FUNCTIONALIZED COVALENT ORGANIC FRAMEWORKS FOR ICE NUCLEATION INHIBITION

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1. ABSTRACT

Development of passive icephobic surfaces are highly desirable due to their energy, economic and safety implications in various sectors such as aircrafts, wind turbines, power lines and infrastructure. Among few, inhibiting ice nucleation is one of the most primitive strategy in designing effective icephobic surfaces. In this work, we show that surface-grown covalent organic frameworks (COFs) with pore size ~1.8 nm can effectively inhibit the nucleation of ice due to nanoconfinement effect. The effectiveness in delaying ice nucleation is further enhanced by post-functionalization with flexible alkyl chains. It is observed that the flexibility and molecular chain length can also affect the ice nucleation on such surface and this work can help in advancing the design for practical solution against undesirable icing on surfaces.

2. INTRODUCTION

Unwanted ice accretion on surfaces is one of the fundamental problems in nature which poses a serious hazard to the safety and operation of a wide range of applications such as aircrafts, wind turbines, power lines and infrastructure[1, 2]. In the recent years, there has been a growing interest in developing icephobic surfaces, which mainly involve surface modifications to achieve one of the following functionalities: i) repellence towards incoming water droplets ii) delaying ice nucleation and iii) lowering the ice adhesion strength to underlying substrate[2]. According to the classical nucleation theory, nucleation is the first step in the phase transformation from water to ice[3]. Hence inhibiting ice nucleation could be the most effective and primitive strategy in designing icephobic surfaces. The predominant methods of ice nucleation inhibition rely on decreasing the ice nucleation temperature. For example, classical nucleation theory suggests that surface concave nanotextures which are smaller than the critical nucleus radii (often below 5 nm) can potentially inhibit the nucleation of ice[4]. However, fabrication of such textured surfaces with a few nanometer manufacturing precision is an extremely challenging task. Bottom-up nanofabrication approach allows to build up nanostructures through the self-assembly of atoms and molecules and allows to control the pores and surface roughness with high precision. We recently showed that reticular porous materials, covalent organic frameworks (COFs) assembled through solid-vapor interfacial polymerisation offers ~2 nm defect-free nanotexture was able to delay the ice and lime scale nucleation, significantly[5]. Extending on these findings, herein, we have investigated the effect of molecular chain length and flexibility on the ice nucleation used to functionalise the surface-grown COFs. The surface grown COF is prepared using our previously reported methodology and then functionalised with flexible alkyl silanes (Figure 1) of increasing chain length (6, 12 and 18 carbon) and also with a rigid

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fluoroalkyl silane (10 carbon). Perfluoro compounds have been used for the fabrication of liquid repellent surfaces for passive prevention of ice due to their lowest surface energy (< 10 mN m^{-1}) among others. However these compounds have serious health and environmental concerns. To overcome this issue, herein we have utilized alkyl silanes to functionalize the COF surface and have compared their anti-icing performance with the COF surface functionalized with fluoro silane.The fabricated surfaces are characterised for wettability, morphology, roughness and anti-icing performance using various techniques.

3. METHDOLOGY

3.1 Materials: Polished aluminium sheets (1 mm thick and 99.99% purity) were purchased from Alfa-Aesar (Product code - 11333798). All the chemicals including acetone, ethanol, isopropanol, n-hexane, 3-aminopropyl triethoxysilane (APTES), trichloro(hexyl) silane, trichloro(dodecyl) silane, trichloro(octadecyl) silane, perfluoro(decyl) trimethoxy silane, p-phenylenediamine (PDA), octanoic acid, triformylphloroglucinol (TFP) were purchased from Sigma Aldrich. All the chemicals were used without further purification.
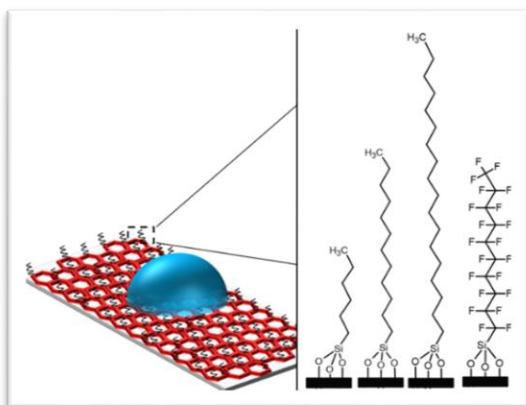

Figure 1 Schematic showing a water droplet on a functionalized COF substrate silanized with four different silanes - (left to right) hexyl silane, dodecyl silane, octadecyl silane and perfluorodecyl silane.

3.2 APTES functionalization: As a first step, aluminium substrate was functionalised with APTES to obtain a layer of amine groups (-NH$_2$) on the top surface which acted as binding site for the COF linker. For this, the aluminium substrates (2.5 cm x 2.5 cm) were washed with acetone, followed by isopropanol and DI water and then dried under a stream of nitrogen gas. The substrates were immersed into 1% n-hexane solution of APTES at room temperature for two hours and then incubated in an oven to cure for one hour at 120 °C. Then the substrtates were rinsed with n-hexane and then dried with nitrogen gas.

3.3 COF fabrication on the aluminium substrate: Nanometre thick COF film was fabricated on aluminium substrates pre-functionalised with APTES [5]. In brief, substrates were placed horizontally in a glass petri dish on a hot plate at 80 °C. TFP (first COF linker) solution was prepared in DMF with a concentration of 5 mg/mL and was spread onto the aluminium substrate with the help of a pipette. The aluminium substrate was covered with another petri dish for 2 hours. After 2 hours, the upper petri dish was removed to let the aluminium substrate dry. Second COF linker, PDA was dissolved in octanoic acid at a concentration of 2 mg/mL in a 100 mL glass beaker with round edges. The substrates were then placed at the edges of this beaker containing the PDA solution such that the TFP coated side of the substrates were directed downwards inside the beaker. This beaker was then placed inside a big glass container (1 L) and the edges of the container was sealed with aluminium foil. The container was then placed in an oven at 150 °C for 12 hours to allow solid-vapor interfacial polymerization reaction. After 12 hours when the polymerization reaction was completed, the substrates were extensively washed with DMF and chloroform and then dried for 12 hours under vacuum at 80 °C.

3.4 Functionalisation of the COF substrates: The as synthesised COF surfaces were functionalised with four different silanes – trichloro(hexyl) silane, trichloro(dodecyl) silane, trichloro(octadecyl) silane and perfluoro(decyl) trimethoxy silane. COF substrates were dipped into 1% of n-hexane solution of the above silanes in a petridish and incubated for 2 hours at room temperature and then cured for 1 hour at 120 °C. The substrates were then thoroughly rinsed with n-hexane to remove the physiosorbed silane molecules and then dried with nitrogen gas.

3.5 Ice nucleation temperature measurement: A benchtop setup was designed to evaluate the ice nucleation temperature. The setup consisted of a peltier element mounted on the top of a four pass copper tube heat exchanger through which a mixture of water and ethylene glycol was pumped. The peltier element was powered with the help of a power supply and a microcontroller. A thermocouple mounted on the peltier was used to monitor and log its' temperature during the experiments. A LabVIEW program was written to measure and log the temperature in an excel file. The substrate was attached to the peltier using a thermal paste. Around 30 droplets, each of 2 μl were then pipetted onto the substrate using a pipette, while the substrate was kept at room temperature. Then, the temperature of the substrate was reduced at a rate of 1°C/min till all the droplets had frozen. A LabVIEW code was used to produce a log of temperature against time and to record an image series from the camera, at a rate of one frame per second. Hence, the temperature of the substrate at each frame was known. Frozen droplets could be easily distinguished from the liquid droplets as they appeared white in the images due to increased light scattering. The information obtained from the images was used to determine the fraction of frozen droplets f_{ice} as a function of temperature using the below equation.

$$f_{ice} = n_{ice}(T)/n_{tot} \qquad (1)$$

In the above equation, $n_{ice}(T)$ represented the number of water droplets which had frozen at a specific temperature T and n_{tot} represented the total number of water droplets pipetted onto the substrate which was 30 in the experiments.

4. RESULTS

Figure 1 shows the schematic, three flexible alkyl molecular chains of various lengths and a rigid fluroroalkyl chain were used in functionalising reticular COF surface. The four different surfaces were characterised to confirm the chemical and morphology of COF surfaces and then subjected to ice nucleation experiments. Pristine (unfunctionalised) COF surface, bare aluminium substrate were used as a control to compare against functionalised regime. The obtained data is shown in Figure 2 A and B. Clearly, pristine COF is excellent in suppressing the ice nucleation compared to bare aluminium substrate as the last few drops freeze at ≈-26°C compared to ≈-23°C on bare aluminium. Furthermore, silanized COF substrates are even better in delaying the ice nucleation compared to the pristine COF substrate with the last few drops freezing at ≈-26.5°C, -27.6°C, -28°C and -27°C on hexyl silane, dodecyl silane, octadecyl silane and fluoro silane respectively.
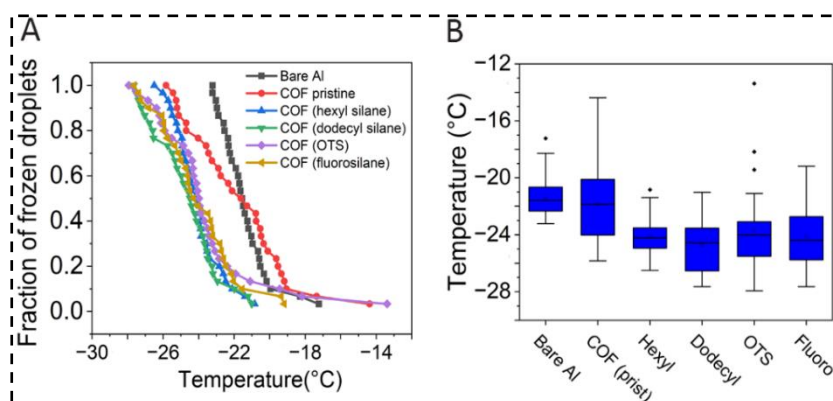

Figure 2 (A) Ice nucleation graph showing fraction of frozen droplets against temperature range comparing different surfaces. (B) Box plot graph showing median nucleation temperature for different surfaces.

5. CONCLUSIONS

Herein, it was concluded that functionalisation with long and flexible alkyl chains has significant impact on ice nucleation. Specifically, the ice nucleation temperature was reduced as the chain length of the alkyl silanes was increased from 6 to 18.

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