Colloids and Surfaces A 538 (2018) 140–147

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Research Paper

Designing a transparent organogel layer with self-repairing property for the inhibition of marine biofouling

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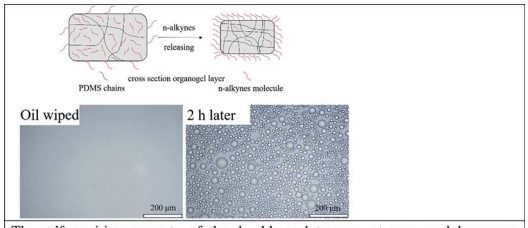
GRAPHICAL ABSTRACT



The self-repairing property of the durable and transparent organogel layer was realised by releasing the n-alkanes between the PDMS chains over the surface.

ARTICLE INFO

Keywords:
Organogel
N-alkanes
Self-repairing
Bacterial inhibition
High under-water transmittance

ABSTRACT

The presence of a biofilm on an optical window of a sensor is one of the main threats to the continued successful operation of marine sensors. A self-repairable and transparent organogel layer (OG) was designed by swelling cross-linked polydimethylsiloxane (PDMS) with the nontoxic *n*-alkanes to restrict the biofilm attachment. Compared with the traditional slippery liquid-infused porous surfaces in the marine biofouling inhibition, the as-prepared OG has a self-repairing property and can maintain high underwater transmittance. Its self-repairing property was verified by the optical microscope images of releasing *n*-alkanes. Meanwhile, the potential of OG to inhibit biofilm formation was verified by a bacterial settlement experiment in a stimulated marine environment. Compared with the bare glassBG and PDMS, the as-prepared OG can efficiently inhibit the bacterial attachment and maintain high underwater transmittance under the static and dynamic conditions. The effect of the chain length of *n*-alkanes on bacterial inhibition was also studied, and results showed that the OG with *n*-alkanes of shorter chain exhibited better performance in bacterial inhibition. This study demonstrates that the as-prepared OG has the potential to protect the marine optical sensor from biofouling.

1. Introduction

Recently, the utilisation of long-term optical marine sensors has paved the way for the monitoring of global climate change and marine environments [1]. However, the biofilm on the optical window is one of the main threats to the utilisation of the marine optical sensors [2,3]. The accumulation of microorganisms on the optical window weakens its underwater transmittance. In turn, the monitoring sensitivity and accuracy are reduced and data acquisition is disrupted.

To date, various strategies have been proposed to control biofouling. Mechanical scraping [4] is effective in cleaning the coastal optical window. However, it is limited by its mechanical complexity

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http://dx.doi.org/10.1016/j.colsurfa.2017.10.079
Received 20 August 2017; Received in revised form 26 October 2017; Accepted 30 October 2017
Available online 31 October 2017
0927-7757/

and expensive cost. The biocide method [5], which is realised by releasing biocides [3,6], is convenient and economical. However, it negatively affects the environment. Given that photocatalytic technology can potentially control biofilm formation [7], photocatalytic nanomaterials have been widely studied [8–11]. However, the photocatalyst can only work when the light is adequate. To address these limitations, many novel strategies have been developed to inhibit the biofouling of marine optical windows. Among them, slippery liquid-infused porous surface (SLIPS), a type of biomimetic material inspired by Nepenthes pitcher plant [12,13], has been extensively reported with the capability to inhibit the bacterial attachment [14–17]. The potential application of SLIPS to marine biofouling control has also been explored [18–20]. Recently, our research group has proposed a novel method for fabricating SLIPS over glass. The as-fabricated SLIPS materials present high underwater transmittance and outstanding anti-biofouling property [21]. The traditional SLIPS is realised by infusing the lubricant into the porous micro-structure over a substrate with the assistance of capillary force [22–25]. However, the slippery property is lost when the lubricant layer is destroyed. Hence, the mechanical stability of the liquid layer should be improved for the practical application of SLIPS in marine environment.

In the current study, a novel organogel layer (OG) with slippery and self-repairing properties and high underwater transmittance was designed and fabricated by swelling the biocompatible polydimethylsiloxane (PDMS) [26] with the *n*-alkanes (*n*-dodecane, *n*-tetradecane, and *n*-hexadecane). The self-repairing property of the as-prepared OG was verified by the optical microscope images of the *n*-alkanes releasing process. The *Pseudoalteromonas* sp. settlement analyses of bare glass (BG), PDMS and OG were conducted to investigate the potential of OG in controlling bacterial attachment. The as-prepared OG can efficiently inhibit the bacterial attachment and maintain higher underwater transmittance compared with BG and the PDMS. In addition, the effect of solvent on the OG was investigated. All these discussions reveal that the OG can be further utilised in marine optical sensors. This research aims to provide a novel method to solve the biofouling problem of marine optical sensors.

2. Materials and methods

2.1. Chemicals and materials

Slide glasses were purchased from Yancheng Feizhou Bosu Co., Ltd., China. N-alkanes (*n*-dodecane, *n*-tetradecane, and *n*-hexadecane) were obtained from Kermel Chemical Reagent Co., Ltd., China. All chemicals were used as received, without any further purification.

2.2. Preparation of OG

PDMS (Dow, Sylgard 184) was prepared by mixing the base and the curing reagent (weight ratio 10:1). Subsequently, the standard mixture was stirred for 20 min to stimulate the reaction. The resulting product was centrifuged at a speed of 4500 rpm for 6 min to remove bubbles. Then, the obtained product was poured into a glass pattern. Finally, the glass pattern with the product was placed horizontally in an oven at 80 °C overnight for curing.

To prepare the OG, the cured PDMS was cut into cubic pieces and immersed in different types of *n*-alkane (*n*-dodecane, *n*-tetradecane and *n*-hexadecane) baths at different temperatures (80 °C, 100 °C, 120 °C, 140 °C and 160 °C) for different lengths of time (1, 2, 4, 6, 8, 12 and 16 h) (Fig. 1). Finally, the swollen PDMS was taken out of the hot solvent and cooled down to room temperature.

2.3. Swelling ratio measurement

The swelling ratio (*SR*) was calculated by the following equation:

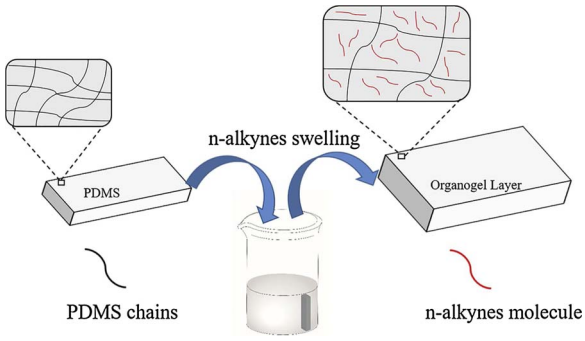

Fig. 1. Preparation of OG: Cross-linked PDMS was immersed in *n*-alkanes, resulting in the diffusion of *n*-alkane molecules into the cross-linked network of the PDMS.

$$SR = V_a/V_b, \quad (1)$$

where V_b represents the volume of the PDMS, which was not soaked into the solvent, and V_a represents the volume of the swollen PDMS.

2.4. Static contact angle and sliding velocity measurement

The static contact angle was measured by a contact angle meter (Powereach, JC200C1, Shanghai, China). Three different water droplets were deposited on different areas of the sample surface. The reported values of the water contact angle represent the average values ± standard deviations of the three replicates. The water sliding disparities of the different OGs were also measured by the contact angle meter (Powereach, JC200C1, Shanghai, China). Before the test, the *n*-alkanes on the OG surfaces were wiped using oil-absorbing sheets. After 2 h, the water droplets (3 μL) were deposited on the OG surfaces with the same titled angle (< 10°). The images of the sliding water droplets were captured one piece per second to determine the distance at which the water droplet dropped in five seconds.

2.5. Transmittance measurement

The underwater transmittance of the samples was measured by an ultraviolet (UV) spectrophotometer (Hitachi, UV-2900, Tokyo, Japan). The BG samples and the samples covered with PDMS films or OG films were immersed into distilled water. The transmittance in the spectral range of 800–300 nm was subsequently tested. To avoid the influence of thickness, the selected PDMS and OG films were set with the same thickness of 10 mm.

2.6. Self-repairing characterisation

An optical microscope (Olympus, ix71, Tokyo, Japan) was utilised to characterise the self-repairing property of OG. The lubricant layer over the OG surface was first wiped by the oil-absorbing sheet, and then the releasing process of *n*-alkanes was observed and recorded with an optical microscope.

2.7. Bacterial settlement analysis

The bacterial settlement experiment was carried out in the culture solution inoculated with model bacteria *Pseudoalteromonas* sp., after which the seed bacteria were injected into the sterilised culture medium prepared by adding 1.00 g yeast extract, 5.00 g peptone and 0.01 g Fe_2SO_4 into 1 L sea water. The as-prepared culture solution was utilised for the bacterial settlement experiments. The BG, PDMS and OG samples were all sterilised by UV radiation for 30 min before attaching vertically onto the wall of the 250 mL beaker using the hot glue. Then, 200 mL as-prepared culture solution was poured into the 250 mL beaker. The bacterial settlement experiments were conducted under static and dynamic environments at 30 °C. To simulate a dynamic