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A biomimetic nano hybrid coating based on the lotus effect and its anti-biofouling behaviors

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ABSTRACT

To develop an environmentally friendly anti-biofouling coating in virtue of bionics, a block copolymer containing fluorine (**Coplm_F**) of low surface energy was prepared by copolymerization. The Ag-loaded mesoporous silica (**Ag@SBA**) acting as a controlled-release antifoulant was prepared from the mesoporous silica (SBA-15). The nano hybrid coating (**Ag@SBA/Coplm_F**) composing of the **Coplm_F** and **Ag@SBA** was to biomimetically simulate the lotus microstructure. The concentration of fluorine element on surface was analyzed by the energy dispersive spectroscopy (EDS) and found rising to 1.45% after hybridation, which could be explained by the driving effect of SBA-15 via the hydrogen bond. This nanoscale morphology of the hybrid coating was measured and found highly semblable to the microstructure of the lotus surface. The contact angle was determined as 151° which confirmed the superhydrophobicity and lotus effect. The adhesion behaviors of *Pseudomonas fluorescens*, *Diatoms*, and *Chlorella* on the surface of the nano hybrid coating (**Ag@SBA/Coplm_F**) were studied and good effects of anti-biofouling were observed.

1. Introduction

The biofouling is a serious problem in all aspects of marine engineering such as shipping, defense, recreation, harbors, drilling platforms and fishery, which are suffered from the accumulation and settlement of barnacles, macroalgae, microbial slimes, and other organisms on man-made surfaces immersed in seawater. Marine biofouling can significantly increase friction resistance and lead to more fuel consumption. Thus, the anti-biofouling coatings are provided to decrease the adhesion of marine organisms and remove them as well. In the recent decades, use of environmentally friendly coatings to replace the traditional tributyl tin [1] and copper containing coatings [2] has attracted researchers' interests. In the last few years, the electrografting technique for reduction of biofouling has been investigated as well [3].

The silver particle has been regarded as an effective, safe, broad and permanent fungicide, and could be regarded as a candidate for the antifoulant [4,5]. Taking into account of both the cost and sustained release, the silver particle is often loaded in mesoporous materials such as the molecular sieves [6,7]. The SBA-15 mesoporous material has generated a great deal of interests in the field of catalysis, drugs, sensing, and adsorption due to its high surface areas and large ordered nano-pores with narrow size distributions [8]. In this study, the silver particle is designed to be embedded into the nano-pores of SBA-15 by ions exchanging and the following reduction. Another trend in the antifouling coating is the using of materials with low surface energy specifically silicone or fluoropolymer based systems, which could minimize the adhesion strength between fouling organisms and the surface of vessels [9–11]. Practically both control-release silver particles and copolymers of low surface energy are complementary functional ingredients in design of hybrid anti-biofouling coatings. The fluorinated multilayered polyelectrolyte films such as PEI/PAA and PEI–Ag(I) complex were prepared and used as the anti-biofouling and superhydrophobic coatings [12–14].

Meanwhile, materials possessing nanoscale topographical features also display the remarkable hydrophobicity and bactericidal activity [15], in addition to the other bioinspired applications such as anti-icing, anti-corrosion coatings, microfluidic devices, textiles, oil/water separation, water desalination/purification,

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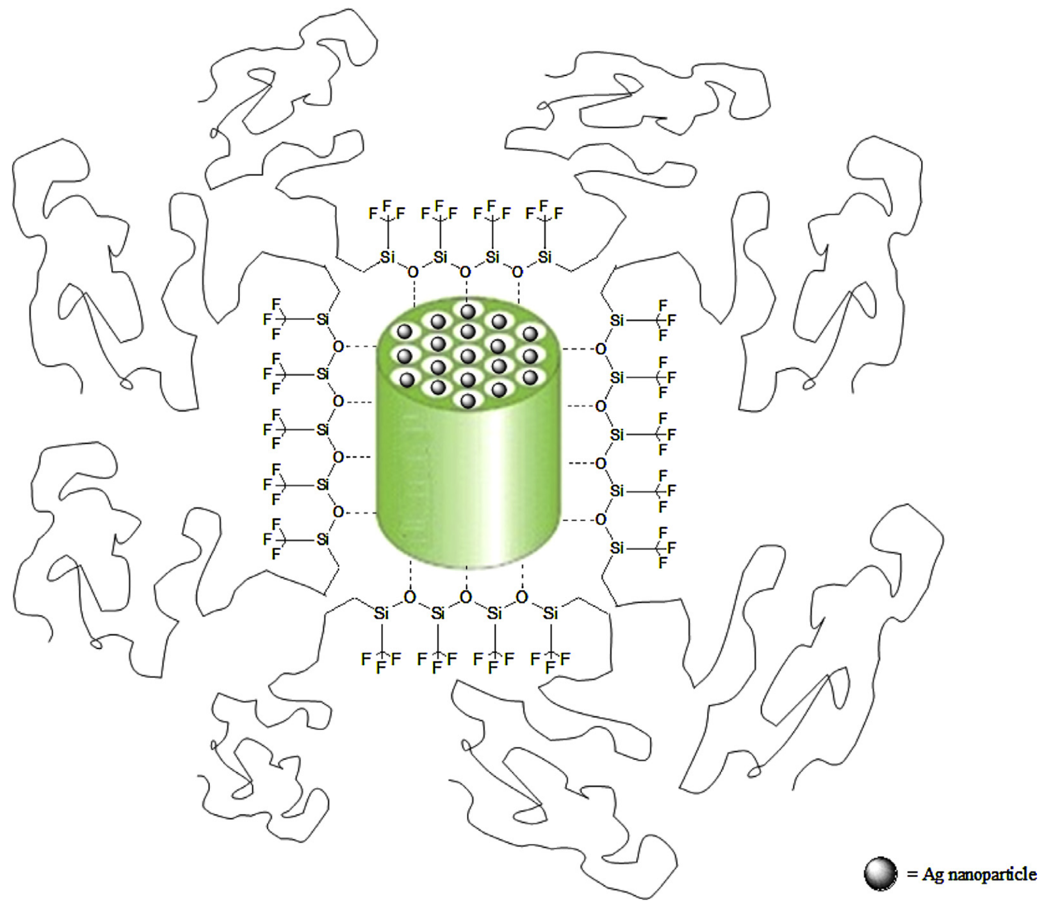

Fig. 1. The schematic view of the biomimetic nano hybrid coating for anti-biofouling.

optical devices, sensors, batteries and catalysts [16]. H. Yang et al. [17] reported a novel lotus-leaf-like antibacterial film fabricated by the microcapsule-supported Ag nanoparticles which was prepared by adsorbing of Ag(I) ions on the surface of sulfonated polystyrene beads via electrostatic interaction and protection by polyvinylpyrrolidone.

Then we are inspired to design a block copolymer containing fluorine in which the Ag-loaded mesoporous silica (**Ag@SBA**) is embedded. The block copolymer containing fluorine (**Coplm_F**) could be prepared from the styrene–butadiene–styrene polymer (SBS) and vinyl fluoride silicone (BD-FT-LSR). The hydrogen bond will be formed between the polysiloxane unit and the hydroxyl group in the outer edge of SBA-15, so a nanoscale hydrophobic region is constructed by the fluorinated groups linking to the polysiloxane unit, which is a rigid phase separation region. The SBS segments of the copolymer are flexible and may act as the molecular hooks to connect the separated rigid regions containing **Ag@SBA** into a macroscopically homogeneous coating by means of the Velcro Effect (Fig. 1). The design purpose of this nano hybrid coating is to biomimetically simulate the lotus microstructure to achieve the marked effect in anti-biofouling.

2. Experimental

2.1. Materials

The styrene–butadiene–styrene polymer (SBS) and vinyl fluoride silicone (BD-FT-LSR) were supplied by Shanghai Sunvea Chemical Material Co., Ltd. The azodiisobutyronitrile (AIBN) was crystallized from an industrial product (Tianjin Guangfu Fine Chemical Research Institute). The other chemical reagents were used as commercially received (Sinopharm Chemical Reagent Co, Ltd.). *Pseudomonas fluorescens*, *Diatoms* and *Chlorella* were supplied by Guangdong Microbiology Culture Center.

2.2. Preparation of the block copolymer containing fluorine (*Coplm_F*)

10 g of SBS (0.16 mol of ethylene unit) and 100 mL of tetrahydrofuran (THF) were taken in a 500 mL round bottom flask and stirred for 0.5 h at room temperature. Then 4.32 g of BD-FT-LSR (0.12 mol of ethylene unit) and 0.1 g of AIBN were added to the flask and stirred for 5 h at 65 °C. The reaction mixture was left overnight and followed by addition of 300 mL of ethanol on stirring. The product precipitated from the solution was filtrated and washed with 2× 30 mL of ethanol. After dried in a vacuum oven at 50 °C for 1 h, 12 g of the white resin-like material (**Coplm_F**) was obtained. The ^{1}H NMR spectra was recorded on a Mercury plus 400 instrument (Varian) for solutions in $CDCl_3$ using $(CH_3)_4Si$ as an internal standard. ^{1}H NMR for **Coplm_F** (400 MHz, $CDCl_3$, δ): 7.09(Ar–**H**), 6.59(Ar–**H**), 5.40(–C**H**$_2$–CF_3), 4.95(Si–O**H**), 2.06(–C**H**$_2$–C–CF_3), 2.03(C**H**$_3$–Si–C–C–CF_3), 1.25–1.43 (butadiene), 0.09 (Si–C**H**$_3$). The infrared spectra (IR) were recorded on a Tensor 27 FT-IR Spectrometer (Bruker). The number-average, weight-average and viscosity-average molecular weight were measured as 114,200, 124,200 and 133,800 respectively by a gel permeation chromatography system (HLC-8320GPC EcoSEC, Tosoh) using tetrahydrofuran (THF) as mobile phase and polystyrenes as the standards.