface on PMMA. In this technique hierarchical structures are produced on surface of PMMA by sanding PMMA sheet with sand paper and etching it by oxygen plasma. After fabrication of hierarchical structures on polymers they are coated with a fluorinated silane. This simple technique was able to successfully produce a superhydrophobe surface on PMMA. Having a hierarchical structure on PMMA will decrease the surface fraction of solid in contact with water droplets (Cassie's model). Presence of silane molecules on surface also repels water preventing it from wetting inside the grooves causing the static contact angle to increase more than 150° and water to slide on surface at sliding angle 2°.

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REFERENCES

[1] Z. Yang, C. Chiu, J. Yang and J. Yeh, "Investigation and Application of an Ultrahydrophobic Hybrid-Structured Surface with Anti-sticking Character", Journal of Micromechanics and Microengineering, 19, 2009.
[2] Z. Guo and W. Liu, "Biomimic from Superhydrophobic Plant Leaves in Nature: Binary Structure and Unitary Structure", Plant Science ,172, 1103-1112, 2007.
[3] X. F and L. Jiang, "Design and Creation of Superwetting/Antiwetting Surfaces", Advanced Materials, 18, 3036-3078, 2006.
[4] J. Ou, B. Perot, and J. P. Rothstein, "Laminar Drag Reduction in Microchannels Using Ultrahydrophobic Surfaces", Physics of fluids, 16, 4635-4643, 2004.
[5] J. Ou and J. P. Rothstein, "Direct Velocity Measurements of the Flow Past Drag-reducing Ultrahydrophobic Surfaces", Physics of fluids, 17,103606, 2005.
[6] M. Callies and D. Quere, "On Water Repellency", Soft Materials, 1, 55-61, 2005.
[7] B. Bhushan, Y. Jung, and K. Koch, "Micro-, Nano- and Hierarchical Structures for Superhydrophobicity, Self-cleaning and Low Adhesion", Philosophical Transactions of the Royal Society, 367, 1631-1672, 2009.
[8] M. Sun, C. Luo, L. Xu, H. Ji, Q. Ouyang, D. Yu, and Y. Chen, "Artificial Lotus Leaf by Nanocasting", Langmuir, 21, pp. 8978-8981, 2005.
[9] H. E. Jeong , M. K. Kwak , C. I. Park, K. Y. Suh, "Wettability of Nanoengineered Dual-roughness Surfaces Fabricated by UV-assisted Capillary Force Lithography", Journal of Colloid and Interface Science, 339, 202–207, 2009.
[10] Y. Lee, S. H. Park, K. B. Kim, and J. K. Lee, "Fabrication of Hierarchical Structures on a Polymer Surface to Mimic Natural Superhydrophobic Surfaces", Advanced Materials, , 19, 2330–2335, 2007.
[11] Y. Kwon, N. Patankar, J. Choi and J. Lee, "Design of Surface Hierarchy for Extreme Hydrophobicity", Langmuir Article, 25, 6129-6136, 2008.