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Superhydrophobic Surfaces Engineered Using Diatomaceous Earth

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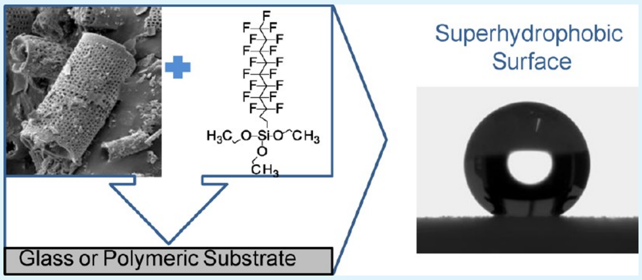

ABSTRACT: We present a simple method to prepare superhydrophobic surfaces using siliceous exoskeleton of diatoms, a widespread group of algae. This makes diatomaceous earth an accessible and cheap natural material. A micro/nanoscale hierarchical topography was achieved by coating a glass surface with diatomaceous earth, giving rise to a superhydrophilic surface. Superhydrophobic surfaces were obtained by a further surface chemical modification through fluorosilanization. The wettability of the superhydrophobic surface can be modified by Argon plasma treatment in a controlled way by exposure time variation. The chemical surface modification by fluorosilanization and posterior fluorinated SH surface modification by plasma treatment was analyzed by XPS. Using appropriated hollowed masks only specific areas on the surface were exposed to plasma permitting to pattern hydrophilic features with different geometries on the superhydrophobic surface. We showed that the present strategy can be also applied in other substrates, including thermoplastics, enlarging the potential applicability of the resulting surfaces.

KEYWORDS: *superhydrophobic surfaces, diatomaceous earth, bioinspiration, surface modification, micropatterning*

INTRODUCTION

In general, superhydrophobic (SH) surfaces are defined as surfaces with a static water contact angle (WCA) higher than 150°.[1,2] These surfaces have attracted much interest in both fundamental and applied research. Different applications for SH surfaces were proposed including in self-cleaning, antifouling, anti-adhesion, microfluidic systems, and high-throughput screening devices.[2−7] The inspiration to produce artificial SH surfaces comes from nature. The most well-known example of a natural SH surface is the Lotus leaf.[8] Hierarchical surface topographies at micro/nanoscale such as those found on Lotus leaves are critically important for this effect. The superhydrophobicity includes a combination of multiscale roughness and a low surface energy of the materials used.[9] Many techniques and strategies to mimic that hierarchical surface topography were developed, including: lithography, polymer reconformation, template method, sol−gel processing, or layer-by-layer methods.[2] One of these strategies involved the spin-coating of a glass slide with a mixture of micro and nanoparticles of silica prepared by sol−gel.[10] Tsai and coworkers also reported a similar strategy to produce SH surfaces through successive Langmuir−Blodgett depositions of micro/nanoparticles on a glass slide surface;[11] after silica deposition, the silanization of the particulate films decreased the surface energy, allowing to obtain a SH surface. Different sizes and number of layers of micro-silica particles were tested. It was demonstrated that the superhydrophobicity increased with the increase of the silica particle size. Other interesting strategy to produce SH surfaces is using natural structures as templates that exhibit the necessary hierarchical structure. Sun et al. have developed a method to produce SH surfaces using a natural lotus leaf as template.[12] They were able to replicate the topography of the lotus leaf by polymer casting, using poly(dimethylsiloxane). The resulting lotus-leaf-like substrate has the same superhydrophobic characteristics of the original lotus leaf. Biomimetic SH polystyrene films were also obtained by replicating the surface pattern of a natural taro leaf, another superhydrophobic natural surface.[13]

These two strategies to produce SH surfaces inspired us to develop a new approach to generate such kind of surfaces. We propose the use of silica-based structures already available in nature to create the necessary hierarchical topography. We hypothesize that these structures can be used directly on the surface and not as templates. The proof-of-principle will be based on the use of diatomaceous earth (DE) to produce the SH surfaces. Diatomaceous or diatoms are unicellular algae and widely spread in both fresh water and seawater playing a crucial role in the earth's carbon cycle.[14,15] Other very appreciated characteristic of diatomaceous is their amazing silica microskeleton and the biomineralization mechanisms associated with its formation. Diatoms are taken as a model for some research works on nanoscale self-assembly and biomimetics.[16,17] The sedimented dead diatoms on the bottom of lakes or sea are called DE or diatomite.[15] The exoskeletons of diatoms are

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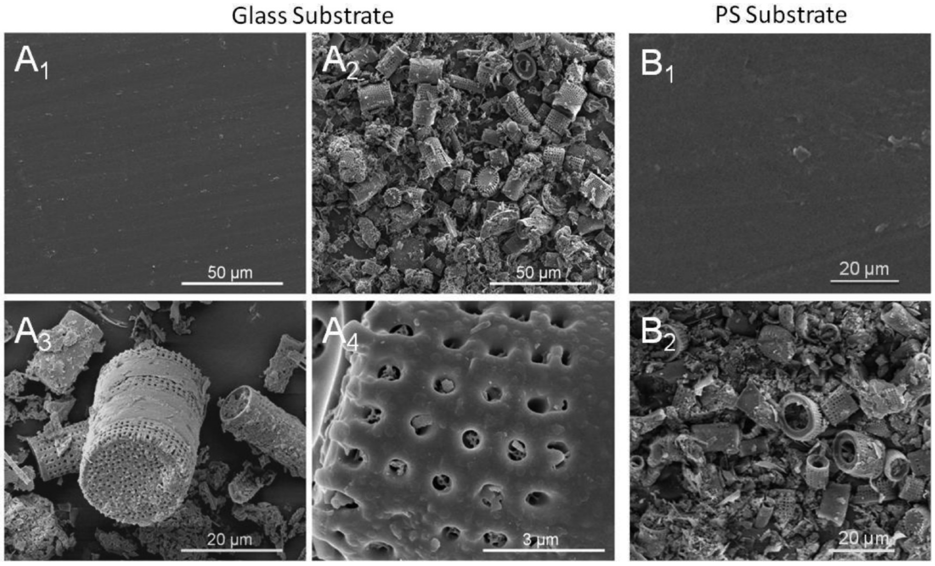

Figure 1. SEM images of glass substrate before (A_1) and after coating with DE (A_{2-4}). Magnification images from both diatomaceous silica microskeleton (A_3) and the nanotexture on their surface (A_4). SEM images of polystyrene substrate before (B_1) and after coating with DE (B_2).

microstructures with nanotextures on their surface and are constituted mostly by amorphous silica. The use of these microstructures to coat smooth surfaces should enable to create a hierarchical structure eliciting extreme wettability properties. We will explore the possibility to create superhydrophobic surfaces by treating such substrates with fluorosilanes.

Simpson and D'Urso have a patent with the idea to produce a superhydrophobic powder using DE.[18] They refer the possibility to use the powder to make superhydrophobic surfaces. On this patent it was proposed that to use a polymer in solution as a binder to adhere the DE particles to the surface. The substrate surface can be coated with superhydrophobic DE particles by painting, dipping or spraying. On this work, we propose to use the intrinsic characteristics of the substrate to promote the binding with DE particles. That can be performed by melting superficially the substrate to get a DE layer locked on its surface. Through this method we believe that a more robust SH surface can be obtained, because DE particles will be trapped and not only deposited on the surface. We explore also the possibility to change the SH surface wettability in a controlled way and to print patterns on the surface. These possibilities make possible to use the patterned substrates both open microfluidic and high-throughput screening applications.[3,4]

■ MATERIALS AND METHODS

Materials Processing. Glass substrates with 2.5 × 2.5 cm were prepared using glass microscope slides. The substrates were cleaned with detergent, acetone, ethanol, and deionized water to remove any surface contaminant and dried in air. A DE suspension was prepared by mixing 1 g of DE (Food-Grade Fossil Shell Fluor from Perma-Guard, Inc; kindly supplied by Agrogreen Canada Inc., Ontario, Canada) in 4 mL of water, followed constant stirring. The DE suspension (500 μL) was dropped on the top of each substrate. Then the substrates with the DE suspension were heated in a furnace under air atmosphere for 1.5 h at 675 °C to obtain a sintered DE film on the surface. The samples were cooled slowly until room temperature and washed with ethanol in a ultrasound bath for 15 minutes to remove DE excess. The washed substrates were immersed in a 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (PFDTS) (from Aldrich Chemistry) solution at 1% in ethanol for 48 h. Subsequently the samples were dried in air and heated to 220 °C for 5 min to promote silane hydrolysis and condensation, thereby forming a stable fluorosilanated layer on the DE surface.

We also used polystyrene (PS) as the substrate instead of glass, to demonstrate that the proposed methodology can be also used at low temperature. Substrates with 2.5 × 2.5 cm were prepared by cutting PS Petri dishes. The substrates were washed with ethanol in a ultrasound bath for 15 minutes and dried in air. Then over the substrates a 2 millimeter-thick layer of PFDTS modified DE was placed. The substrates with DE were heated at 90 °C for 20 minutes and enforcing a pressure of 30×10^5 N m^{-2}. The ensemble was heated and cooled always under pressure. To perform the process a hydraulic press with heating/cooling platens was used. After it was cooled, the DE excess on PS surface was removed washing the surface with ethanol, which was then dried in air. The DE used to coat PS substrates was previously chemically modified with PFDTS. First, DE was heated at 600 °C for 1 h to promote water desorption and expose more silanol groups on diatom surface. A DE suspension was prepared by mixing 1 g of DE with 10 mL of a 1% PFDTS solution prepared in deionized water, the mixture was left to react overnight. Both solid and liquid phases were separated by filtration. After it was dried in air, the solid phase was heated at 220 °C for 5 min to promote silane hydrolysis and condensation. The chemically modified DE was washed with 20 mL of ethanol to remove any unreacted silane. After it was dried, the PFDTS-modified DE was used to perform surface modification onto the PS substrates.

Surface Modification by Plasma Treatment. Surface treatments using a plasma reactor Plasma Prep 5 (Gala Instrument GmbH, Bad Schwalbach, Germany) were performed in the diatom coated glass samples with fluor. Argon gas was used and the pressure in the reactor chamber was controlled in the range of 0.1−0.2 mbar. The treatment was performed using a radio frequency source (13.56 MHz) and a power of 30 W for different time periods.

Surface Morphology Characterization. The morphology of the samples was analyzed using a NanoSEM-FEI Nova 200 Scanning Electron Microscope (FEG/SEM; FEI Company, Hillsboro, OR, U.S.A.). All specimens were pre-coated with a conductive layer of gold. The surface topography of the samples at lower magnification was assessed by a non-contact optical profiling technique using a interferometer profiler (WYKO-Veeco, model NT1100; Veeco, Tucson, AZ, U.S.A.) equipped with the WycoVision 32 analytical software package. The surface of both unmodified glass substrate and DE modified glass substrate was analyzed. For each sample, five different regions with 0.9 × 1.2 mm^2 were measured to determine topographic roughness parameters, namely average roughness (Ra)

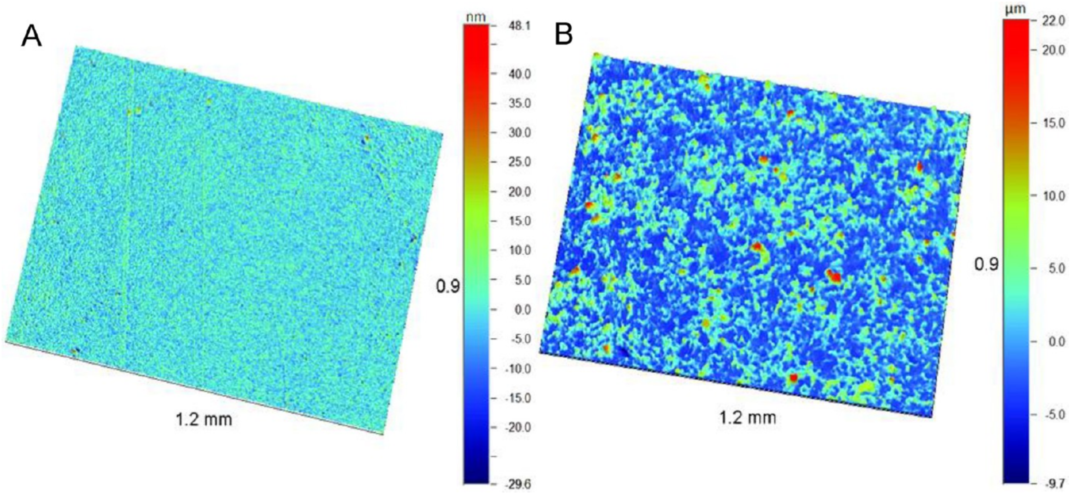

Figure 2. Optical profilometry images of the unmodified glass surface (A) and the glass substrate surface after the coating with DE (B). Images show an area of 0.9 mm ×1.2 mm (magnification 5×).

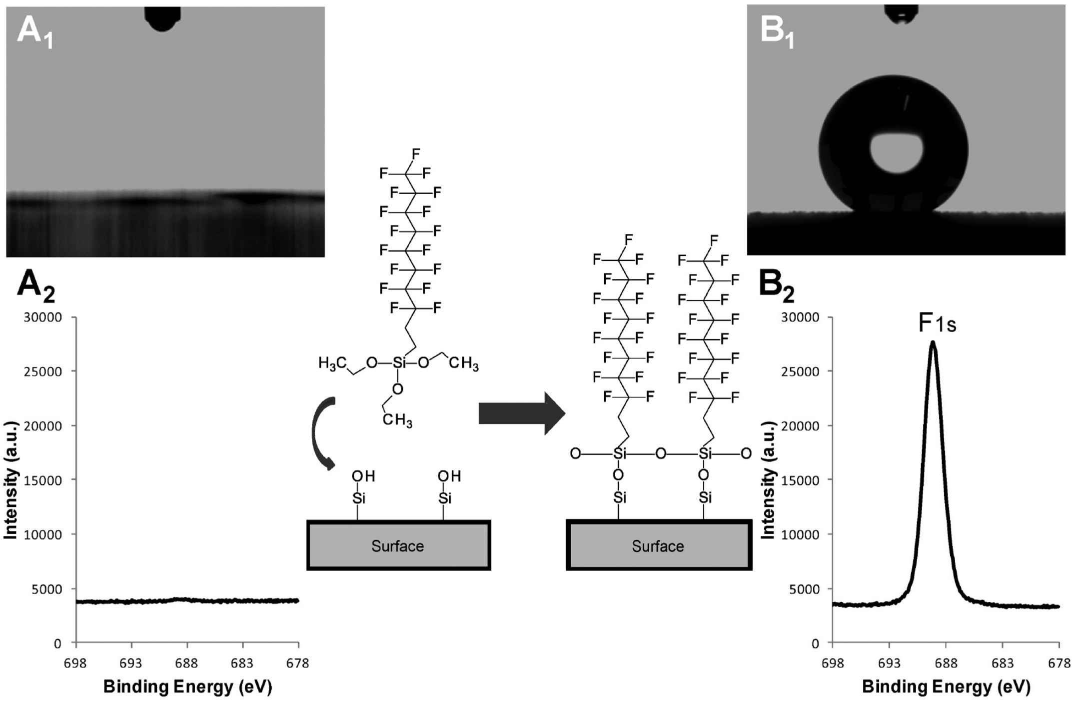

Figure 3. Chemical modification of the DE coated glass surface performed by a fluorosilane transform the initial superhydrophilic substrate (see water profile A_1) to superhydrophobic one (see water profile B_1). The chemical modification was confirmed by XPS analysis: the F_{1s} spectra of the two samples are presented in A_2 and B_2, respectively.

and root-mean-squared (RMS) roughness (Rq). 3D images from both surfaces to show roughness distribution were obtained applying a filter for noise reduction. The water contact angle (WCA) was analyzed for the different samples: unmodified glass slides (G1), glass coated with diatoms (G2), diatom coated glass modified by fluorosilane (G3), and after Argon plasma treatment performed on fluorinated samples (G4). WCA was also determined in the produced surfaces using PS substrates. The WCA was measured in a OCA 15+ goniometer from DataPhysics Corporation (San Jose, CA, U.S.A.) at room temperature. The static WCA was measured by a sessile drop method with a 6 μL water droplet. Using the same method, the WCA hysteresis was determined using a liquid injection rate of 0.3 μL s^{-1}, changing the drop volume between 5 and 8 μL.

Chemical Characterization. The chemical composition of the PFDTS modified DE particles was analyzed on a NanoSEM-FEI Nova 200 Scanning Electron Microscope (FEG/SEM; FEI Company, Hillsboro, OR, U.S.A.), equipped with an EDAX-Pegasus X4M energy dispersive spectrometer. EDS analysis were performed at an accelerating voltage of 15 keV, using conventional ZAF correction procedure integrated on the EDAX-Pegasus software.

The surface chemistry composition of glass samples was analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha ESCA instrument (Thermo VG Scientific, East Grinstead, U.K.) equipped with monochromatic Al (Kα) X-ray source operating at 1486.6 eV. Due to non conductor nature of samples it was necessary to use a low energy flood gun (electrons in the range 0−14 eV) and a low energy Argon ions gun to minimize surface charging. Photoelectrons were collected from a take-off angle of 90° relative to sample surface. The measurements were performed in a Constant Analyzer Energy mode (CAE) with 100 eV pass energy for survey spectra and 30 eV pass energy for high resolution spectra. Charge referencing was carried out by setting lower binding energy C1s photo peak at 285.0 eV C1s hydrocarbon peak. Using the standard Scofield photoemission cross sections, we determined surface elemental composition.

RESULTS AND DISCUSSION

The wetting behavior of a surface is dependent on both surface topography and surface chemistry. We used DE to generate a rough topography on smooth glass. The initial substrate was glass microscope slide that presents a smooth surface, see Figure $1A_1$. The glass is hydrophilic, having a WCA of 31.3 ± 2.6°. The glass was coated by DE suspension and then was heated until 675 °C to induce the agglomeration and stabilization of the diatom layer over the glass surface. Substrates were then cleaned in a ultrasound bath to eliminate the non-sintered fraction of DE. After the cleaning process we obtained a glass with a sintered diatom layer on the surface, see Figure $1A_2$. The DE layer provided roughness to the surface at the microscale level complemented with a nanotexture given by the diatom surface morphology, see Figure $1A_3$ and $1A_4$. To characterize the changes on surface roughness, the surface topography was analyzed by optical profilometry, Figure 2. The glass surface is clearly smooth at the sub-micrometer level, see Figure 2A. After coating with DE, we clearly see a roughness at the microscale level that seems homogenous throughout all the analyzed area, Figure 2B. Unmodified glass surface presented an average roughness (Ra) of 4.2 ± 0.5 nm and the DE coated glass surface exhibited a Ra of 3.0 ± 0.2 μm. On the Figure 2B, a representative profilometry of surface with a 1 mm^2 was presented. On this area, if smaller areas are selected and compared between them these areas present similar morphology. Therefore a homogenous DE coating on substrate surface was achieved at a sub-millimeter level.

The resulting modified surface has superhydrophilic properties, see Figure $3A_1$. This behavior was the result of the combination between surface roughness and the hydrophilic nature of the substrate.[19] In fact, the diatoms are hydrophilic due to the SiO_2 groups on their surface. To decrease the surface energy the substrate was subjected to fluorosilanization.[20] The chemical surface modification was confirmed by XPS analysis. As showed in Table 1 the surface with a DE layer (G2) is mostly constituted by oxygen and silica. The presence of carbon in unmodified glass (G1) and after DE coating (G2) is due to surface contamination.[21] Initially on the DE modified glass the fluor content is almost inexistent and after the silanization process a peak indicating the presence of fluor on the surface appears: compare Figure $3A_2$ with Figure $3B_2$. With the chemical modification, the surface presents a decrease on oxygen from 55.6% to 29.4% and a flour content of 31.8%, sample G3 in Table1. Because of the changes on surface chemistry the initial superhydrophilic surface becomes superhydrophobic with a WCA of 151.0 ± 0.9° and a WCA hysteresis of 5.8 ± 1.4°.

Table 1. Atomic Composition of the Studied Substrates Determined from XPS Analysis[a]

	Atomic Composition (%)			
samples	C_{1s}	O_{1s}	Si_{2p}	F_{1s}
G1	19.3	48.9	22.4	0.5
G2	8.8	55.6	27.6	0.4
G3	18.9	29.4	16.7	31.8
G4	10.8	50.1	26.1	7.4

[a] The present results are for unmodified glass (G1), glass substrate coated with DE (G2), DE-coated glass chemically modified with PFDTS (G3), and DE/PFDTS-modified glass after Argon plasma treatment (G4).

Two theories have been used to explain the occurrence of the SH behavior. The Wenzel model postulated that the hydrophobicity of a surface can be increased by providing roughness to the surface, if the initial smooth substrate is already hydrophobic. In this model, the surface is completely wet since water completely fills all the surface roughness to form a fully wetted interface.[22] The second model, called Cassie model, predicts that air can be trapped in the surface roughness, the air blocks water infiltration into the valleys of the rough surface and the water droplet is partially suspended by air pockets.[9,23,24] For this model, the relation between WCA of the rough surface (θ^*) and the WCA of the smooth surface (θ) is given by the Cassie−Baxter equation

$$\cos \theta^* = f(1 + \cos \theta) - 1 \tag{1}$$

where f is the area fraction of the liquid−solid contact. As the SH substrate obtained in this work showed a lower WCA hysteresis we will assume that the Cassie model could explain its wettability properties. As the WCA of the smooth glass surface modified by fluorosilane was 112.7 ± 2.4°, we can estimate that f = 0.2.

We hypothesis that it is possible to use the same strategy to produce superhydrophobic surfaces using other kind of substrates, such as polymers. Experiments were carried out to modify a polystyrene (PS) substrate with DE. The PS was chosen due to be an amorphous material and when heated the PS undergoes a glass transition to a rubbery state at a relatively low temperature. One of the main vantages of PS is that it is both inexpensive and very accessible material, almost of labs use Petri dishes that are made of PS. The strategy is to melt superficially the substrate to bind DE to the surface, see Figure $1B_2$. In the glass case, first the substrate was coated with DE and after that the coated surface was modified with a fluorosilane. However using PS as substrate the fluor modification of DE was performed prior the deposition onto the PS, that occurs at a temperature sufficiently low to maintain the properties of the fluorosilane. The binding process was carried out applying pressure over the surface with the DE layer to avoid PS substrate deformation due to temperature. As the PS has a glass transition temperature of 80−120 °C, using a temperature of 90 °C the PS exhibits a considerable viscoelastic behavior.[25] Appling pressure on the DE layer over the substrate, the DE particles penetrate on the PS surface. Then with the temperature decrease the PS becomes rigid and the hydrophobic particles stay trapped on PS surface. Initially the PS, obtained from the Petri dishes, presents a hydrophobic behavior. After the treatment with the hydrophobic DE particles the PS shows superhydrophobic properties, see Figure 4. The modified PS substrate with DE present a WCA of 153.6 ± 3.1° and a WCA hysteresis of 3.3 ± 1.1°.

After the chemical modification of the DE particles with PFDTS, the obtained hydrophobic particles were analyzed by EDS. The chemical characterization reveals that the Fluor amount on particles was 2.8 ± 0.3%.

To modify the surface wettability of the obtained SH substrates we exposed the fluorinated glass surfaces to an Argon plasma treatment. By increasing the exposure time, the WCA of the SH surface decreased steadily down to the hydrophilic regime such phenomenon was previously observed in SH polymeric surfaces.[26] The relationship between plasma treat-

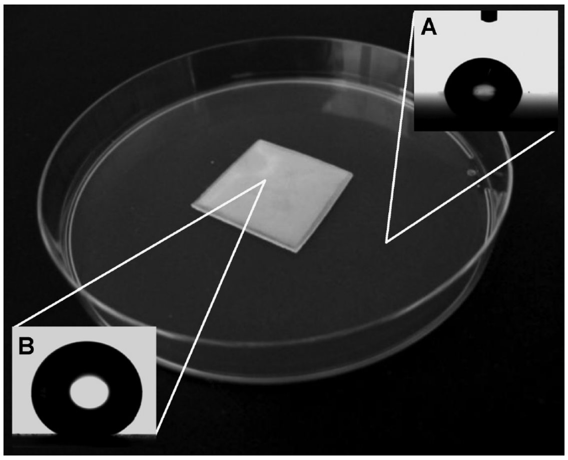

Figure 4. Polystyrene obtained from Petri dishes is a hydrophobic material (see the inset image A). After surface modification with hydrophobic DE particles the polystyrene becomes superhydrophobic (see the inset image B).

ment time and the WCA on the glass substrate surface is showed in Figure 5. When a fluoropolymer is treated by plasma both surface defluorination and oxidation occurs, during which CF_2 carbons are changed by CF, CH_2, C═O, and C−O carbons.[27,28] We believe that the fluorinated SH surface experienced a similar process. The chemical state of carbon on the obtained surfaces was analyzed by XPS before and after plasma treatment (samples G3 and G4 respectively) and the collected results are presented in Table 2. The relative content of CF_2 and CF_3 carbons decreases and C−H, C−O, and O═C−O carbons increase with plasma treatment. With this treatment the fluor content on the surface decreases strongly and a new species in the F1s spectrum at energy 685.5 eV is observed, corresponding to the bond of type Si−F, see Figure 6. Because of defluotination combined with the surface oxidation the surface energy increases and consequently also the surface wettability. After plasma surface modification the surface WCA remains stable until at least 5 days.

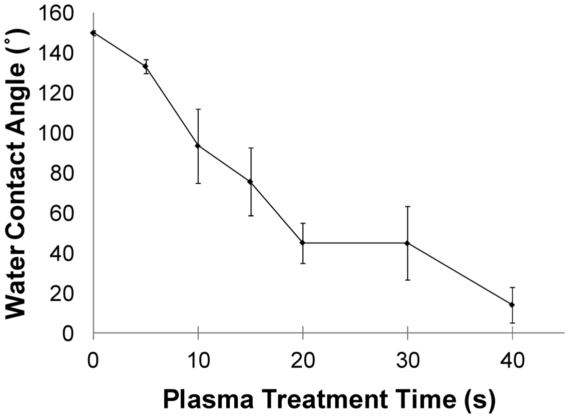

Figure 5. Influence of argon plasma treatment time on the WCA of the initial SH surface using the glass substrate.

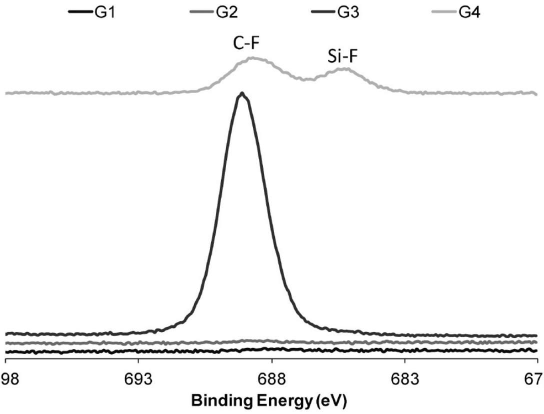

Figure 6. XPS F_{1s} spectra comparison between the different samples: unmodified glass (G1), glass substrate coated with DE (G2), DE coated glass chemically modified with PFDTS (G3), and DE/PFDTS modified glass after Argon plasma treatment (G4).

Surface modification can be performed in selected areas on the surface, so that patterns on the surface can be created. Using appropriate hollowed masks, we can modify only specific areas on the surface. We used masks of plastic sheets in which different shapes were cut, namely, squares, circles, lines, or triangles. The masks were placed over the SH glass substrate and the ensemble was subjected to Argon plasma treatment. The exposed regions gave rise to hydrophilic features with the same geometry in the substrate. Such wettable regions can be wetted and support the confinement of liquids that will not transpose to the surrounding superhydrophobic regions due to the high contrast in surface tension. The patterning of wettable spots with three distinct geometries is shown in Figure $7A_1$−A_3. Through this procedure, we can produce platforms with imprinted patterns with potential to be used in high-throughput screening applications, open microfluidics, and gel fabrication with different shapes, for example. The platform can also be used to generate gradients of different materials in an easy and fast way, see Figure $7A_4$. The hydrophilic stripe imprinted on surface should be prewetted with a solution A. Then using a pipette a solution B can be dropped at one end of the prewetted stripe. The solution B spreads along to the fluid stripe and by convection generates a gradient of material B on the material A. It was proposed that such surface-tension-driven centimeter scale gradients could be used in diagnostics, cell behavior studies, or drug screening.[29] In a similar manner on the PS superhydrophobic surfaces wettable regions can also be patterned, see Figures $7B_1$ and $7B_2$. The surface modification

Table 2. Chemical State Assessment of Carbon Functional Groups on Surface of DE-Coated Glass Chemically Modified with PFDTS (G3) and DE/PFDTS Modified Glass after Argon Plasma Treatment (G4)

		C_{1s}				
		C−C, C−H	C−O	O═C−O	CF_2	CF_3
binding energy (eV)		285.0	286.5 ± 0.3	289.0 ± 0.2	291.5 ± 0.3	293.8 ± 0.3
samples	G3	21.7%	10.5%	8.8%	48.3%	10.7%
	G4	61.1%	14.6%	10.1%	10.3%	3.8%

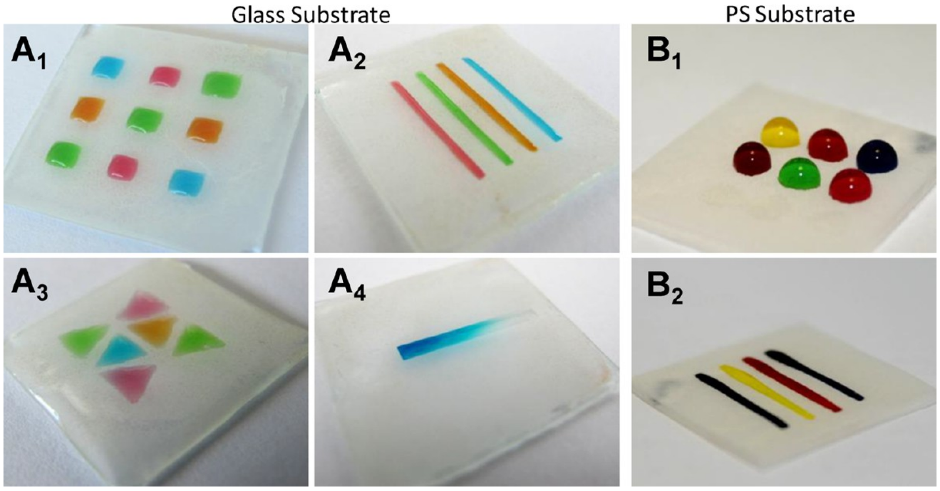

Figure 7. Hydrophilic patterns with different shapes and able to confine liquid volumes can be imprinted on the SH glass surfaces (A_1−A_3), such as on the SH polystyrene surfaces (B_1−B_2). Surfaces with channel-like patterns can be used as platforms to produce material gradients (A_4). The patterns on surface was produced by Argon plasma treatment using masks with the desired shapes.

was also performed by Argon plasma treatment. Because of the possibility of applying the strategy reported on this work in different kinds of substrates, we can envisage the fabrication of devices exhibiting SH surfaces with very distinct properties, aimed to used in different applications.

■ CONCLUSION

We showed here the possibility to produce superhydrophobic surfaces using diatomaceous earth. The natural nano/microstructure of the silica objects provided the necessary rough topography for the surface. After coating a glass surface with diatomaceous earth, the desired hierarchical structure on the surface was obtained because of the anatomic characteristics of the diatom exoskeleton. The wettability of the produced superhydrophobic surfaces can also be precisely controlled by exposing the substrates to plasma treatment for specific times. The control in space of the plasma treatment can be used to imprint hydrophilic patterns on the superhydrophobic surface with well-defined geometries. It was also showed that the proposed strategy could be applied in other substrates, such as polystyrene. This open the possibility to produce superhydrophobic surfaces for specific applications through the choice of the most convenient substrate.

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Notes

The authors declare no competing financial interest.

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