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Flexible Teflon Nanocone Array Surfaces with Tunable Superhydrophobicity for Self-Cleaning and Aqueous Droplet Patterning

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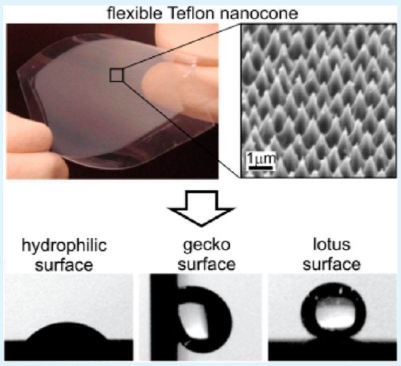
Supporting Information

ABSTRACT: Tunable hydrophobic/hydrophilic flexible Teflon nanocone array surfaces were fabricated over large areas (cm^2) by a simple two-step method involving the oxygen plasma etching of a colloidal monolayer of polystyrene beads on a Teflon film. The wettability of the nanocone array surfaces was controlled by the nanocone array dimensions and various additional surface modifications. The resultant Teflon nanocone array surfaces were hydrophobic and adhesive (a "gecko" type of surface on which a water droplet has a high contact angle but stays in place) with a contact angle that correlated with the aspect ratio/sharpness of the nanocones. The surfaces switched to a superhydrophobic or "lotus" type of surface when hierarchical nanostructures were created on Teflon nanocones by modifying them with a gold nanoparticle (AuNPs) film. The nanocone array surfaces could be made superhydrophobic with a maximum contact angle of 160° by the further modification of the AuNPs with an octadecanethiol (C18SH) monolayer. Additionally, these nanocone array surfaces became hydrophilic when the nanocone surfaces were sequentially modified with AuNPs and hydrophilic polydopamine (PDA) layers. The nanocone array surfaces were tested for two potential applications: self-cleaning superhydrophobic surfaces and for the passive dispensing of aqueous droplets onto hybrid superhydrophobic/hydrophilic microarrays.



KEYWORDS: *nanocone, biomimetics, self-cleaning surface, flexibility, superhydrophobicity*

1. INTRODUCTION

Effective control of interactions between liquids and solid surfaces, such as wettability and adhesiveness, is a major topic of research because of the great importance of hydrophobic and hydrophilic surfaces for the various applications which are directly related to our daily life.[1,2] For instance, superhydrophilic surfaces that exhibit excellent water wettability with a low contact angle around zero degrees can be used as biocompatible and anti-fogging materials.[3] Superhydrophobic "lotus" surfaces which weakly bind to water and repel water droplets, can be used as self-cleaning,[4] anti-bacterial,[5,6] and anti-icing[7,8] interfaces. Adhesive hydrophobic "gecko" surfaces that exhibit a high water contact angle and can pin water droplets can be useful for transporting small volumes of aqueous solutions.[9−11] In addition, creating patterned surfaces with two different hydrophilic/hydrophobic areas is also useful for the fabrication of microfluidic devices and the control of cell adhesion.[12]

There are a number of approaches for controlling the hydrophilic/hydrophobic properties of surfaces, including surface chemistry[2,13] and the formation of microscale and nanoscale surface structures.[1,10,14] Hierarchical periodic micro- and nanostructured surfaces with excellent hydrophobic/hydrophilic properties have been observed in a number of biological systems including lotus leaves,[1] gecko feet,[15] rose petals,[11,16] rice leaves,[17] and butterfly wings.[18] Thus, biomimetic structures based on these surfaces have been intensively studied.[19−21] As the hydrophobic properties of these surfaces depend highly on their microscale and nanoscale shape, size, and periodicity, fabrication techniques enabling precise control of the structures are required. In addition, methods that can easily fabricate these nanostructured surfaces over large areas are required for the successful application of these functional materials. Duplications of the native micro- and nanostructures of biological surfaces are one of the straightforward approaches to modify the wettability of desired surfaces.[16,22] On the other hand, various nanostructure arrays of nanocones,[14,23] nanopillars,[15] nanowires,[20] nanodomes,[4] nanopores,[24] and their hierarchical micro- and nanostructures[3,25−27] have been artificially created, and their surface wettability has been successfully controlled. For the fabrication of these nanostructure arrays, colloidal crystal monolayers are widely used as masks for further etching processes,[23,27−29] or used as templates for deposition of other materials,[3,30,31] in addition to the patterning created by photolithography.[10,25] Anodization is also a powerful method for the fabrication of nanopore arrays over large areas.[24] These studies, however, were typically carried out on rigid solid substrates, even though flexibility is an essential

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feature for coating desired surfaces with superior hydrophobic/hydrophilic materials.

In this paper, we describe the fabrication of flexible nanocone array surfaces with tunable hydrophobic/hydrophilic properties that can be easily created over large areas. The nanocone arrays are made by a straightforward two-step method involving the oxygen plasma etching of a colloidal monolayer of polystyrene beads (PS beads) on a Teflon film. In the present study, the geometric control of the nanocone arrays including the aspect ratio, sharpness and the periodicity is performed and the changes of surface wettability are investigated. Furthermore, we show that the hydrophobic properties of nanocone array surfaces can be enhanced or switched to hydrophilic by surface modification. The Teflon nanocone surface exhibits adhesive “gecko” type hydrophobicity. When the nanocones are modified with gold nanoparticles (AuNPs) by thermal deposition of a gold thin film, the hydrophobicity of the surface is enhanced and is switched to non-sticky “lotus” type superhydrophobicity. The hydrophobicity is even further enhanced by modifying the surface of AuNPs on nanocones with an octadecanethiol (C18SH) monolayer, and alternatively can be switched to a hydrophilic surface by coating the nanocones with a polydopamine (PDA) layer. Finally, two original applications of those nanocone surfaces are demonstrated: first, as self-cleaning surfaces for the removal of mud spots, and second, for the passive dispensing of aqueous solutions.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Materials. All the solvents and chemicals were used as received. The PS beads (Polybead carboxylate, 0.35 μm, 0.5μm, 1.0 μm, and 2.0 μm, 2.5 w/v %) were purchased from Polyscience. The Teflon film (thickness 0.005 in) was obtained from CS hyde Company. Dopamine hydrochloride was obtained from Sigma-Aldrich, and triton-X-100 (TX100) was purchased from Fischer Scientific.

2.2. Fabrication of Nanocone Arrays on Teflon Film. Before spincoating PS beads, a Teflon film was cut into square (typically 3.0×3.0 cm) and cleaned by rinsing with ethanol and Milli-Q water followed by plasma cleaning (PDC-32G, Harrick Plasma) for 3 min. A solution of PS beads (1 mL) were centrifuged and transferred to a mixture containing ethanol and methanol with a 2:1 volume ratio. A surfactant (TX100) was added to the solution at 0.2 vol % in order to improve the wettability of the solution on the Teflon films. The concentration of PS beads was roughly adjusted to from 2.5 to 7.5 w/v % for 0.35 μm to 2.0 μm beads, respectively. The solutions of PS beads with a volume of about 25 μm were then spin-coated on a cleaned Teflon film for 6 sec at 1000 rpm. The films were left in a petri dish at room temperature for few minutes to let the solvent dry slowly. The PS bead/Teflon surface was etched by O_2 plasma (200 mTorr, 50 W, PC2000, South Bay Technology) for the desired time.

2.3. Surface Modifications of Teflon Nanocone Arrays. For surface modifications of Teflon nanocone arrays, a thin gold film with a thickness of 5 nm was deposited by a thermal evaporator (DV-502A, Denton Vacuum). The gold-coated nanocone surfaces were further modified with octadecanethiol (C18SH) or polydopamine (PDA) as desired. For thiol modification, the film was immersed in a 5 mM C18SH solution in EtOH for 30 min, followed by rinsing with EtOH, and dried in a nitrogen stream. For PDA modification, the gold coated nanocone surface was exposed to a 2 mg/mL dopamine solution in Tris Buffer (pH 8.5) for 10 min, rinsed with water, and dried under a nitrogen stream. This protocol leads to the deposition of a PDA layer having a thickness about 1.0 nm.[32]

2.4. SEM and AFM Characterization. For the SEM characterization of the Teflon nanocone arrays, a thin layer of Ir was previously sputtered by ion beam sputter deposition (IBS/e, South Bay Technology) on the surface in order to ensure a good electrical conduction. A FEI Quanta 3D FEG SEM was used for imaging the surfaces. The tilted views were performed using an angle of 52°. The AFM characterization was achieved with an Asylum Research MFP-3D. The analysis of SEM images and AFM images were performed by using ImageJ (U.S. National Institutes of Health, http://imagej.nih.gov/ij/) and Gwyddion, respectively.

2.5. Contact Angle Measurements. Contact angle measurements were carried out based on the static sessile drop method with a home build setup. For the contact angle measurement, water droplets with a volume of 5−10 μL were used. The photographs of water drops were taken at over three different spots for each sample. The data analysis of the photos was carried out with ImageJ.

3. RESULTS AND DISCUSSION

3.1. Nanocone Arrays on Flexible Teflon Films. The fabrication of the Teflon nanocone arrays was adapted from the technique recently reported by our group for the creation of broadband antireflective plasmonic films[33] and is described in detail in the Experimental Section. Briefly, it consists of a two-step process that is shown in Figure 1a. First, a monolayer of hexagonally-packed polystyrene (PS) beads was formed on a flexible Teflon film by spin-coating a solution of PS beads. The surface with the colloidal monolayer was then exposed to oxygen plasma which induced the simultaneous shrinking of the PS beads and the etching of the partially-protected Teflon film. Depending on the etching time and the diameter of the PS beads, this process resulted in the formation of either arrays of Teflon nanocones or Teflon nanocones surmounted with PS beads. Figure 1b shows a macroscopic view of a Teflon nanocone array film obtained using 1 μm PS beads and 10 min of etching. First, one can see that the flexibility of the Teflon film is maintained after the surface treatment, which is of first importance for applications of those films as coatings for complex surfaces. Two different areas can be observed on this transparent film. The first one, located at the edge of the film and glossy, is flat Teflon that was not covered with PS beads. The second area, located in the middle of the film and mat, corresponds to the area covered with the PS beads. This area has been observed by scanning electron microscopy (SEM), as shown in Figure 1c. On this tilted SEM picture, multiple oriented domains of hexagonally packed nanocones with a characteristic size of several tens of micrometers can be seen. The inset of Figure 1c shows the individual nanocones. Those results show clearly that densely packed flexible Teflon nanocone array can be fabricated over a large area (here ~6 cm^2) by using this straightforward and up-scalable two-step process.

3.2. Geometrical Control of the Hydrophobic Properties. The hydrophobic properties of the Teflon nanocone surfaces were controlled by changing the height and the shape of the nanocones. Figures 2a−f show the structural changes of nanocones created with 1 μm PS beads as a function of etching time *t* from 1 min to 20 min. The SEM images in the upper and lower rows show the nanocones before and after removing the PS beads by rinsing the surfaces with toluene, respectively. For the unrinsed samples, the hybrid structures consisting of Teflon nanostructures (bumps or pillars) and the shrunk PS beads on top of them are observed for a short etching time (t < 5 min). As the etching time increased (t = 5−10 min), the height of the nanocones increased, and the head of nanocones got shaper with only small residues of the PS beads remaining on top of them. For further longer etching time (t = 15−20 min), the shape of the head of the nanocones become sharper and string

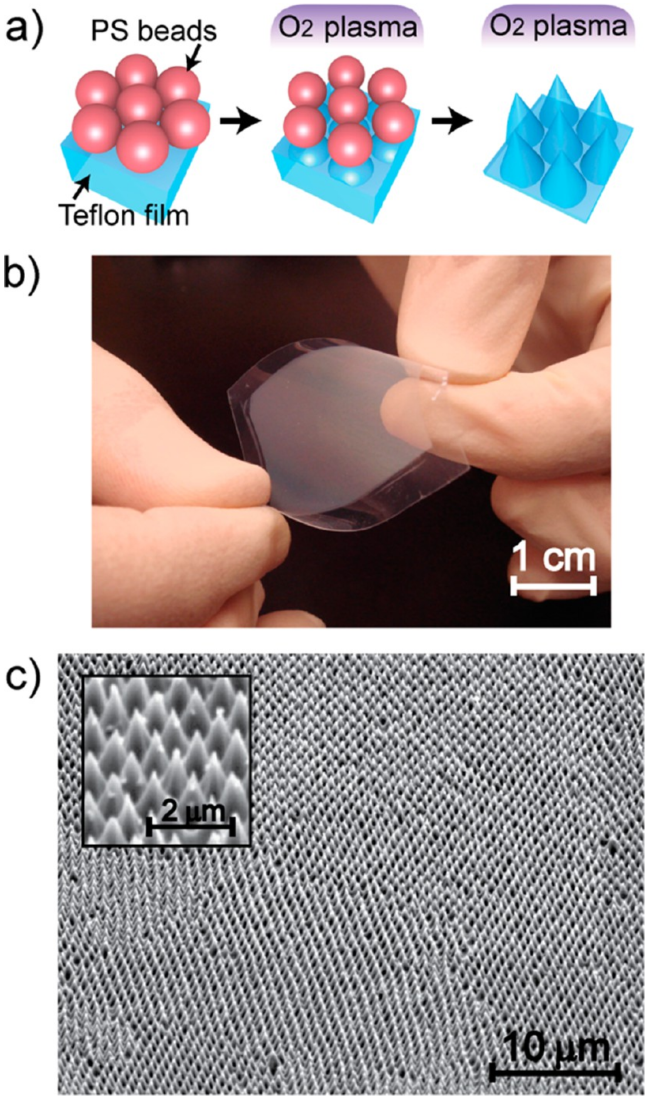

Figure 1. (a) Scheme of the fabrication process of Teflon nanocone arrays. (b) Photograph showing a macroscopic view of flexible Teflon nanocone array. (c) SEM images of the tilted nanocone array. Inset: detailed view of Teflon nanocones.

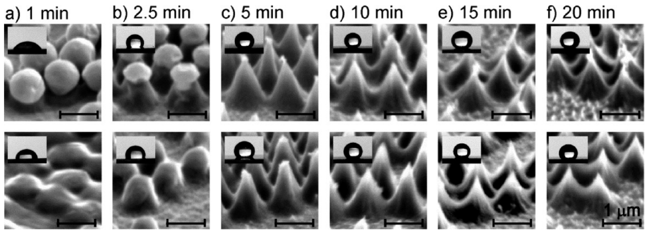

Figure 2. (a–f) SEM images of Teflon nanocones with PS beads (top row) and after dissolution of PS beads (bottom row). The structures are created with different etching times; (a) 1, (b) 2.5, (c) 5, (d) 10, (e) 15, and (f) 20 min. All scale bars indicate 1 μm. The insets show the photos of water droplets (10 μL) on the corresponding samples.

shape residues stick out from the heads of nanocones. For the rinsed samples, the same trend is observed but without PS beads or residues on top of the nanocones. From these SEM images, one can observe that the height of nanocones increased until 10 min etching, and then decreased slightly for longer etching time. On the other hand, the sharpness of the nanocones was enhanced as the etching time increased. The insets of Figures 2 show the shapes of 10 μL water droplets on the corresponding nanocone array surfaces. Those pictures show that both unrinsed and rinsed samples exhibit a similar trend of hydrophobicity as a function of etching time: an increase at first (t = 1−10 min) followed by the reaching of a plateau at high contact angle values for longer etching times (t > 10 min).

The measured contact angles θ_c of both unrinsed and rinsed Teflon nanocone array surfaces are plotted as a function of etching time in Figure 3a. As it was observed in Figure 2a, the Teflon nanocone arrays exhibited slightly hydrophilic properties with measured contact angle of 65 and 84° for both unrinsed and rinsed surfaces created by 1 min O_2 plasma etching. The surfaces switched to hydrophobic (contact angle $\theta_c > 90°$) when the etching time was increased to 2.5 min. The contact angles of nanocone array surfaces dramatically increased from 1 to 5 min etching time for both unrinsed and rinsed surfaces, then reached plateaus after 10 min etching time. Let us note that the unrinsed nanocone array surfaces were highly hydrophilic for t = 1 min and turned to highly hydrophobic for the longer etching time (t > 2.5 min) with respect to the rinsed nanocone arrays. As shown in Figure 3b, the height of the rinsed nanocones (obtained by AFM measurements) was plotted as a function of the etching time. The corresponding AFM images and height profiles are shown in Figure S1 in the Supporting Information. As it was observed in the SEM images in Figure 2a–f, the height of nanocones dramatically increased as the etching time increased from 1 min to 5 min. The nanocones exhibited a maximum height at t = 10 min and the height slightly decreased for longer etching times.

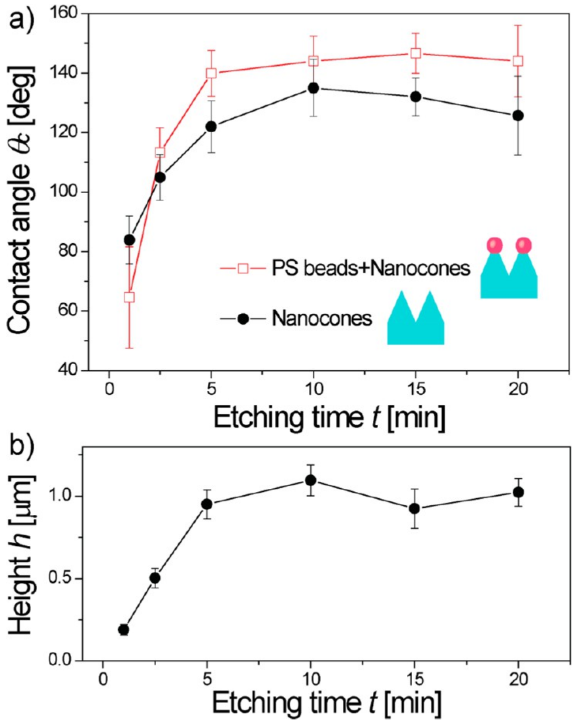

Figure 3. (a) Plot of measured contact angles of Teflon nanocone array surfaces with (red curve)/without (black curve) PS beads on top as a function of etching time t. (b) Height of rinsed nanocones h as a function of etching time t.

This trend totally follows the contact angle measurements in Figure 3a.

These results indicate that the hydrophobic properties of nanocone arrays highly depend on the aspect ratio of the nanocones and the shape of their top. Now, the mechanism controlling the wettability of the nanocone arrays will be discussed. We consider the effects of (i) changes of chemical composition of Teflon films and PS beads and (ii) changes of the shape of nanocones induced by oxygen plasma treatments. It has been reported that Teflon, which is originally hydrophobic, turns weekly hydrophilic by a short oxygen plasma etching treatment accompanied with the increase in oxygen on the surface.[34] After certain etching time, the amount of oxygen at the Teflon surface decreases to that of untreated surface and the surface returns hydrophobic.[34,35] The polystyrene (PS) surfaces is also initially hydrophobic but is known to become highly hydrophilic by oxygen plasma treatment,[36] with a change more pronounced than for Teflon surfaces. The hydrophilic chemical nature of the surface of the nanobump arrays and its hybrid structure with PS beads, presented in Figure 2a, is attributed to the hydrophilic properties of O_2 plasma treated Teflon and PS beads. In addition to the changes in surface chemistry, the geometry of nanocone arrays plays an important role. D'Urso et al. reported changes in the hydrophobic properties of glass nanocone arrays modified with fluorinated self-assembled monolayer as a function of aspect ratio.[37] According to their model, the sharp nanocone arrays with low apex angles restrain a water drop to penetrate into the interspaces of nanocones resulting in highly hydrophobic properties due to existence of air bubbles in the interspaces. When the apex angle of the nanocone is large, the surface tension of a water droplet pulls the water into the interspace of nanocones, which leads to a slight depression in the measured contact angle with respect to that of the flat surface. This trend agrees well with our experimental results. This shows that the wettability of the Teflon nanostructured surfaces can be controlled by changes in surface chemistry, the height of the nanostructures, and the shape of their tips induced by the oxygen plasma.

In the next set of experiments, the size and periodicity of nanocone arrays were varied and the hydrophobic properties of nanocone array surfaces were investigated. PS beads with various diameters from 0.35 to 2.0 μm were used to control the size and the periodicity of the nanocones. The contact angle measurements were carried out and plotted in Figure S2 in the Supporting Information as a function of etching time from 1 min to 20 min. A similar trend between the measured contact angle and the etching time was observed for both small and large nanocone arrays. For the nanocone array surfaces created with small PS beads (0.35 μm), the measured contact angles reached a plateau for t = 2.5 min. The etching time for which the nanocone array surface exhibited highly hydrophobic properties increased with the size of PS beads. Figures 4a−d present the typical SEM images of tilted nanocone arrays fabricated with PS beads with various sizes and an optimized etching time corresponding to the plateau (marked in the plot in Figure S2 in the Supporting Information). The inserted pictures show photographs of a water drop (10 μL) on the corresponding nanocone array surface. The periodicity and height of the nanocone array was determined by using fast Fourier transform (FFT) analysis of SEM images of nanocones from top view and AFM measurements (shown in Figure S3 in the Supporting Information), respectively. The period, height, aspect ratio and the measured contact angle, for each bead diameter are summarized in Table1.

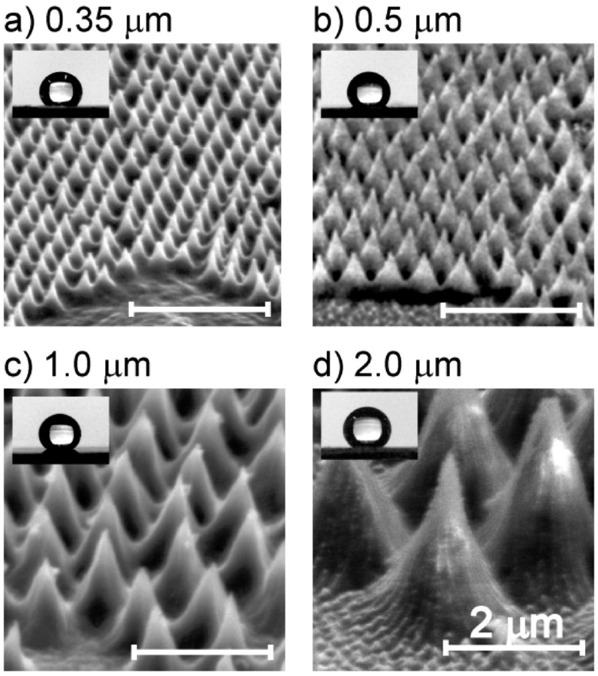

Figure 4. SEM images of tilted Teflon nanocone arrays fabricated with PS beads of different diameter and etching time: (a) 0.35, (b) 0.5, (c) 1.0, and (d) 2.0 μm. The scale bars in all images indicate 2.0 μm. The insets show photographs of water drops on the corresponding sample.

Table 1. Diameter of the PS Bead, Optimum Etching Time, and the Measured Contact Angles

	bead diameter (μm)			
	0.35	0.5	1.0	2.0
etching time (min)	2.5	5	10	15
period (μm)	0.33 ± 0.01	0.45 ± 001	0.87 ± 0.03	1.87 ± 0.17
height (μm)	0.45 ± 0.05	0.65 ± 0.1	1.10 ± 0.09	2.39 ± 0.32
aspect ratio	1.37	1.45	1.27	1.27
contact angle (deg)	134.5 ± 5	137 ± 6	134 ± 10	145 ± 16

3.3. Tailoring the Hydrophobicity from Gecko to Lotus Surface and Switching to Hydrophilic with Surface Modifications.

The hydrophobic properties of nanocone array surfaces will be now tuned by surface modification. In these experiments, the nanocones were created with 1 μm PS beads and 10 min etching time. Interestingly, the Teflon nanocone arrays exhibit a "gecko" type hydrophobicity, which is also referred to as adhesive and hydrophobic, even though Teflon originally has a low surface energy and low adhesion to water. Figure 5a shows a water drop that exhibits a high contact angle on top of the Teflon nanocone arrays with measured contact angle of 134°. As shown in this figure and in video V1, when the film was tilted to 90 and 180°, the water drop doesn't roll off and sticks to the nanocone array surface. The water drop on the Teflon nanocone array surface exhibited high contact hysteresis of 41° with measured advancing and receding contact angles of 139 and 98°, respectively, when the surface was tilted to 90°. This result indicates that the Teflon

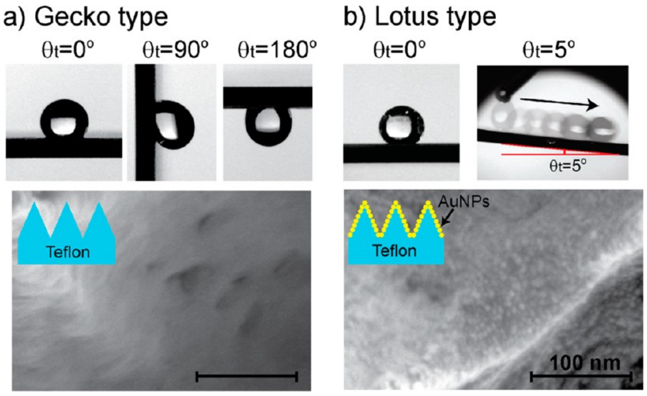

Figure 5. (a) Photographs of a water droplet on top of a Teflon nanocone surface at tilted angles θ_t = 0, 90 and 180° (top row). High-magnification SEM image of a Teflon nanocone (bottom). (b) Photograph of a water droplet on top of gold-coated Teflon nanocone surface at θ_t= 0° (top left), and an overlaid sequential photograph showing a water droplet rolling off on the nanocone surface at tilted angle θ_t = 5° (top right). High-magnification SEM images of the surface of a gold-coated Teflon nanocone (bottom). The scale bars in the SEM images indicate 100 nm.

nanocone array surface likely holds the Wenzel state, in which hydrophobicity of the surface is enhanced by increasing the roughness.[38] As it has been reported that the contact angle hysteresis of Teflon surfaces can be significantly reduced or enhanced depending on the surface nanostructures and roughness,[34,39,40] we attributed the adhesive hydrophobicity of the Teflon nanocone arrays to their specific shape and periodicity. The nanocone array surface switched to "lotus" type, which is also referred to as superhydrophobic, after a 5 nm thick gold film was deposited on the nanocone surfaces, see Figure 5b. By depositing the gold thin layer, the hydrophobicity of the surface was enhanced with a measured contact angle of 153°. The top right picture in Figure 5b is the overlaid sequential photographs showing a water droplet which is rolling off on the surface at a tilted angle of 5°. This experiment is also shown in video V2 in the Supporting Information. This experimental result indicates low contact angle hysteresis of the gold coated nanocone array surface and that the water drop weekly binds to the surface suggesting that the gold coated Teflon nanocone surface holds Cassie–Baxter state, in which the air bubbles fill in the nanocone interspaces and repel a water drop.[38,41] These results provide important insights into the hydrophobic properties of nanocone arrays because the Teflon exhibits more hydrophobic properties (contact angle θ = 105°) compared to that of gold (θ = 52°) when they are flat. SEM observations were performed in order to observe the detailed surface topography of nanocone arrays. As shown in the bottom row in panels a and b in Figure 5, the gold film formed nanoparticles (AuNPs) with diameters of several nanometers on the surface of Teflon nanocones, which conferred to the nanocone a much rougher surface. The result agrees with the previous study reporting the formation of AuNPs by thermal vapor deposition of several nanometer thick gold film on glass substrate.[42] In addition, it has been shown that the roughness of thermally evaporated gold films on fluoropolymer surfaces is enhanced with respect to that on glass substrate due to the low surface energy.[43] The SEM observations revealed that the deposition of a gold thin film resulted in the formation of hierarchical nanostructures on the Teflon nanocone surface. Hierarchical micro- and nanostructures can be found in various biological superhydrophobic surfaces, and previous researches reported that creating nanoscale roughness on the microstructures enhanced the hydrophobicity of the interface and reduced adhesion to a water drop.[26,27,44,45] We attribute the superhydrophobicity of the gold-coated nanocone array surface to the hierarchical structures consisting of Teflon nanocones and gold nanoparticles. Even if gold is originally hydrophilic, it has been shown that nanostructured gold surfaces can exhibit hydrophobicity without any surface modifications with hydrophobic compounds.[31,46]

The hydrophobicity of gold-coated nanocone array surfaces is further enhanced by modifying the AuNPs with hydrophobic alkanethiols. The gold-coated nanocone surface was immersed in a 5 mM octadecanethiol (C18SH) solution in EtOH for 30 min, followed by rinsing with EtOH, and dried in a nitrogen stream. Figure 6a shows a water droplet on the nanocone arrays modified with C18SH-AuNPs. Because of the formation of the hydrophobic self-assembled monolayer, the measured contact angle was increased to 160°. On this sample, the water droplets can be easily rolled-off with a roll-off angle around 0°, indicating a strong water repellency of the surface.

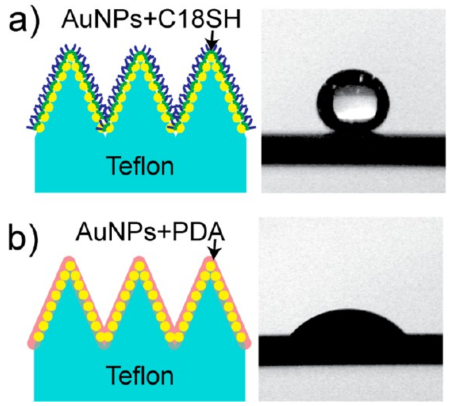

Figure 6. Schematic of Teflon nanocones (left column) and photographs of a 10 μL water droplet (right column) on AuNPs-nanocones modified with (a) C18SH and (b) PDA.

On the other hand, we can switch the wettability of the AuNP-coated nanocones surface to hydrophilic by modification with a hydrophilic layer. In this experiment, we employed a coating of polydopamine (PDA) to make the nanocone array surface hydrophilic. PDA is a biomimetic adhesive polymer inspired by marine mussel foot proteins, and it has great advantages for surface modification.[47] First, it can be applied on any kind of surface by exposure to an alkaline dopamine solution. Second, PDA film can serve as an attachment layer for biomolecules containing amino or thiol functional groups.[32,48,49] Furthermore, it has been reported that modifing superhydrophobic surfaces, consisting of anodic aluminum oxide membranes coated with fluorosilane, with PDA thin films switched the surface to hydrophilic.[50] In this experiment, the AuNP-modified nanocone surface was exposed to a 2 mg/mL dopamine solution in Tris Buffer (pH 8.5) for 10 min, which corresponds to the deposition of a PDA layer having a thickness about 1.0 nm.[32] The surface was rinsed with water and dried under a nitrogen stream. Figure 6b shows a photograph of a water droplet on PDA modified nanocone surface showing that the measured contact angle dramatically reduced from 153 to 44°. It revealed that the superhydrophobic

AuNP-modified nanocone surface turned to hydrophilic through successfully coating of a PDA layer. This result agrees with the previous research.[50] The measured contact angles for all the samples are reported in Table 2.

Table 2. Surface Modification of Nanocone Surfaces, Measured Contact Angles, and Hydrophobicity Type

	nanocone surface			
	Teflon	AuNPs	AuNPs +C18SH	AuNPs +PDA
contact angle (deg)	134 ± 10	153 ± 6	160 ± 5	44 ± 8
type	gecko	lotus	lotus	hydrophilic

3.4. Self-Cleaning Surfaces. Having shown that the hydrophobicity of the flexible nanocone arrays can be finely tuned, we will now demonstrate the utility of the superhydrophobic nanocone films as self-cleaning surfaces. In these experiments, the self-cleaning action was demonstrated by the removal of a dried mud spot by rinsing the surface with water. Figure 7 shows the sequential photographs of the experiment with a cleaned microscope slide (Figures 7a−c) as a control and with the nanocone array modified with AuNPs and C18SH (Figures 7d−f). The surface modification of the nanocone array was carried out in the same manner as described in the previous section. Videos V3 and V4 in the Supporting Information also show the cleaning process for both the control and the nanocones, respectively. First, a 10 μL droplet of muddy water was spotted on both surfaces. As shown in Figure 7a, the droplet spread on the glass slide due to its hydrophilicity. On the contrary, Figure 7d shows that the droplet beaded up upon the nanocone surface, due to its superhydrophobicity. The both surfaces were dried in an oven at 70 °C for 30 min in order to evaporate all the water. Images b and e in Figure 7 show the surface after the drying step for the glass and the nanocone surface, respectively. As expected, the shape of the dried mud was defined by the initial shape of the wet mud for the glass slide. In contrast, the dried mud adopted a disklike shape caused by the settlement of the mud particles and the evaporation of water on the nanocone arrays. Finally, the surfaces were rinsed with water using a wash bottle in order to simulate the action of rain. Figure 7c shows the glass slide after 9 sec rinsing. In this picture and in video V3, it is clear that some mud remain on the surface after the rinsing. Figure 7f shows the nanocone surface after 2 s rinsing. As it can be seen in video V4, the mud disk did not attached to the surface and was removed straight after the water was flushed on it, leading to a much cleaner surface. This striking evidence of the self-cleaning action of the superhydrophobic nanocone arrays suggests great expectation of those films for applications in self-cleaning coatings.

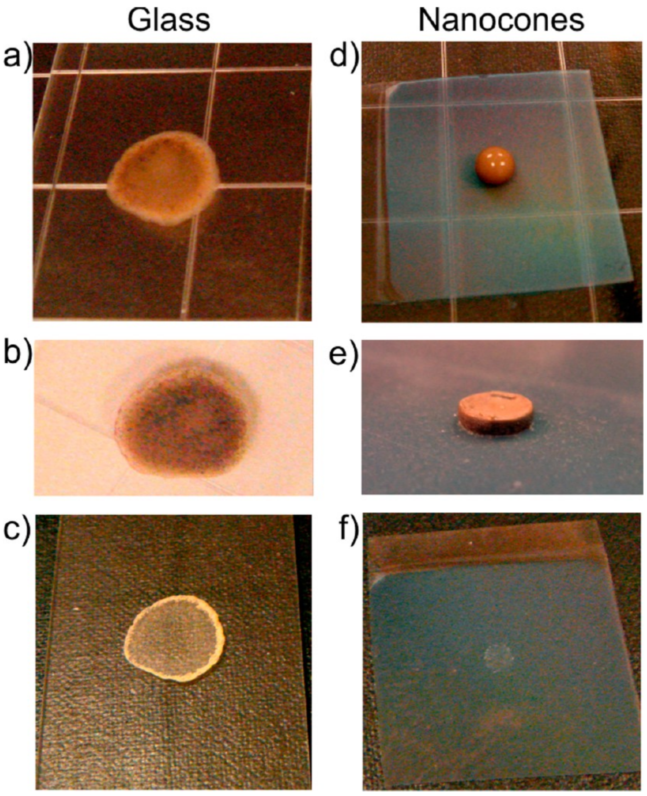

Figure 7. Photographs of a droplet of muddy water on a hydrophilic glass slide (left column) and on a superhydrophobic surface with nanocone arrays modified with AuNPs and C18SH (right column), (a, d) before and (b, e) after drying, and (c, f) after rinsing with water.

3.5. Passive Dispensing of Water Droplets. Having demonstrated the self-cleaning properties of superhydrophobic nanocone surface, we will now describe the fabrication of a superhydrophobic/hydrophilic hybrid nanocone surface which can be used for the passive dispensing of aqueous solutions. The fabrication of surfaces that can be used for passive dispensing of aqueous solutions is a current area of strong research for applications such as patterning of complex geometries with liquids and the fabrication of cells microarrays.[12] The hybrid surface consisting of a superhydrophobic surface with hydrophilic spots was fabricated on the AuNP-modified nanocone surface by spotting 1 μL droplets of PDA solution as depicted in Figure 8a. The passive dispensing of aqueous solutions, which consists of wetting hydrophilic areas without wetting the hydrophobic background without a direct spotting of the solution, was achieved by sliding a droplet of water held by the tip of a syringe over the surface. This is shown in the series of sequential photographs in Figures 8b−d and in the video V5 (see the Supporting Information). In these pictures, it is clear that water was selectively dispensed on the hydrophilic areas, generating water droplets with a diameter of about 0.8 mm, as defined by the size of the initial PDA spots. After drying the surface under a nitrogen stream, sequential dispensing cycles could be performed. These results shows clearly that passive dispending can be achieved by using this hybrid surface, which is of a strong interest for the easy patterning of aqueous solutions on the surfaces.

4. CONCLUSIONS

In this paper, we have presented the tunable hydrophobic/hydrophilic properties of flexible nanocone surfaces and shown two possible applications of those functional surfaces. The nanocone arrays were fabricated by a simple two-step method involving the oxygen plasma etching of a colloidal monolayer of polystyrene beads on a Teflon film. The wettability of those surfaces was controlled by both geometry and surface modifications with an enhanced hydrophobicity for the nanocones with high aspect ratios. The hydrophobicity of nanocone arrays was retained over the wide range of the nanocone size and periodicity from 0.35 to 2 μm. The Teflon nanocone array exhibited "gecko" adhesive hydrophobic

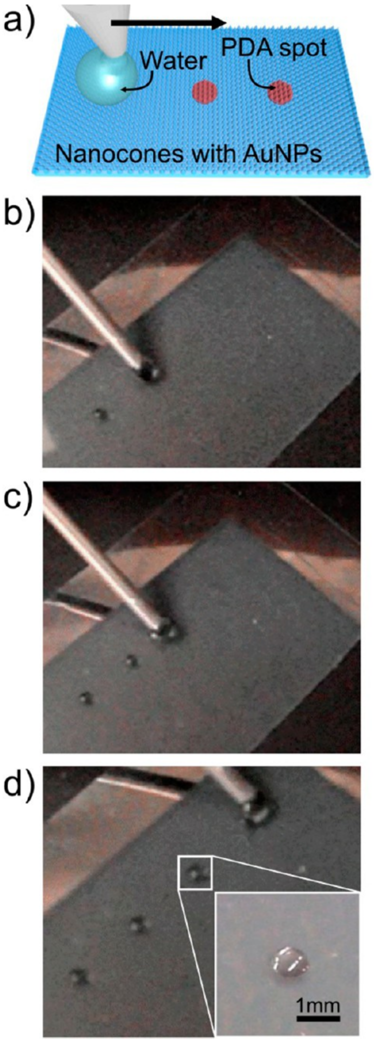

Figure 8. (a) Schematic illustration of the passive dispensing of water on a hybrid surface composed of superhydrophobic and hydrophilic nanocones. (b–d) Series of photographs showing the water droplets selectively dispensed on the PDA spots. Inset: enlarged picture of the water droplet.

properties that could be changed to a "lotus" superhydrophobic surface by creating hierarchical nanostructures by modification with AuNPs. The hydrophobic property was further enhanced by modifying the AuNPs with octadecanethiol. This surface exhibits excellent water repellency and can be used as a self-cleaning surface as we demonstrated for the removal of mud spots. The AuNP-modified nanocone array surface can be made hydrophilic by coating the surface with polydopamine. The passive dispensing of aqueous solution was demonstrated on a hybrid surface consisting of superhydrophobic AuNP–nanocone surfaces with hydrophilic PDA spots. The presented results hold the potential of nanocone arrays surfaces for various applications including water repellency, self-cleaning surfaces, or simple techniques for spotting aqueous solutions with the great advantage of their flexibility.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information and videos. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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