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Slippery liquid-infused surface from three-dimensional interconnecting net structure via breath figure approach and its usage for biofouling inhibition

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ABSTRACT

Optical sensors having transparent windows act as the eyes in marine exploration. However, biofouling is a critical problem to blind them. In this report, transparent glass is used as the substrate to grow robust SiO_2 onto the surface via a facile breath figure approach under the temperature of 40 °C. After grafting of long-chain organic molecule, a hydrophobic surface is obtained. The three-dimensional interconnecting net configuration acts as the reservoir for accommodating the lubricant to form the liquid-infused surface. After lubrication with oil phase, SiO_2 performs as the transparent medium for light to transmit. Taking diatom as the representative organism, the surface can effectively inhibit biofouling growth. Time-dependent fluorescent images are used to trace the inhibition effect of the liquid-infused surface. Even immersed in seawater for 11 days, the inhibition efficiency can still maintain 96.1%.

1. Introduction

Biofouling is one ubiquitous phenomenon in different fields related to water environment, such as the medical care, food industry and marine engineering. When solid material is exposed in water environment having living organisms, the biofilm and community composed by bioactive species will build onto the surface, resulting in the biofouling [1–3]. From the interests of human beings, mainly, biofouling is unwelcome. For example, biofouling is a big problem to health care. The NIH estimates that biofilm accounts for over 80% of microbial infection in the body [4]. Although drastically different from the human body, seawater is another environment to introduce the biofouling, due to the existence of many living organisms in this biofluid. The biofouling on shiphulls needs extra energy to consume for the navigation, resulting in the higher cost and more greenhouse gas discharge into the atmosphere. Moreover, other problems can also be caused due to the biofouling, such as the alien species invasion, biocorrosion and so forth [5,6].

Optical sensors having transparent windows act as the eyes to serve in marine exploration fields, and the biofouling is a critical hurdle for its application. Although typical marine engineering, e. g., shiphull, suffers from biofouling, it can still work by paying extra energy consumption. However, once biofouling organisms grow on an optical window, the consequence is serious. The biofouling is mainly composed by the slimy biofilm and other opaque organisms, so that the light to transmit glass window will be unequivocally blocked and attenuated [7–9]. Therefore, the optical information cannot be efficiently achieved, and the eyes in the sea are regarded as blind.

The inhibition of biofouling on optical window is of high significance for marine exploration and research. Several available techniques by using copper and organotin as the biocide have been proposed and employed for alleviating this problem. However, the shortage is that the biocide can also kill other untargeted species in seawater, leading to environmental and ecological concerns. Another efficient way is chlorine generation by consuming the electrical energy. In previous reports, *in situ* electrochemical generation of chlorine has been introduced to prevent glass from biofouling in seawater environment [9–13]. Using conductive glass, chlorine can be produced by electrolyzing Cl^- in seawater. Since Cl^- has an infinite storage in seawater, the antifouling agent precursor is inexhaustible. However, electrical energy is needed, and it only has limited storage for marine usage, which is drastically different from the municipal regions. Therefore, an efficient and energy-saving approach is highly desired for underwater optical window to prohibit biofouling.

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Slippery liquid-infused porous surfaces (SLIPS) have been introduced as the fouling inhibition strategy since 2010 by Aizenberg group [14]. By versatile preparation approaches, the solid surface can be constructed with an oil layer, on which the organisms have low affinity to settle down. Therefore, the attachment will significantly decrease. Based on SLIPS, different fields such as medical care and marine engineering have seen the exceptional biofouling inhibition [15–23]. Up to now, the study focusing on SLIPS to realize marine antifouling of glass surface still remains rare [24]. For constructing SLIPS onto glass surface to prohibit biofouling, several criteria need to be satisfied. Firstly, the surface should be hydrophobic for oil phase to wet. Secondly, the as-prepared hydrophobic matrix should be porous to afford micro/nano scale channels or pores for anchoring oil phase, so that a static liquid oil layer will be constructed on soild surface. Thirdly, as the layer to prohibit the biofouling on the optical window, SLIPS is necessary to be transparent for light to transmit. SiO_2, a typical inorganic material, is easy to be constructed onto glass surface with porous morphology via the facile hydrolysis reaction. On the other hand, breath figure method can be used to fabricate the porous material. For breath figure method in material science, it is another example of inspiration from nature. During breathing, water vapor coming from the human mouth will become the fog. When contacting with a cold surface such as window glass, the fog behaves as droplets with regular array distribution, and the breath figure is observed. Provided an immiscible fluid layer is constructed on cold substrate surface, with the participation of breath figure array, i. e., ordered water droplet, the versatile pattern will finally be achieved. Therefore, breath figure has worked as a facile and sophisticated approach to prepare a variety of materials for over two decades [25–28]. In this report, taking transparent glass as the substrate, robust SiO_2 having three-dimensional interconnecting net configuration has been constructed onto the surface via a facile breath figure approach. The grafting of long-chain organic molecule achieves a hydrophobic surface, which acts as the reservoir for accommodating the lubricant to form the liquid-infused surface. Using diatom as the representative organism, the surface shows highly effective biofouling inhibition to prohibit diatom to grow.

2. Experimental

2.1. Preparation and characterization of porous SiO_2/glass and slippery liquid-infused surface

A piece of bare glass was respectively washed for 5 min in ethanol and acetone bath by using an ultrasonic cleaner. After the drying, it was fixed on a spin coating apparatus (Setcas, KW-4B, Beijing), and a small amount of tetraethyl orthosilicate (TEOS, Ruijinte Chemicals Co. Ltd, Tianjin) was dropped on glass surface. By adopting the speed of 2000 rps for 30 s, the liquid distributed homogenously and evenly on glass surface. Later, the glass carrying TEOS was put into the ammonia gas for 10 min, and temperature was maintained at 40 °C. Small water droplets were formed on the glass surface due to the evaporation of water. Then the glass was taken out of the ammonia gas and put into the drying oven at 40 °C for 20 min. A rough surface with white deposit was achieved.

The modification of the as-formed rough surface is achieved via evaporation of 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (Qinba Chemicals) at the temperature of 120 °C for 4 h in a sealed reactor. After cooling down to room temperature, the hydrophobic surface was obtained. The surface wettability of the glass modified at the different stages was revealed using a contact angle meter (CAM-101, KSV Instruments), and a water droplet (3 μL) worked as the probe at room temperature (25 °C). Droplets were deposited at different places of the bare and as-modified glass, and at least 10 readings were made to determine the average value.

X-ray diffraction (XRD, Bruker D8 Advance) was used to verify the phase composition of the as-formed deposit on glass surface. Field emission scanning electron microscopy (FE-SEM, Zeiss, Ultra 55) and energy dispersive spectroscopy (EDS, INCA Energy, Oxford) were employed to detect the morphology and element distribution of the as-formed surface. For SEM characterization, Pt sputtering coating was used to improve the surface conductivity for acquiring the high resolution image. The surface topology was characterized with atomic force microscopy (AFM, SPI 3800N-SPA 400, Seiko Instrument), and silicon nitride cantilever (Seiko, spring constant 0.02 N/m) was used in imaging process by adopting the contact mode.

For preparing the slippery liquid-infused surface, perfluorinated lubricant (PFL, Nascent FX 6200) and silicone oil (polydimethyl siloxane fluid, dynamic viscosity ca. 500 mm^2/s at 25 °C, Tianjin Zhiyuan Reagent Co., Ltd) was dipped onto the as-prepared surface for realizing the liquid infusion. Spin coater with the speed of 500 rad/min was used for homogeneously infusing the lubricant phase and getting rid of the excess oil on the surface. Water droplet worked as probe for illustrating the sliding property of the slippery liquid-infused surface, and contact angle meter was used for capturing the sliding scenario with time interval of 2 s.

2.2. Diatom suspension preparation

Culture of *Navicula minima* was carried through in the State Key Laboratory for Marine Corrosion and Protection, Qingdao, China. These diatoms were originally isolated from benthic biofilm in Qingdao coast. Solution (5 ml) of f/2 nutrient [29] was added into 1 L filtrated seawater, which was autoclaved at 121 °C for 30 min. The sterile solution for culturing diatom was brought out of the autoclave and cooled down to room temperature. Diatom suspension was endured ultrasound for 2 min and put into the Erlenmeyer flask, which was maintained at 20 °C under a 12:12 h light:dark photocycle.

2.3. Biofouling inhibition of the as-prepared slippery liquid-infused glass surface

The bare slide glass worked as the reference for illustrating the antifouling efficiency of the slippery liquid-infused surface. For evaluating antifouling capability, the glass was intermittently brought out of the diatom suspension for surface status observation using a fluorescence microscope (Leica, DM2500) to count the number of the attaching diatoms. UV–vis spectrophotometer (Hitachi U-2800) was used for measuring the light transmission after immersion for certain days with the light wavelength range from 300 to 800 nm.

3. Results and discussion

3.1. Preparation of three-dimensional interconnecting SiO_2 structure on glass via a facile breath figure method

As shown in Fig. 1a and b, the glass surface is homogeneously covered by the interconnecting net structure. The deposit exists as the net-like wall, which divides the surface to numerous pores with the scale of several micrometer. Using AFM characterization, the surface topology and wall height has been revealed. Fig. 1c shows the uneveness of skeleton and the neighboring area, and peak to valley value reaches as high as 371 nm. In the sampling area, the parameters R_a (arithmetical mean deviation of the profile), R_{rms} (root mean square roughness) and R_z (mean roughness depth) are used to characterize the surface roughness, and the corresponding value is 29.98, 37.42, and 115.0 nm, respectively. Moreover, the plain surrounded by the wall is also sampled for measuring the surface topology, which is shown as Fig. 1d. It is observed that the height variation of the plain is 79.6 nm, which is much smaller than that shown in Fig. 1c. Also, the roughness of plain surface is smaller than the area covering the wall, and R_a, R_{rms} and R_z is 10.46, 13.04, and 40.31 nm, respectively, indicating the flat feature of the surface. With XRD technique, the as-formed deposit is