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Superhydrophobic and self-cleaning surfaces prepared from a commercial silane using a single-step drop-coating method

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ABSTRACT

A simple and time-saving approach for preparing superhydrophobic and self-cleaning surfaces from a commercial silane, Octadecyltrichlorosilane (ODTS) is reported in this study. A solution of the silane was prepared by dissolving in hexane. Prior to film deposition, the substrates were treated with oxygen plasma etching to remove organic contaminants from the surface followed by immediate immersion in deionized (DI) water to form hydroxyl groups. A few drops of the prepared silane solution were then placed on the treated surface and allowed to dry under ambient conditions. The modified surfaces exhibited superhydrophobic behavior with advancing water contact angles (WCA) in the range 160–170° and the contact angle hysteresis (CAH) less than 10°. Surface characterization with scanning electron microscopy (SEM) and atomic force microscopy (AFM) showed the presence of dual-scale roughness. Dust particles readily adhered to and were washed away with the rolling water droplets placed on the deposited film. Furthermore, the resulting surface was able to maintain these characteristics under the impact of a water jet. It should be mentioned that the demonstrated efficiency of this method makes it very feasible candidate for preparing self-cleaning surfaces for a variety of industrial applications.

1. Introduction

Non-wetting surfaces are very important for several industrial applications such as textiles, electronic devices, battery and fuel cells, etc. Many biological surfaces, particularly some plant leaves, exhibit remarkable non-wetting characteristics [1,2]. The well-known superhydrophobicity of lotus leaves have attracted a lot of attention and have generated great interest in fundamental research [3], as well as in industrial applications. It is well-known that there are two major factors influencing the wettability of a solid surface: surface chemistry, and surface topology [4]. An appropriate combination of a chemical composition that gives low surface energy and a morphology that results in intermediate surface roughness usually result in superhydrophobic behavior.

A wide variety of methods have been adopted to synthesize water-repellent surfaces and their possible applications discussed [5–7]. Several researchers have tried to fabricate patterned surfaces with superhydrophobic characteristics using expensive instrumentation and cumbersome procedures [8]. Moreover, some routes for creation of such surfaces require the repetition of the entire experimental process, which is time-consuming and laborious; hence diminishing their feasibility [9–11]. Therefore, the development of a simple and straightforward technique for preparing superhydrophobic surfaces is currently a major challenge in the area of surface science and technology.

In view of the above, we present here a simple and economical method for the fabrication of superhydrophobic and self-cleaning surfaces on different substrates. A commercially available silane, ODTS, was chosen because of its well-known ability to form self-assembled monolayer (SAM) thin films on various oxidic substrates [12]. The above characteristic has made it very popular especially in semiconductor industry where it is used to form SAM thin films on silicon dioxide substrates. In addition, a large number of commonly used water repellent surface treatments are based on perfluorinated organic compounds (PFC). It has been shown that several perfluorinated compounds (e.g. PFOA and PFOS) are persistent, bioaccumulative and pose a severe risk to human health and the environment [13,14]. Hence, the growing need for the synthesis of

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a fluorine-free superhydrophobic surface was also a driving force behind this work.

2. Experimental procedure

2.1. Materials

The surface coating was prepared from Octadecyltrichlorosilane (ODTS) (>98%), and hexane (anhydrous, 99%) purchased from Sigma Aldrich, USA. All the chemicals were used as received without any further purification. Substrates made of glass micro-slides and plastic holders with removable caps, which were purchased from Somatco Inc., Saudi Arabia were coated with ODTS silane.

2.2. Surface modification

Prior to the silane coating, the glass micro-slides and plastic holder substrates were subjected to oxygen plasma etching to prepare the surface. This type of cleaning involves the removal of impurities and contaminants from surfaces through the use of an energetic plasma or Dielectric barrier discharge (DBD) plasma created from gaseous species. A plasma activated species include atoms, molecules, ions, electrons, free radicals, metastables, and photons in the short wave ultraviolet (vacuum UV, or VUV for short) range.

The plasma is created by using a high frequency voltage to ionise the low pressure gas. The VUV energy is very effective in the breaking of most organic bonds (i.e., C—H, C—C, C=C, C—O, and C—N) of surface contaminants. This helps to break apart high molecular weight contaminants. A second cleaning action is carried out by the oxygen species created in the plasma (O2+, O2−, O3, O, O+, O−, ionised ozone, metastable excited oxygen, and free electrons). These species react with organic contaminants to form H_2O, CO, CO_2, and lower molecular weight hydrocarbons. These compounds have relatively high vapour pressures and are evacuated from the chamber during processing. The resulting surface is usually ultraclean.

The samples were placed inside an Oxygen Plasma Cleaner (Harrick Plasma, Ithaca, NY) and the chamber evacuated with the help of a vacuum pump. After generation of sufficient vacuum (∼100 mbar), the plasma was switched on for a period of 2–3 min. Immediately after that, the specimens were removed and immersed in DI water to hydroxylate the surface. The presence of OH groups on the surface serves as potential binding sites for the silane to be deposited subsequently.

The ODTS solution was prepared by dissolving the silane in hexane with the help of a magnetic stirrer. The concentration of ODTS in the resulting solution was around 0.2 M as was the case for similar silanes in previous studies [15]. The ODTS solution was then poured onto the treated surface drop-by-drop with the help of a disposable dropper. The droplets were added until the solution covered the surface of glass/plastic substrate. The samples were then left for drying overnight under ambient conditions.

2.3. Characterization

The surface morphologies of the coatings were analyzed using a field emission scanning electron microscope (FE-SEM) (Hitachi, S-4800) with images taken from different locations and at various magnifications. The samples were sputter coated with a very thin film of gold for less than a minute to make them electrically conductive. Optical photographs of the specimens with water droplets on them were taken with a digital camera. The water contact angles on the coated surface were measured using a model DM-501 contact angle goniometer (Kyowa Interface Science, Japan) with FAMAS (interFAce Measurement & Analysis System) software. Both static and dynamic (advancing/receding) angles were measured from 5 to 7 different locations and the mean value calculated. Due to high values of WCAs and the not-so spherical shape of the droplet, the tangential method was used to measure the angles from both sides.

Since surface roughness is an important parameter, the surface topology was analyzed using an Atomic Force Microscope from Brukers, Inc. A silicon nitride cantilever was used in the tapping (non-contact) mode with a scan size of 5 μm. The measurements were performed on different locations to obtain a general picture. After the scans, representative 2-d and 3-d images and the roughness profiles were generated from linear sections.

A qualitative assessment of the self-cleaning capabilities of the modified surface was done in the following manner. Dust particles accumulated on the surfaces of solar panels were collected and sprinkled onto the coated specimen. Droplets of DI water were then carefully placed on the surface and the adsorption of dust particles to the droplet was then visually observed. In practical applications, water is sprayed onto surfaces for cleaning purposes. For this reason, the stability of the silane coating was tested under the impact of impinging water jets at high speeds.

3. Results & discussion

3.1. Surface morphology

Generally, surfaces with low energy and high roughness demonstrate high water repellency. Fig. 1a–f shows FE-SEM images of the ODTS coating on plastic substrate at different magnifications. The images at lower magnifications (Fig. 1a and b) show the presence of peaks and valleys with the depth in a few microns. This morphology is expected to allow a large amount of air to be entrapped which is one of the principal requirements of superhydrophobicity.

After a survey of the surface, the peaks were focused to study the morphology at intermediate magnifications. These images reveal the presence of a network of cylindrical fibers with plenty of pores in between (Fig. 1c and d) A similar surface morphology although with much thinner fibers has also been reported by Lichao et al. who fabricated a perfectly superhydrophobic surface using trichloromethylsilane (TCMS) [16] together with toluene and ethanol to form a 3-D methylsiloxane network. The combination of FE-SEM images at varying resolutions (Fig. 1a–d) confirm the presence of dual scale roughness that is most commonly associated with hierarchical structures for natural superhydrophobic surfaces [17–19].

The above findings with regard to the surface morphology may be somewhat surprising because of the hypothesis that alkylchlorosilanes form a self-assembled monolayer with smooth surfaces due to horizontal polymerization on a surface with hydroxyl groups. In fact, several studies with ODTS on different substrates strengthen the idea of well-ordered SAMs that is believed to follow a 3-step process [20]: (i) hydrolysis of chloro moieties of the ODTS at the hydrophilic substrate surface to generate a silanetriol $Si(OH)_3$, (ii) physisorption onto the substrate via hydrogen bonding, (iii) formation of bonds with the substrate and oxygen as well as cross-linking adjacent chains of ODTS molecules.

However, Fadeev et al. [21] in a comprehensive study showed that self-assembly is not the only reaction possible between alkyltrichlorosilanes hydroxylated surfaces. Under certain conditions, especially in the presence of sufficient moisture, vertical polymerization occurs, resulting in the formation of a 3-D siloxane network (Fig. 2). A similar network structure is also proposed by Gao and McCarthy [16] who worked with methyltrichlorosilane (MTCS). The morphology observed in the present study is pretty much similar to Lichao's surface with the only difference being thicker fibers (∼80 nm as compared to ∼40 nm) with lower porosity.