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Effect of surface topological structure and chemical modification of flame sprayed aluminum coatings on the colonization of *Cylindrotheca closterium* on their surfaces

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ABSTRACT

Biofouling is one of the major problems for the coatings used for protecting marine infrastructures during their long-term services. Regulation in surface structure and local chemistry is usually the key for adjusting antifouling performances of the coatings. In this study, flame sprayed multi-layered aluminum coatings with micropatterned surfaces were constructed and the effects of their surface structure and chemistry on the settlement of typical marine diatoms were investigated. Micropatterned topographical morphology of the coatings was constructed by employing steel mesh as a shielding plate during the coating deposition. A silicone elastomer layer for sealing and interconnection was further brush-coated on the micropatterned coatings. Additional surface modification was made using zwitterionic molecules via DOPA linkage. The surface-modified coatings resist effectively colonization of *Cylindrotheca closterium*. This is explained by the quantitative examination of a simplified conditioning layer that deteriorated adsorption of bovine calf serum proteins on the zwitterionic molecule-treated samples is revealed. The colonization behaviors of the marine diatoms are markedly influenced by the micropatterned topographical morphology. Either the surface micropatterning or the surface modification by zwitterionic molecules enhances antimicrobial ability of the coatings. However, the combined micropatterned structure and zwitterionic modification do not show synergistic effect. The results give insight into anti-corrosion/fouling applications of the modified aluminum coatings in the marine environment.

1. Introduction

As one of the persistent problems for marine infrastructures, biofouling causes huge negative impacts on marine economy [1,2]. Biofouling is a complex process in which the settlement of diatoms plays an important role in deciding the following colonization of other fouling species, such as barnacles, bryozoans and polychaetes [3]. In response to the vast demands for antifouling techniques, a variety of antifouling systems were developed. Yet, none of the available antifouling systems, either toxic antifouling paints or environment-friendly fouling-release coatings, has the capability of effectively preventing the settlement of marine diatoms [4]. Hence, emerging ongoing research efforts have been devoted to developing diatom-resistant systems for marine applications.

To control the settlement of marine diatoms, it is essential to inspect the microenvironmental variables that crucially determine the fate of the diatoms contacting the surfaces of the marine materials. Surface topological structure [3,5–7] and local chemistry [8,9] are the two major factors among those that have been extensively examined. The surface topographies with varying geometry like meshes, pillars, grooves, bumps or holes were fabricated by mimicking the natural topographies of marine organisms [10,11]. Recent studies show that antifouling properties of the artificial structures do not follow a linear relationship with the size of the topographical feature [12,13]. Available studies on the influence of local chemistry of a submerged surface, which is another important factor mediating the settlement of diatoms, are usually based on the use of polymeric materials. Polyethylene glycol (PEG) modified surfaces have shown a competent restriction against protein adsorption, in turn resisting effectively the settlement of marine fouling organisms [14]. However, the intrinsic property limitation is a major hurdle for long term application of the PEG modified surfaces. Recently,

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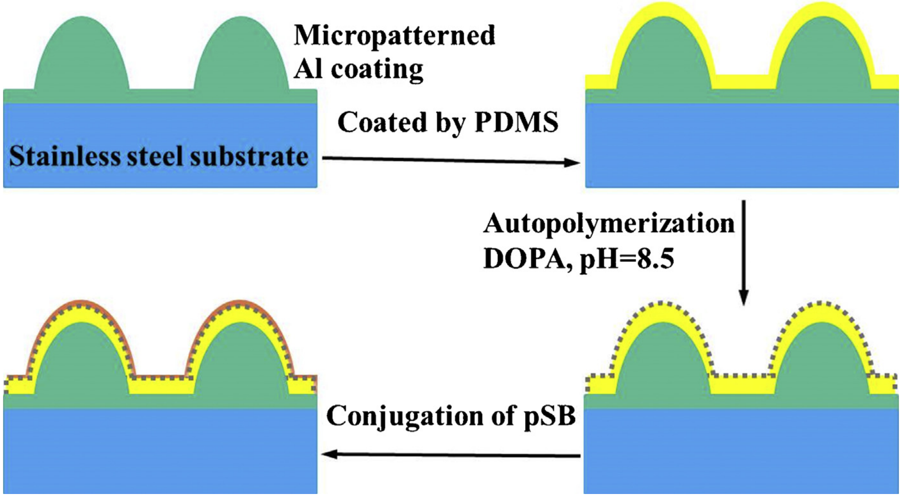

Fig. 1. Schematic depiction showing the construction of the micropatterned Al coatings with additional surface modification.

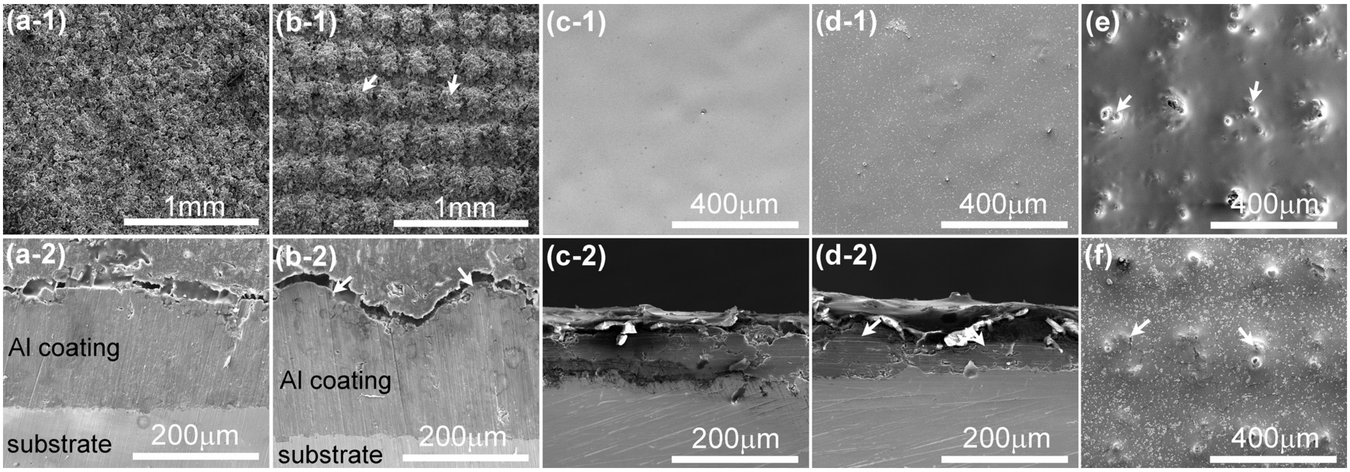

Fig. 2. SEM images of (a) the flat Al coating (a-1: surface view, and a-2: cross -sectional view), (b) the micropatterned Al (b-1: surface view, and b-2: cross -sectional view), (c) the flat Al-PDMS coating sample (c-1: surface view, and c-2: cross-sectional view), (d) the micropatterned Al-PDMS coating sample (d-1: surface view, and d-2: cross-sectional view), (e) the flat Al-PDMS-DOPA-pSB coating sample, and (f) the micropatterned Al-PDMS-DOPA-pSB coating sample. The white arrows point to typical asperities of the patterned aluminum coating.

zwitterionic molecules, such as [2-(Methacryloyloxy) ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) which is neutrally charged in seawater, have been identified effective in reducing adsorption of proteins [15–18]. Effect of the zwitterionic molecules on protein absorption was well demonstrated. However, the mechanism of the resistance of zwitterionic molecules to the settling of marine diatoms keeps unknown. Alterations in either surface topography or surface chemistry have shown a certain success in preventing marine diatom settlement. Appropriate approaches for attaining the alterations are still lacking. Further studies are necessary for developing effective foul-resistant topographies. In addition, several studies have implied that an effective antifouling solution would require multiple physico-chemical properties of a surface [19,20]. Quantitative models involving the combined effects of both surface topography and chemistry on the adhesion tendency of *Ulva* spores have been reported [21,22]. However, to the best knowledge of the authors, there are so far few research publications focusing on the combined effect of surface topography and chemistry on diatom behaviors. This study aims to construct a new aluminum-based coating system with a multi-layered structure for enhanced antifouling performances. The surface micro-topological structure of the coatings was produced by surface micropatterning during flame spraying and further chemical modification was made by depositing a silicone elastomer layer and following zwitterionic molecules via DOPA linkage. The effect of the combined effect of micro-topography (micropattern) and chemical cue (pSB-functionalization) on the settlement of the typical marine diatom *Cylindrotheca closterium* was investigated and elucidated.

2. Experimental setup

2.1. Sample preparation

Commercial pure aluminum powder with the size range of +15 to 45 μm (Beijing General Research Institute of Mining & Metallurgy, China) was used as the starting feedstock. The Sylgard 184 silicone elastomer (Dow Corning, USA) and the zwitterionic molecule [2-(Methacryloyloxy) ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) and 3,4-dihydroxyphenylalanine (DOPA) (Sigma-Aldrich, USA) were used as received. Stainless steel (316 L) plates with the dimension of 20 × 20 × 1.5 mm were used as the substrates. The Al coatings were deposited by flame spray using the FS-4 multi-functional powder flame spray torch (Wuhan Research Institute of Materials Protection, China). Acetylene was used as the fuel gas with a flow rate of 1.5 Nm^3/hr and working

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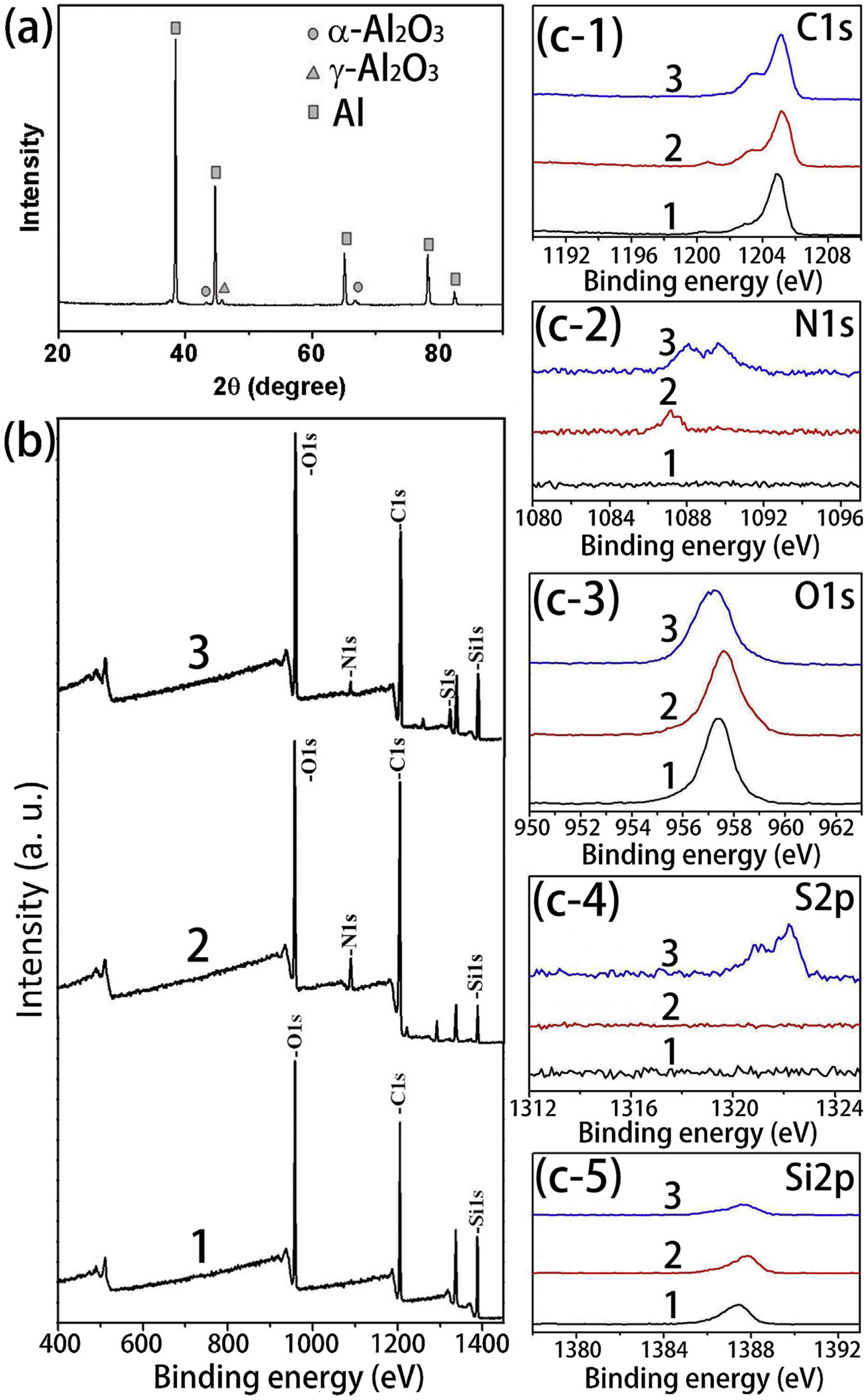

Fig. 3. XRD curve of the Al coating (a), XPS spectra of the surface treated coating samples (b), and high resolution XPS spectra of C 1s, O 1s, Si 2p, N 1s, and S 2p (c). The XPS spectra were acquired from 1: the flat Al-PDMS coating sample, 2: the flat Al-PDMS-DOPA coating sample, and 3: the flat Al-PDMS-DOPA-pSB coating sample.

pressure of 0.1 MPa. The pressure and flow rate of oxygen were 0.5 MPa and 2.5 Nm^3/hr, respectively. The spray distance from the nozzle exit to the substrate surface was 150 mm. Micropatterned topographical morphologies were constructed through the shielding by a stainless steel mesh with the size of 125 μm during the top layer deposition. For following further surface treatment, the micropatterned Al coatings were washed with distilled water and subsequently dried at 60 °C.

Sylgard 184 silicone elastomer was prepared by thoroughly mixing base material and the curing agent (10:1), and then placed standing for 1 h to remove the bubbles. The silicone mix was deposited on both the flat coatings (flat Al-PDMS) and the surface-micropatterned coatings (micropatterned Al-PDMS) using scraping method. After curing at 60 °C for 12 h, the flat Al-PDMS and the micropatterned Al-PDMS samples were immersed in the solution of 50 ml DOPA (2 mg/ml) and 10 mM Tris buffer (pH 8.5) for 12 h in dark. The treated samples were rinsed with distilled water to remove residual DOPA for further treatment. The DOPA-modified samples were then immersed in 50 ml pSB solution (80 ng/ml) with 10 mM Tris buffer (pH 8.5) and treated for 12 h at room

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temperature. Afterwards the samples were rinsed with phosphate buffer saline (PBS) to remove physically adsorbed pSB and dried at room temperature for subsequent characterization. In this paper, the DOPA-modified flat and micropatterned Al-PDMS were designated as flat Al-PDMS-DOPA and micropatterned Al-PDMS-DOPA, respectively. The pSB grafted DOPA-modified samples were designated as flat Al-PDMS-DOPA-pSB and micropatterned Al-PDMS-DOPA-pSB, respectively.

2.2. Surface characterization and antifouling property assessment of the coatings

Microstructure of the coatings was characterized using field emission scanning electron microscopy (FESEM, FEI Quanta FEG250, the Netherlands). Phases of the samples was examined by X-ray diffraction (XRD, Bruker AXS, Germany) with a scanning rate of 0.1 s^{-1} using Cu Kα radiation operated at 40 kV. Chemical composition of the samples was detected using X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Japan). Hydrophobicity/hydrophilicity of the coatings was evaluated by measuring the contact angle of deionized distilled water droplet spreading on their surfaces using a contact angle measurement instrument (Dataphysics OCA20, Germany). And three specimens were measured for each coating sample.

Adsorption of proteins/polysaccharides on marine structures is virtually the key phenomenon involving formation of a conditioning layer that participates as the first step in overall biofouling. Examination of protein adsorption was performed using the same protocol reported previously [23]. The coating samples were placed in 6-well plates containing 1 ml 10% bovine calf serum (BCS, Gibco), followed by incubation for 4 h at 37 °C, and subsequent washing with PBS for three times. The samples were then transferred to the clean well plate that contains 0.5 ml 1 wt.% sodium dodecyl sulfate (SDS) solution in each well. The plate was shaken for 1 h at room temperature to remove the proteins adsorbed on the surfaces of the samples. The protein collected in the SDS solution was quantified by using the MicroBCA protein assay reagent kit.

The marine diatom *C. closterium* (NMBguh002-2, provided by Ningbo University, China) was employed in this study. The diatoms were cultured in artificial seawater-based culture media under sterile conditions at 20 °C. The artificial seawater was prepared following the international criteria ASTM D1141-98 and sterilized before use. Adhesion of the diatoms on the different surfaces was measured in this study. After incubation for 24 h at room temperature, the samples were washed with PBS for three times, fixed by 2.5% glutaraldehyde for 2 h, and dehydrated through the critical point drying using 25%, 50%, 75%, 90%, and 100% ethanol solution. After the fixation, the samples were stained using 150 μl propidium iodide (PI) for 30 min followed by PBS washing for 3 times. The PI stained samples were observed by a confocal laser scanning microscopy (CLSM, TCS SP5, Leica, Germany). Three samples were examined in each group for an average value.

3. Results and discussion

The multilayered structures of the constructed coatings are schematically shown in Fig. 1. Upon fabrication of micropatterned Al coatings, additional surface modification by PDMS, DOPA, and pSB was made successively. Dense Al coatings with the thickness of ~200 μm and relatively flat surface morphology have been fabricated by flame spray (Fig. 2a-1, a-2). The surface micropatterned Al coatings with unique asperities with the size of ~150 μm were readily fabricated (Fig. 2b-1). The surface protuberance of the asperities shows the height of ~70 μm standing on the surfaces of the coatings (Fig. 2b-2). It is noted that the additional construction of the PDMS layer altered the topological feature of the Al coatings without shielding treatment by the steel mesh (Fig. 2c-1, c-2). However, due to the sharp nature of the surface asperities of the mesh-treated coatings, the coatings retained in much extent their topological feature after being coated with the PDMS layer (Fig. 2d-1, d-2). Further treatment by DOPA and following conjugation with pSB can also be clearly seen on the surfaces of the PDMS treated coatings (white particles in Fig. 2e, f). It is likely that polydopamine was formed during the treatment [24].

Table 1
XPS chemical compositions of the samples.

Samples	C (at.%)	O (at.%)	Si (at.%)	N (at.%)	S (at.%)
Flat Al-PDMS	48.80	27.78	23.41	0	0
Flat Al-PDMS-DOPA	50.19	25.97	22.63	1.21	0
Flat Al-PDMS-DOPA-pSB	55.16	26.16	13.68	2.54	2.46

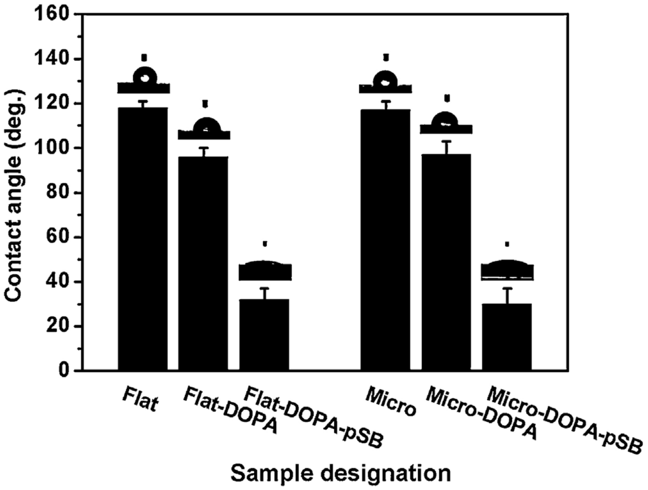

Fig. 4. Water contact angles of the samples.

To examine the Al coatings before and after the additional modification, chemistry of the surface layers was characterized. XRD curve detected from the surface of the Al coating suggests the major component as Al, apart from appearance of Al_2O_3 due to the oxidation of certain amount of Al during the spraying (Fig. 3a). XPS spectra (Fig. 3b) exhibit the peaks for elements C, O and Si, indicating favorable coverage of PDMS on the Al coatings. Additional peak for *N* element can be observed for the flat Al-PDMS-DOPA coating (Fig. 3b, curve 2), which is derived from amino groups of DOPA molecules. Further high resolution XPS spectra for the individual elements show more details about their state in the layers (Fig. 2c). The quantitative data acquired from the XPS detection (Table 1) shows a relatively high content of *N* element, 1.21%, evidencing formation of DOPA on the PDMS layer. After the conjugation with pSB onto the PDMS-DOPA surfaces, the content of *N* further increased to 2.54% (Table 1), which is likely due to a higher content of element *N* in pSB molecules than that in DOPA molecules. Moreover, the high content of 2.46% for element S suggests the presence of pSB film on the PDMS-DOPA surfaces, further confirming successful conjugation of pSB on the surfaces of PDMS. This result is consistent with the results reported in previous studies [25,26].

The wettability of both the flat Al-PDMS-DOPA-pSB and the micropatterned Al-PDMS-DOPA-pSB coatings was also examined with water contact angle measurements (Fig. 4). The contact angle of the flat Al-PDMS-DOPA coatings is ~96°, much lower than that of the flat Al-PDMS coatings (~118°). This result agrees well with a previous study that water contact angle of the samples decreased significantly after DOPA modification [27]. However, the flat Al-PDMS-DOPA-pSB displays a hydrophilic property with a water

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contact angle of ~32°, which is predominately due to the wettable nature of the zwitterionic polymer pSB layer. This is consistent with previous studies that zwitterionic structure exhibits high hydrophilicity [26]. The micropatterned coating samples exhibit similar tendency (Fig. 4), once again confirming successful fabrication of the flat Al-PDMS-DOPA-pSB and the micropatterned Al-PDMS-DOPA-pSB.

It is known that adsorption of extracellular polymeric substances occurs as the first event on submerged substrata in seawater [28], promoting in turn the diatom to settle. Herein, controlling the protein adsorption is a key to mediating the settlement behavior of diatoms. In this study, the protein adsorption on different substrates was quantized with a BCA kit. It is found that PDMS benefits the protein adsorption (Fig. 5). This is why many methods have been attempted to modify the PDMS surface chemically to minimize the protein absorption [5,29,30]. In this study, the effect of the modification by the micropatterning or the pSB functionalization of the PDMS surfaces was investigated. Significantly weakened adsorption of BSA proteins was realized on the flat Al-PDMS-pSB surface as compared to that on the flat Al-PDMS surface (Fig. 5). This could be attributed mainly to the higher hydrophilicity of the samples after the additional pSB modification. In this case, the "surface hydration" theory likely prevails, suggesting a tightly bound water layer formed around the hydrophilic surface [31]. In addition, the electrostatic interaction between BSA and dipole moments of sulfobetaine groups in the zwitterionic polymer as observed by other researchers [32,33] could also account for the antifouling performances. Similar adsorption of albumin was also observed for the micropatterned Al-PDMS and the micropatterned Al-PDMS-DOPA-pSB. The pSB modified samples exhibit similar tendency (Fig. 5). This could explain the constrained settlement of the diatoms on the pSB treated samples.

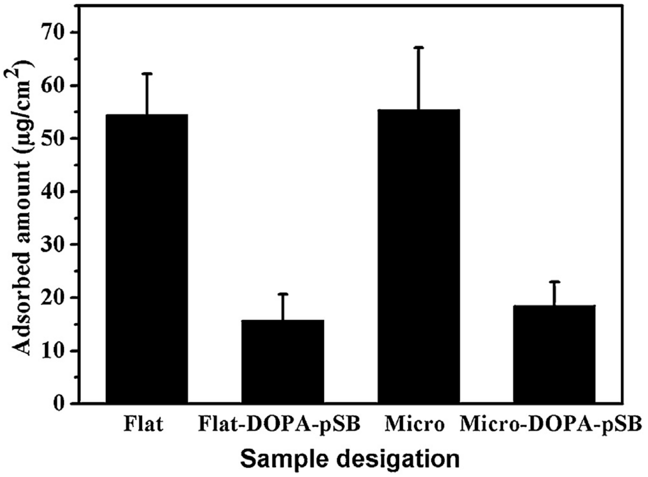

Fig. 5. Quantitative examination of the protein adsorbed on the samples after incubation with bovine calf serum for 4 h. Flat: the flat Al-PDMS sample; Flat-pSB: the flat Al-PDMS-DOPA-pSB sample; Micro: the micropatterned Al-PDMS sample; Micro-pSB: the micropatterned Al-PDMS-DOPA-pSB sample.

To elucidate the joint effects of surface chemistry and topography on the settlement of diatoms, the *C. closterium* cultured on the flat Al-PDMS, the flat Al-PDMS-DOPA-pSB, the micropatterned Al-PDMS and the micropatterned Al-PDMS-DOPA-pSB were also characterized. The morphologies of the *C. closterium* adhering to the samples are shown in Fig. 6. The diatoms opt to adhere to flat surface rather than the island-like structure, which might physically inhibits the diatoms from spreading on the top of the island (Fig. 6c, d). This phenomenon could be explained by the

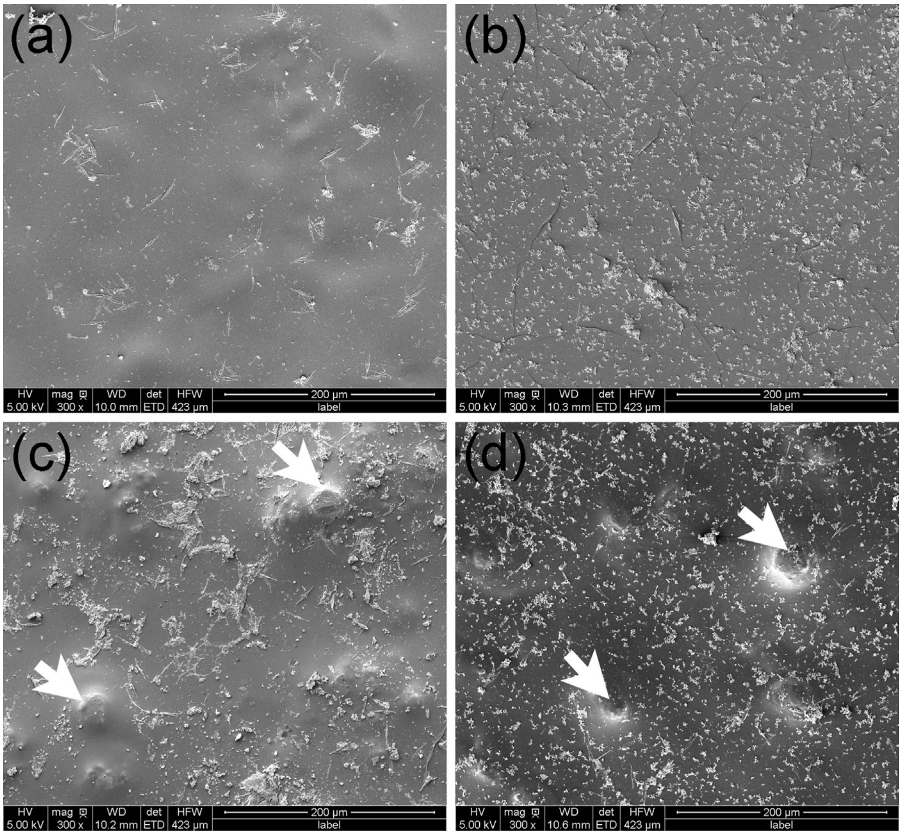

Fig. 6. Images showing the colonization of the diatoms on different samples after 24 h culture. (a) the flat Al-PDMS sample, (b) the flat Al-PDMS-DOPA-pSB sample, (c) the micropatterned Al-PDMS sample, and (d) the micropatterned Al-PDMS-DOPA-pSB sample. The white arrows point to typical asperities of the patterned coatings after the additive modification.

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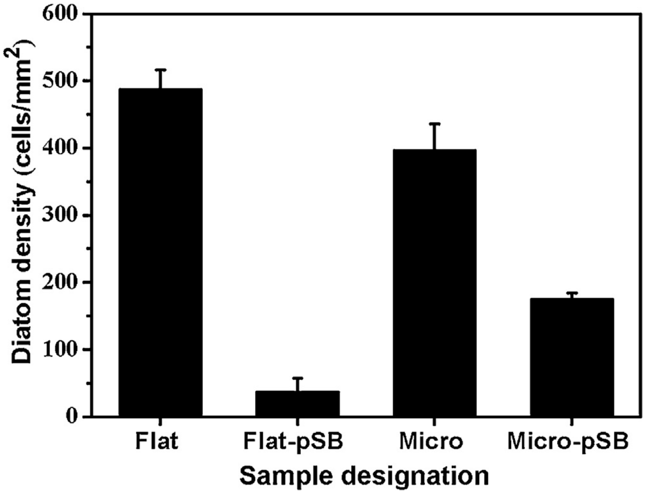

Fig. 7. Quantitative assessment of the diatoms colonized on the surfaces of the samples after 24 h culture. Flat: the flat Al-PDMS sample, Flat-pSB: the flat Al-PDMS-DOPA-pSB sample, Micro: the micropatterned Al-PDMS sample, Micro-pSB: the micropatterned Al-PDMS-DOPA-pSB sample.

attachment point theory that the settlement of diatoms strongly depends on the relative contact surface area between the organisms and the surfaces immerged in seawater [6]. Statistical analysis shows that the micropatterned Al-PDMS surfaces recruit fewer diatoms than the flat Al-PDMS surfaces (Fig. 7). And more diatoms are seen on the unmodified flat/micropatterned Al-PDMS surface, whereas fewer diatoms attach on the flat/micropatterned Al-PDMS-DOPA-pSB surface. The perfect resistance of zwitterionic polymer pSB to protein adsorption likely accounts for the enhanced antifouling performances. Moreover, it is worth to notice that more diatoms adhere to the micropatterned Al-PDMS-DOPA-pSB surface than to the flat Al-PDMS-DOPA-pSB surface, which is likely due to increment of specific surface area of the coatings after the pSB modification. In addition, the interval size of the topological structure is also an important factor affecting the attachment of the diatoms. For the topological structure with small interval sizes, the effect of attachment point theory plays dominant roles in resisting the settlement of the diatoms. In this study, however, the interval size of the topological structure is relatively large. It might not be the key variable participating in mediating the settlement behaviors of the diatoms. To further clarify the distribution and orientation of the diatoms adhered to the coatings, the samples were preliminarily examined by PI staining for CLSM observation. It is well established that upon immersion of a clean surface in sea water, formation of a conditioning layer and following biofilm on the surface usually takes place within minutes to hours. In this study, the incubation time of 24 h was typically chosen for the adhesion assays. After 1 day cultivation of the *C. closterium* on the micropatterned samples, it is realized that the diatoms prefer to adhere to the flat surface and the area around the island-like micro-structure rather than top of the island (Fig. 8). This oriented adherence might be related to the fact that the diatoms reoriented themselves and moved along the surface into preferred positions after their initial settlement on the surfaces. This nevertheless suggests that the topographies of the submerged surfaces strongly influence the settlement behaviors of the diatoms, which has already been proven by the SEM observation (Fig. 6). Our ongoing efforts are

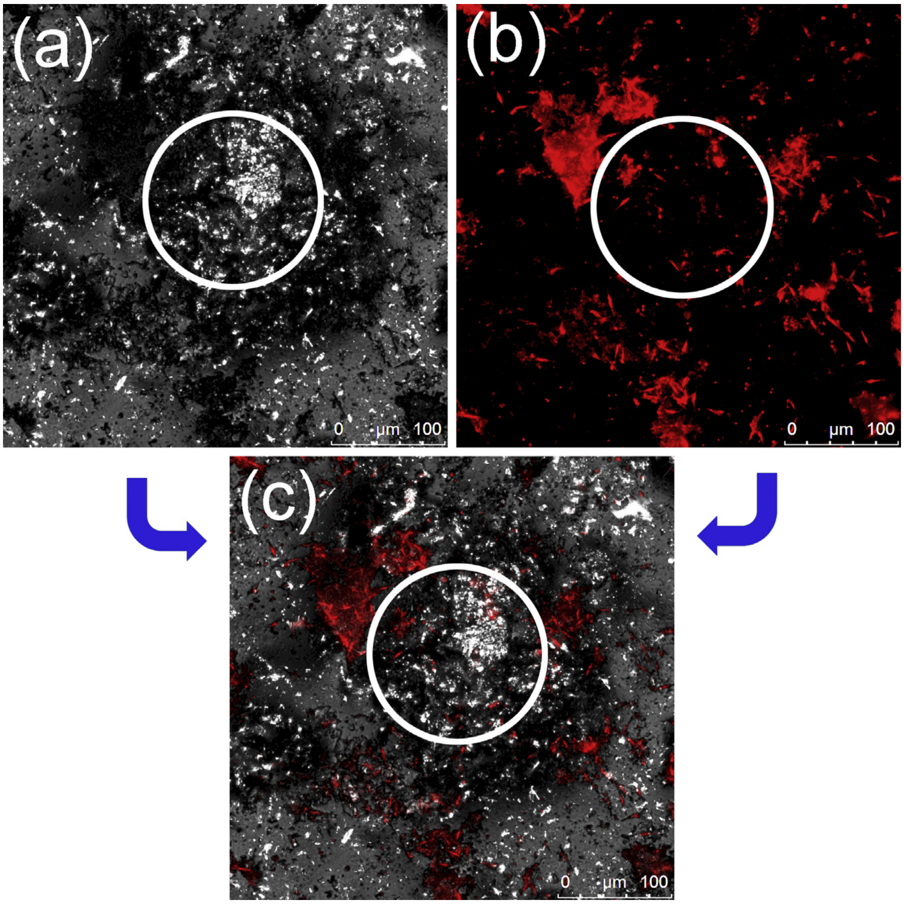

Fig. 8. Morphologies reconstructed from CLSM image stacks showing the colonization of diatoms on the micropatterned Al-PDMS sample after incubation for 24 h. (a) the micropatterned Al-PDMS sample alone, (b) colonized diatoms (in red color), (c) merged image from (a) and (b). The white ring circles the asperity of patterned topographical structure of the coating. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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therefore being devoted to elucidating the effect of the scale of surface topological structure and chemical modification on the settlement behaviors of the diatoms.

4. Conclusions

A multi-layer structure with micro-topological morphology was constructed and further surface chemical modification was made for flame sprayed aluminum coatings. The *C. closterium* diatoms tend to settle on the areas around the locations with protruded topographical features. The zwitterionic polymer-modified surface brought about marked retardation in protein adsorption and diatom adhesion. The micropatterned surfaces show enhanced antimicrobial performances, while the additional pSB surface treatment plays the most significant role in promoting the capability of the coatings to resist settlement of the diatoms on their surfaces. This study provides a simple yet efficient platform for investigating the combined effects of surface topography and chemistry on the colonization behaviors of marine diatoms on marine infrastructures.

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