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Modification of nanostructured fused silica for use as superhydrophobic, IR-transmissive, anti-reflective surfaces

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ABSTRACT

In order to mimic and enhance the properties of moth eye-like materials, nanopatterned fused silica was chemically modified to produce self-cleaning substrates that have anti-reflective and infrared transmissive properties. The characteristics of these substrates were evaluated before and after chemical modification. Furthermore, their properties were compared to fused silica that was devoid of surface features. The chemical modification imparted superhydrophobic character to the substrates, as demonstrated by the average water contact angles which exceeded 170°. Finally, optical analysis of the substrates revealed that the infrared transmission capabilities of the fused silica substrates (nanopatterned to have moth eye on one side) were superior to those of the regular fused silica substrates within the visible and near-infrared region of the light spectrum, with transmission values of 95% versus 92%, respectively. The superior transmission properties of the fused silica moth eye were virtually unchanged following chemical modification.

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1. Introduction

Nature has provided numerous examples of materials with surfaces having nanoscale features that serve a practical survival purpose for living species. The material that comprises a moth's eye is one such surface. Upon close examination, it has been revealed that the moth eye comprises an array of nanoscopic features that are responsible for anti-reflection (AR) character [1,2]. The moth eye transmits a large fraction of incident light, allowing the moth to see in dimly lit areas [3]. The AR property of moth eye also allows moths to go visually undetected from predators [4]. In order to mimic the AR quality of moth eye, periodic and randomly nanopatterned surfaces have been produced in an array of materials [4–8]. Finally, though there are some research reports in which substrates are modified with a surface coating to impart moth eye-like AR properties [4–6], directly patterning an AR structure into substrates is a preferable alternative because coatings are subject to delamination under thermal cycling [9].

When nanoscale features are patterned into the surface of a transparent substrate, the shape and dimensions of those features determine the light transmission as a function of wavelength. These features may be ordered or random as long as the features are sub-wavelength in scale. Fused silica is a common substrate material that transmits in the near-infrared (NIR) region of the light spectrum. Although it has been observed that some materials, such as arsenic trisulfide (As_2S_3) glass fibers that were "stamped" or imprinted with a moth eye pattern exhibited superhydrophobicity [10], fused silica is typically hydrophilic and exhibits superhydrophilicity when imprinted with a moth eye pattern [11]. However, if the surface is chemically modified with compounds that contain hydrophobic end groups, the surface could then be made to be hydrophobic [11–14]. In general, surface modified, nanopatterned materials may be useful in numerous field applications such as visible and infrared optical lenses that function in environments where visibility is obstructed due to moisture. Herein we outline a method for the chemical modification of moth eye patterned fused silica for use as self-cleaning, visible and near IR-transmissive, and anti-reflective surface coatings.

2. Experimental

2.1. Materials

1H,1H,2H,2H-perfluorooctyl trichlorosilane (PFOTS) and n-hexanes were purchased from Sigma-Aldrich and used as received.

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UV grade fused-silica substrates were each patterned with random moth eye structures on only one side.

2.2. Surface modification of moth eye substrate

UV grade fused-silica substrates, which were randomly pre-patterned on one side, were subjected to an $O_{2(g)}$ atmosphere for 10 min in a March Plasma Reactive Ion Etcher under a pressure of 320 mTorr, and at a power of 200 W. The substrates were then removed, immersed and wafted for 30 s in hexanes that contained 0.5% PFOTS. The substrates were immediately rinsed with hexanes, blown dry with $N_{2(g)}$ and placed in an oven to bake for 15 min at 120 °C. Finally, the substrates were removed from the oven and allowed to cool.

2.3. Spectroscopic data collection

UV–visible-NIR data were obtained both before and after surface modification using an Agilent Technologies Cary 7000 Universal Measurement Spectrophotometer in the range of 250–2300 nm. Specifically, percent transmission and percent reflectance data were obtained.

2.4. Scanning electron micrograph images

Scanning Electron Micrograph (SEM) images of the substrate surfaces were taken using a Carl Zeiss LEO Supra 55 scanning electron microscope. Images were taken at 0°, 10°, 20° and 30° to better visualize the surface topology.

2.5. Water contact angle measurements

Water contact angle measurements were taken using a Ramé-Hart instrument, model #590-F4. 10 μL droplets of room temperature, deionized water were placed on the surface of the moth eye substrates. Measurements were taken in a 3 by 3 grid fashion, with 9 contact angle values recorded for each substrate (Fig. SI 1). The best value and an average of all 9 values were determined for each substrate. The area of the 10 μL droplets of water that were in contact with the moth eye surfaces was determined by the Cassie-Baxter equation using the average water contact angle values for each substrate. Advancing (CA_{Adv}) and receding (CA_{Rec}) water contact angles were determined using the "sessile drop" method [15].

2.6. Seawater incubation tests

Artificial seawater (meeting ASTM standard D1141-98) was purchased from Lake Products Company, LLC, and used as received. The surface modified fused silica moth eye substrate was subjected to 20 h incubation in artificial seawater. Following incubation in the seawater, CA measurements were obtained in the same fashion as mentioned before (using deionized water, not seawater).

3. Results and discussion

3.1. Surface features and characteristics

The nanopatterning of the fused silica substrates extended ~800 nm into the surface of the material (Fig. 1). The overall surface topology of the nanopatterned surface included randomly distributed, jagged and pointed features of various heights that protruded vertically from the surface of the fused-silica. The tips of the pointed features were tens of nanometers in diameter. These features were unaltered following the chemical surface modification process. Although the moth eye features were jagged and pointed, the PFOTS chemical modification prevented water droplets from being penetrated by these protrusions, and thus the modified fused silica moth eye surface is best described by the Cassie-Baxter surface wetting model rather than the Wenzel surface wetting model [16,17].

3.2. Chemical modification

In order to obtain optimal hydrophobicity, it is important to make the already hydrophilic surface optimally hydrophilic prior to chemical modification. It is equally important to use a cleaning process that does not damage the nanoscale features of the moth eye surface. To accomplish this cleaning task, the surfaces were cleaned using a plasma etching device under an $O_{2(g)}$ atmosphere. Following the plasma etch, the substrates were wafted for 30 s in a solution of hexanes that contained 0.5% PFOTS. This short wafting time in the hexanes/PFOTS solution prevented the buildup of non-specifically bound PFOTS on the surface of the material that could potentially cloud the surface, which would cause a decrease in transmission. Finally, the substrates were thermally cured at 120 °C to solidify bonding between the fused silica and the PFOTS molecules.

Superhydrophilicity was obtained by forming hydroxyl moieties on the fused silica surfaces via the plasma etch process. Because trichlorosilanes readily form self-assembled monolayers (SAMs) on hydroxyl containing surfaces, the etching process made the surface features more amenable to attachment with the trichlorosilane end of the PFOTS molecule [12]. As a consequence, this aligning of the PFOTS molecule on the surface caused the formation of an array of fluorine molecules (which are on the opposite end of the PFOTS molecule) to interface with the air. These fluorine molecules individually occupied a large spatial area, while their collective SAM alignment above the fused silica surface made the entire surface superhydrophobic. This superhydrophobic character can be seen as water droplets come in contact with the surface (SI Movie).

3.3. Water contact angle analysis

Water contact angle (CA) measurements of cleaned fused silica and cleaned fused silica moth eye substrates were taken before and after the surface modification of each substrate. The non-moth eye fused silica substrates returned CA values indicative of a hydrophilic surface (Table 1). For all moth eye substrates, the CA prior to surface modification was found to be nearly 0° (i.e. superhydrophilic) because the fluid readily spread out along the substrate surface upon contact, rendering both the slide angle (SA) and CA immeasurable (Table 1).

Following the surface modification, the fused silica moth eye surface exhibited superhydrophobicity, with the greatest CA being 176° (Fig. 2). The average CA_{After} was 172.8 ± 4.5°, with the error being given in standard deviation of the data set. To determine the amount of water in contact with the low-wettability moth eye surface, the Cassie-Baxter equation was employed:

$$\cos CA_{avg} = \varphi_S(\cos\theta_S + 1) - 1$$

where CA_{avg} is the average water contact angle, θ_S is the intrinsic water contact angle for unmodified, non-moth eye fused silica, and φ_S is the area of the substrate surface in contact with the water. Using this equation, it was determined that the fraction of the water droplets in contact with the moth eye surface was 0.01 (Table 2). By comparison, the Cassie-Baxter value for non-moth eye fused silica was determined to be 0.47, indicating that much more of a single 10 μL droplet of water was in contact with the non-moth eye surface than the fused silica with a moth eye surface topography (Table 2).