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Functionalizing aluminum substrata by quaternary ammonium for antifouling performances

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ABSTRACT

Due to the great loss induced by biofouling, developing new strategies for combating biofouling has attracted extensive attention. Quaternary ammonium salts are potent cationic antimicrobials used in consumer products and their use for surface immobilization could create a contact-active antimicrobial layer. Here we report the facile preparation of a contact-active antifouling coating by tethering polyethyleneimine (PEI) onto flat/nanostructured aluminum surface by hydrogen bonding between PEI and AlOOH. Quaternized PEI (QPEI) is obtained through quaternization reactions. Biofouling testing suggests excellent antifouling performances of the samples by declining the adhesion of 95% *Phaeodactylum tricornutum* and 98% of *Chlorella pyrenoidosa*. The antifouling properties of PEI/QPEI are attributed predominantly to their hydrophilic and antimicrobial nature. The technical route of PEI/QPEI surface grafting shows great potential for modifying marine infrastructures for enhanced antifouling performances.

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1. Introduction

Biofouling, a phenomenon occurred by undesirable accumulation of organic substances and microorganisms on submerged infrastructures, is a worldwide problem [1–3]. Biofouling brings a series of detrimental effects such as increased fuel consumption and frictional resistance [4], deteriorated corrosion [5], clogging of membranes and heat exchangers [6], and so on. Biofouling has been fought throughout the history of sailing [7]. Extensive research efforts have been devoted to developing antifouling techniques [8–10]. The most effective technology to minimize or prevent biofouling is the use of paints and coatings comprising biocides (e.g. TBT and copper-based antifoulants) to kill the colonizers [6,9,11,12]. Regardless of their remarkable antifouling performances, copper and TBT still have many concerns as used as antifoulants, for example microalgae and amphora are tolerant to copper while brown and green algae and certain diatoms are resistant towards TBT [13]. Further, use of TBT/Cu-containing coatings has been restricted because of their negative impacts on environment [14]. In addition, the TBT/Cu-based antifouling coatings would lose their antifouling activities as the biocidal substances

get continuously released into the surrounding environment or solution. It is therefore highly desirable to find innovative environment-friendly solutions to combat biofouling [2].

Unlike the release-based antimicrobial substances like TBT and copper ions, quaternary ammonium salts (QAS) offer long-lasting contact-based antimicrobial functions [9,15]. Meanwhile, QAS derivatives have shown broad-spectrum antifouling activity for bacteria, fungi, viruses and algae [16]. It was also found that QAS exhibits amazing antibacterial activities even at very low dosage (15 mg/L) and a short contact duration (4 min) with bacterial cells [17]. The excellent antifouling property of QAS is attributed to the high charge density of QAS, which is responsible for strong electrostatic interactions with the negatively charged cell walls of microorganisms for consequent contact killing [17–19]. It is even likely that QAS could combine with the cytoplasmic membrane of microorganisms and destroys their membrane, resulting in release of intracellular content [17,20], in turn leading to death of the species [17,21].

QAS with effective antimicrobial activity was attempted as environment-friendly antifouling layer for marine applications [9,22,23]. Majumdar et al. fabricated a diversity of polydimethylsiloxane (PDMS) coatings with tethered QAS moieties that have both antifouling and enhanced fouling-release characteristics [18,19,24]. Liu et al. designed PDMS materials incorporated with QAS to accomplish antifouling properties [25]. Shi et al. modified QAS on poly(vinylidene fluoride) (PVDF) dual-layer hollow fiber

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to decrease albumin adsorption and bacterial adhesion [21]. Waschinski et al. proposed an environmentally friendly antifouling approach by bonding quaternary ammonium groups to poly(methyloxazoline) to render contact-active antimicrobial against Gram-positive bacteria [26]. Asri et al. covalently tethered QAS onto hyper-branched polyuria coatings to investigate their contact-antimicrobial activity [27]. Most of the antifouling research on chemically-bound QAS involves modification of polymers, such as polysiloxane [18], cotton, wool, nylon, and polyester [15], reports on constructing QAS layer on metal surface are not seen. Aluminum and its alloys are important engineering materials in many industrial fields in particular marine structures owing to their low density, high specific strength and promising corrosion resistance [28]. In this study, a simple processing route was proposed to assemble QAS on aluminum plates. The typical marine algae *Chlorella pyrenoidosa* and *Phaeodactylum tricornutum* were used as the model microorganisms for antifouling testing. Excellent antifouling properties of QPEI-functionalized aluminum samples were revealed and further elucidated. The inspiring results might give insight into developing effective ways of utilizing QPEI to regulate formation of biofilms on marine infrastructures for enhanced performances.

2. Materials and methods

2.1. Preparation of samples

Aluminum plate substrates with the dimension of 20 mm × 20 mm × 2 mm were used in this study. Before PEI layers were constructed, the substrates were polished to remove the oxide layer, and then ultrasonicated sequentially in acetone and ethanol for 10 min in turn. Subsequently, the substrates were washed with deionized water and dried in vacuum. The surface-polished aluminum substrates were activated by UV irradiation following the following reactions: $3\text{O}_2 + h\nu = 2\text{O}_3$, $\text{O}_3 + \text{H}_2\text{O} + h\nu = \text{O}_2 + \text{H}_2\text{O}_2$, and $\text{H}_2\text{O}_2 + h\nu = 2\cdot\text{OH}$. To achieve different surface roughness, some of the aluminum substrates were boiled in water and the hydroxylation was made following: $2\text{Al} (\text{s}) + 3\text{H}_2\text{O} (\text{g}) = \text{Al}_2\text{O}_3 (\text{s}) + 3\text{H}_2 (\text{g})$, and $\text{Al}_2\text{O}_3 (\text{s}) + \text{H}_2\text{O} (\text{g}) = 2\text{AlOOH} (\text{s})$ [29,30]. The surface-roughening by boiling water treatment is usual for aluminum alloys [31,32], which is attained by both the chemical reaction of Al with H_2O and physical erosion of the air bubbles [30].

PEI ($M_w = 70,000$, 50% in water) was purchased from Sigma Aldrich. It was well established that PEI with primary and secondary amino groups can be easily adsorbed onto any hydroxylated solid surfaces through hydrogen bonds and van der Waals forces [33]. In this case, PEI layer was prepared on the aluminum samples surfaces by immersing the samples into 2 g/L PEI tris buffer solution (15 mM, pH 8.5), and the reaction was carried out for 24 h. After that, the samples were taken out and washed with deionized water to remove unreacted PEI. The PEI treated samples were then soaked in cold ethanol solution of CH_3I (9 mL CH_3I in 15 mL ethanol, Xiya Reagent, China) for quaternization. For the quaternized PEI preparation, after reacting for 24 h in dark room, the samples were washed with excess ethanol and then deionized water to remove unreacted molecules. The reaction procedures are schematically depicted in Fig. 1.

2.2. Characterization of the samples

Microstructural features of the samples were examined by field emission scanning electron microscopy (FESEM, FEI Quanta FEG 250, USA). Further characterization was made by atomic force microscopy (AFM, Bruker Dimension FastScanTM) under PeakForce quantitative nanomechanical mapping (PeakForce QNM) mode.

Changes in chemical composition of the samples were examined by X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Japan) using $\text{Al-K}\alpha$ as radiation resource. Wettability of the samples was assessed by measuring the contact angle of deionized water droplets using a water contact angle measurement instrument (OCA20, Data-physics, Germany).

2.3. Preparation of algal strains and algal adhesion testing

Antifouling performances of the samples were assessed by examining the adhesion of typical marine alga on their surfaces. The adhesion testing was conducted in artificial seawater (ASW) prepared according to ASTM D1141-98. All reagents and solvents were used as received without any further purification. Marine strains *Chlorella pyrenoidosa* (NMBluh015-1) and *Phaeodactylum tricornutum* (NMBguh001) (Ningbo University, China) were typically chosen for the adhesion testing. The spherically shaped *Chlorella pyrenoidosa* was categorized as one of the colonizers on artificial surface in the marine environment [2,34]. *Phaeodactylum tricornutum* is coastal marine pennate diatom that is usually considered as model organism for diatom-related research [35,36], and they participate in the early stage of biofouling and often dominate the fouling [37]. *Chlorella pyrenoidosa* was cultured in enriched filtered sterilized seawater with Guillard's F/2 growth medium, while *Phaeodactylum tricornutum* was cultured in sterilized seawater with silicate-enriched Guillard's F/2 growth medium. The algae were cultured in an incubator with a 12 h: 12 h light/dark cycle at 22 °C. The algae used were in the exponential phase of growth.

4 mL algal suspension with the algal concentration of $5 \times 10^6 \text{ mL}^{-1}$ were used for the adhesion testing. The samples were soaked by the algal suspension in shaker (to avoid deposition) for 7 days with a 12 h:12 h light/dark cycle at 22 °C. After the incubation, the wafers were washed with sterile seawater to remove the algae that did not adhere and then fixed by 2.5% glutaraldehyde in ASW for 2 h. The samples were characterized by confocal laser scanning microscopy (CLSM, Leica TCS SP5, Germany) and FESEM. For the FESEM observation, dehydration of the samples was made through the critical point drying using 25%, 50%, 75%, 90%, and 100% ethanol solution successively.

3. Results and discussion

SEM observation clearly shows the remarkably different topographical morphologies of the samples (Fig. 2). Close view of the surfaces of the boiling-water treated Al plates shows appearance of distinctive topographical features, that is, porous and roughened surface are seen (Fig. 2b–2). Formation of the unique grains is attributed to the chemical reaction between Al and H_2O and physical erosion of air bubble [30–32]. In addition, it is noted that successful grafting of PEI is accomplished on the Al plates (Fig. 2c and d). The additional modification of quaternization by CH_3I brings about non-observable changes in SEM morphology (Fig. 2e and f). For the surface-roughened surfaces of Al plates (Fig. 2b), the grafting of PEI and QPEI both obscured the nanostructures triggered by the boiling water treatment (Fig. 2d and f).

To further recognize the covalent coupling of PEI layer on the surfaces of the Al plates, AFM measurement was conducted (Fig. 3). Results show that the surface roughness of the Al plate is 5.35 nm (Fig. 3a). After the self-assembly of PEI, the surface roughness is significantly increased to 14.3 nm (Fig. 3c). The further quaternization gives rise to an increased roughness of 11.1 nm and clear presence of nanoparticles with an average diameter of ~50 nm (Fig. 3e). The boiling-water treated Al plate shows the topographical features already revealed by SEM observation that

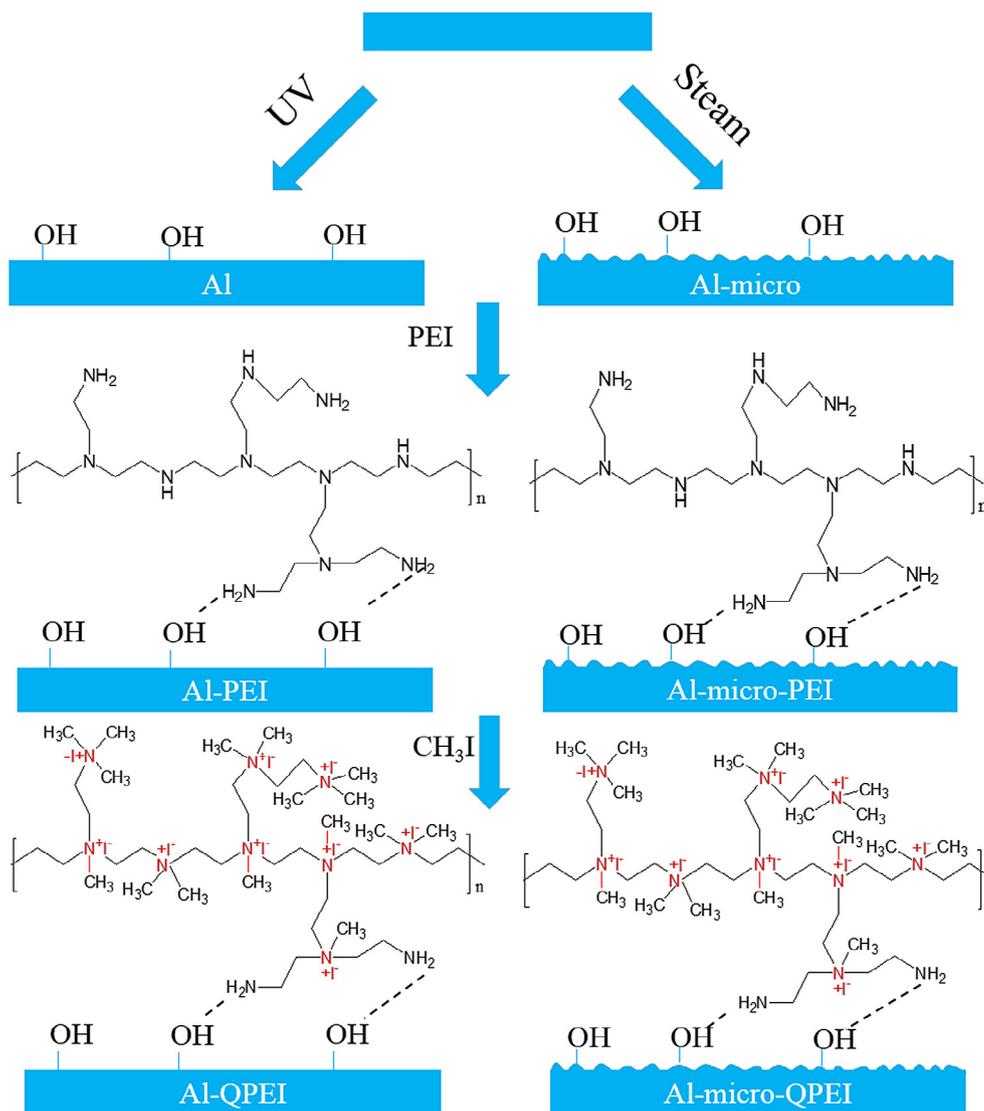


Fig. 1. Schematic depiction showing the surface functionalization of the samples.

the surface consists of patterned grains of ~ 80 nm in height (Fig. 3b), with a surface roughness of 20.9 nm. However, the further grafting of PEI on the patterned Al plate reduces the surface roughness to 10.4 nm, which is likely due to the entire coverage of functionalized PEI (Fig. 3d). The Ra value further drops to 8.07 nm after the quaternization (Fig. 3f). These topographical features together with the altered surface chemistry would affect the bio-fouling behaviors of the samples.

XPS examination further evidences the successful grafting of the functional groups on Al plates (Fig. 4). The XPS spectra for the elements Al, C, O, and N are clearly seen. The N element seen on the curves for the functionalized surfaces is derived from amino groups of PEI molecules. Quantitative data acquired from the XPS detection (Table 1) reveals much higher content of N element on the PEI treated surfaces, 3.739 at.% for the PEI grafted Al plate, and 6.747 at.% for the PEI grafted water-treated Al plate, 1.539 at.% for the Al plate and 0.559 at.% for the water-treated Al plate. This in turn indicates further enhanced grafting of PEI on the surface-nanostructured Al plate (6.747 at.% versus 3.739 at.%). This trend was further retained for the samples even after the quaternization treatment (3.677 at.% for QPEI treated Al plate versus 5.168 at.% for the QPEI/boiling-water treated Al plate). PEI can be easily adsorbed onto any hydroxylated solid surfaces through hydrogen bonds and

van der Waals forces [33]. It is not surprising that since the boiling-water treated Al plate has more active sites on its surface for PEI reaction [29], the plate showed higher N content than other flat samples.

Carbon peak is usually used for internal calibration purposes. The XPS detection already revealed different content of N in the top layer of the samples. The N 1s peaks have their envelopes fitted with one or two components (Fig. 5), showing little amount of N detected for the Al plate and the boiling-water treated Al plate (399.56 eV). The surface of the PEI grafted Al plate is mainly composed of N–C/–NH₂(–NH) (399.80 eV) [38]. It appears that N signal detected from the PEI/boiling water treated Al plate is mainly assigned to C–N in imine (398.64 eV) [38,39] and N–C/–NH₂(–NH) (399.8 eV) [38,40]. In addition, N–C/–NH₂(–NH) peak at 399.50 eV and C–N⁺ peak at 401.50 eV are the main peaks seen for the PEI and PEI/quaternization treated samples [40,41]. The C1s spectra show similar results (Fig. 5), illustrating the binding energy of 284.60–288.15 eV. This suggests the predominate presence of C/C–H/C–C at 284.6 eV [38]. The appearance of a shoulder on the high-binding-energy side of the samples indicates the existence of C–N comprising C–N, C–H (285.70 eV) [38] and C–N (288.00 eV). All the results clearly evidence successful grafting of PEI molecules and the additional

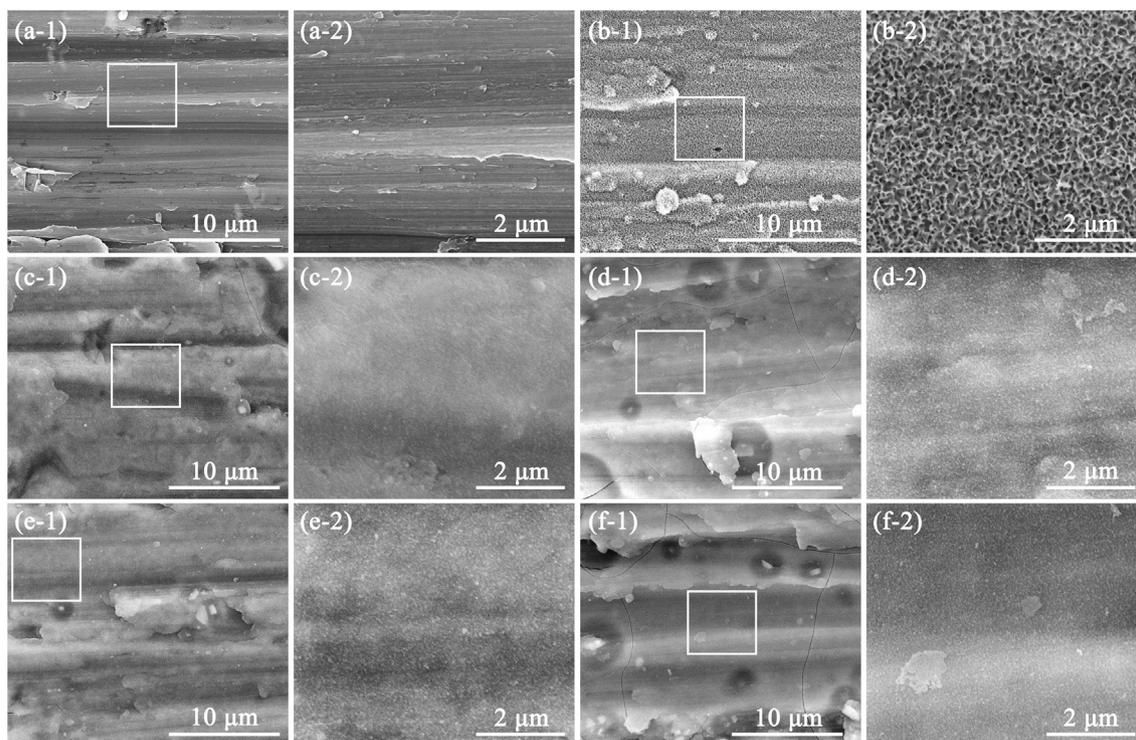


Fig. 2. SEM images showing the topographical morphologies of the Al plate (a), the boiling-water treated Al plate (b), the PEI treated Al plate (c), the PEI/boiling-water treated Al plate (d), the QPEI treated Al plate (e), and the QPEI/boiling-water treated Al plate (f). (–2 is high magnification view of the boxed area in –1, respectively).

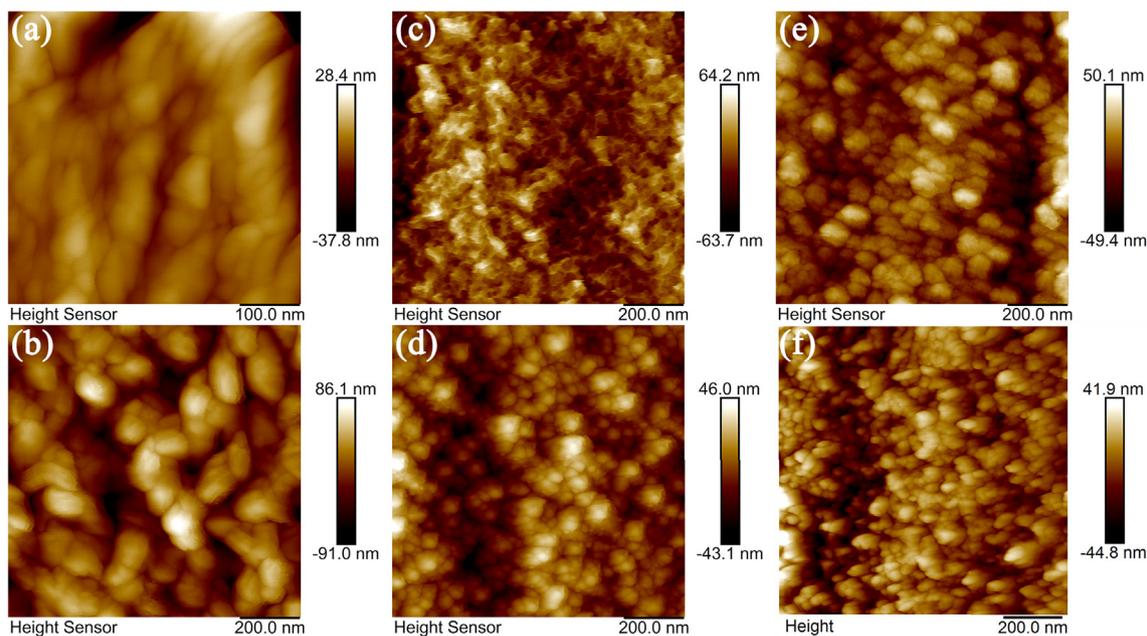


Fig. 3. AFM images showing the surface morphology of Al plate (a), the boiling-water treated Al plate (b), the PEI treated Al plate (c), the PEI/boiling-water treated Al plate (d), the QPEI treated Al plate (e), and the QPEI/boiling-water treated Al plate (f).

quaternization. The PEI/QPEI treated aluminum surface might offer the surface antifouling functions.

The antifouling testing against adhesion of the algae indeed suggests excellent antifouling performances of the PEI/QPEI functionalized aluminum surfaces (Fig. 6). After 7 days incubation in the ASW containing *Phaeodactylum tricornutum* and *Chlorella pyrenoidosa*, the non-treated Al plate already shows entire coverage of the microorganisms (Figs. S1 and S2). It is exciting to note

that the Al plates with surface functionalization of PEI or QPEI show significantly inhibited adhesion and colonization of the algae (Figs. S1 and S2). Statistical analyses of the adhesion were made from at least ten CLSM images for each sample using *ImageJ* software (Fig. 6a). Adhesion rate is defined here as the rate of adhesion area of algae to total surface area of substratum. The adhesion rate of *Phaeodactylum tricornutum* is 10.78% on the Al plate, 0.42% on the PEI treated Al plate, and 0.79% on the QPEI treated Al plate.

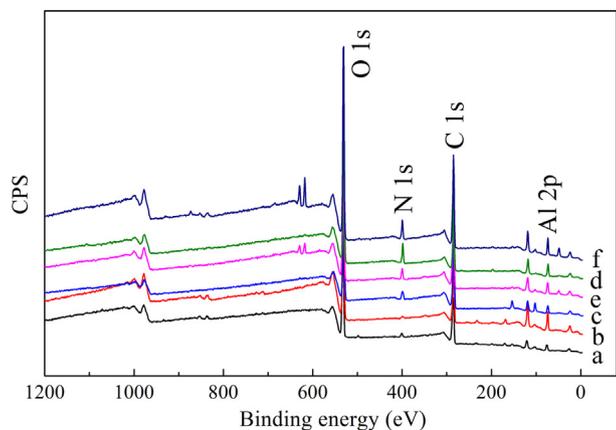


Fig. 4. XPS spectra detected on the surface of Al plate (a), the boiling-water treated Al plate (b), the PEI treated Al plate (c), the PEI/boiling-water treated Al plate (d), the QPEI treated Al plate (e), and the QPEI/boiling-water treated Al plate (f).

Surprisingly, it is noted that the Al plate with nano-patterned structures shows significantly decreased adhesion of *Phaeodacty-*

Table 1
XPS quantitative analysis results.

| Samples | O (at%) | C (at%) | N (at%) | Al (at%) |
|-------------------------------------|---------|---------|---------|----------|
| Al plate | 35.804 | 52.977 | 1.539 | 9.68 |
| Boiling-water treated Al plate | 43.288 | 37.795 | 0.559 | 18.358 |
| PEI treated Al plate | 30.318 | 56.243 | 3.739 | 9.7 |
| QPEI treated Al plate | 35.009 | 49.768 | 3.677 | 11.547 |
| PEI/boiling-water treated Al plate | 34.884 | 46.772 | 6.747 | 11.647 |
| QPEI/boiling-water treated Al plate | 34.771 | 47.852 | 5.168 | 12.209 |

lum tricornutum, 2.82%, which is about four times less than that of the Al plate with relatively smooth surface. Further surface grafting of PEI or QPEI results in further decrease in the adhesion rate, 0.63% and 0.69%, respectively. In addition, similar phenomena are also seen for the adhesion of *Chlorella pyrenoidosa* on the samples (Fig. 6b). The adhesion rate of *Chlorella pyrenoidosa* is 41.80% on the Al plate, 1.20% on the PEI treated Al plate, and 0.86% on the QPEI treated Al plate. Surprisingly, it is noted that the Al plate with nano-patterned structures shows significantly less adhesion of *Chlorella pyrenoidosa*, 13.62%, which is about 32% of the Al plate with relatively smooth surface. Further surface grafting of PEI or QPEI results in further decrease in the adhesion rate, 0.50%.

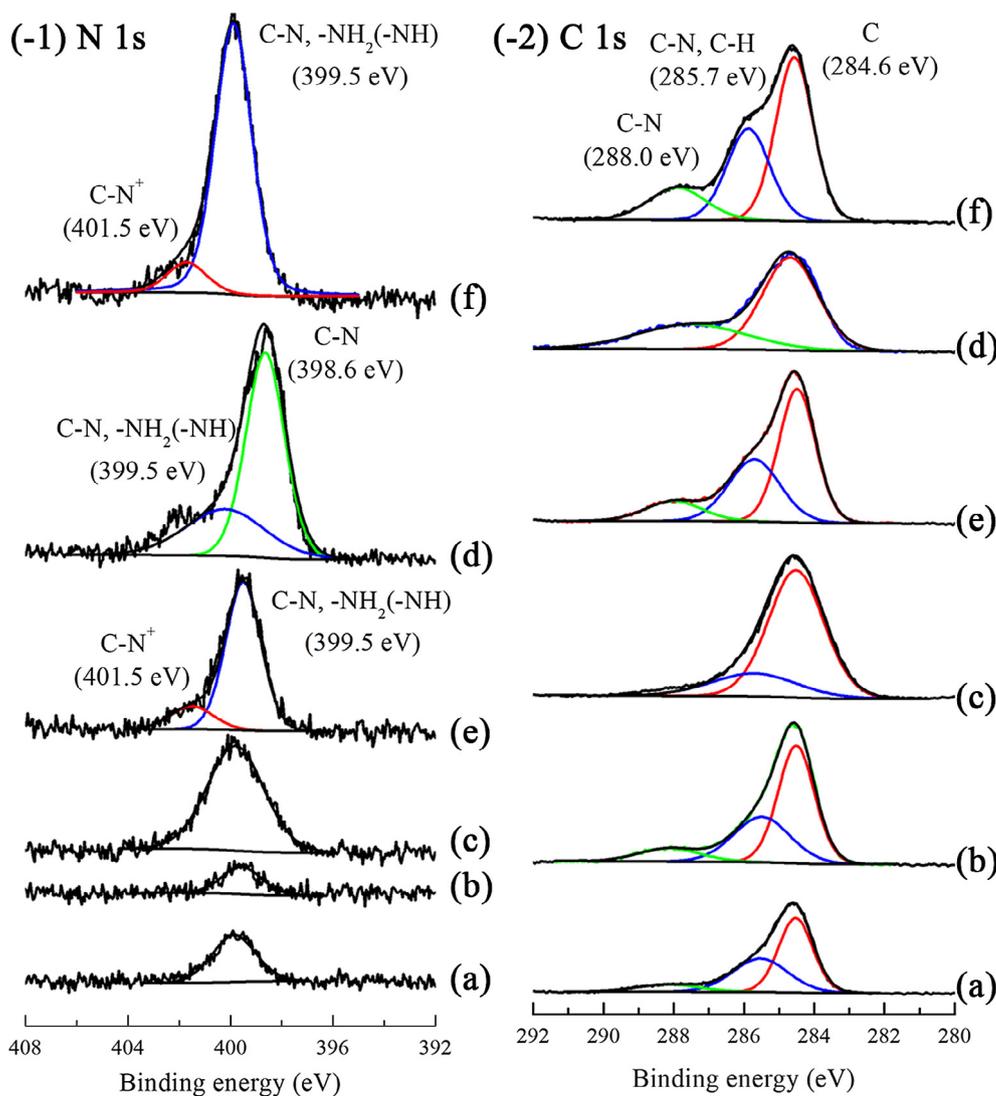


Fig. 5. High-resolution XPS spectra of N 1s (-1) and C 1s (-2) detected on the surface of Al plate (a), the boiling-water treated Al plate (b), the PEI treated Al plate (c), the PEI/boiling-water treated Al plate (d), the QPEI treated Al plate (e), and the QPEI/boiling-water treated Al plate (f).

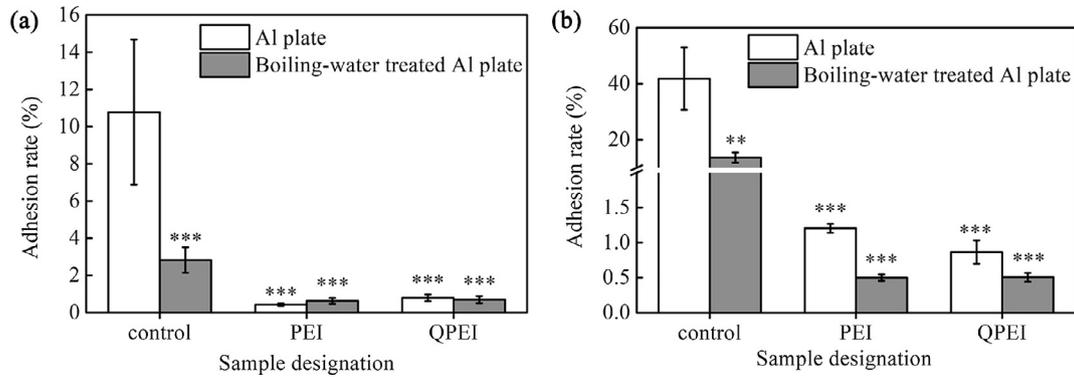


Fig. 6. Statistical adhesion testing results of *Phaeodactylum tricornutum* (a) and *Chlorella pyrenoidosa* (b), error bars are shown as \pm SD ($n = 10$). ***: $p < .005$ as compared with the control groups.

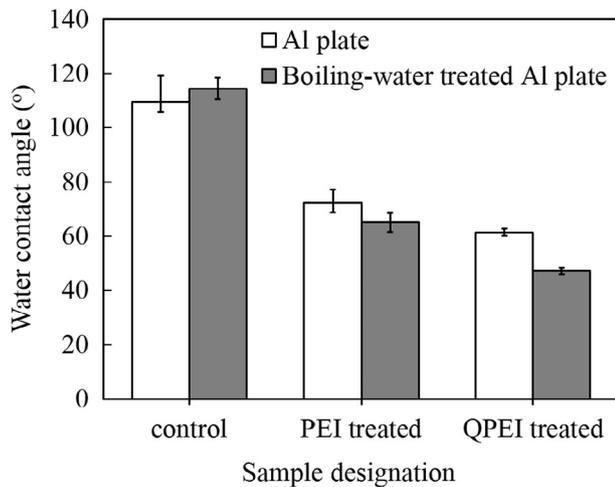


Fig. 7. Water contact angles of the samples.

A variety of factors such as surface tension, surface chemical composition and surface roughness [42,43] play important roles in regulating the adhesion behaviors of microorganisms. The surface nanostructures exhibited by the treated Al plate (Fig. 2b-2) likely give rise to a bridging effect for algae adhesion, since the size is much larger than the spacing between two adjacent nano-grains. Deteriorated attachment is anticipated, which would in turn reduce the adhesion [29]. It is well established that antifouling surfaces prevent microorganisms' attachment not only due to the presence of an unfavorable surface topography, but also owing to surface chemistry [15]. The surfaces grafted by PEI/QPEI already exhibited excellent antifouling properties. Wettability testing shows that the nanostructure of the Al plate attained by boiling-water treatment results in slightly increased water contact angle (114.5° versus 109.6°) (Fig. 7). The surfaces become more hydrophilic after the grafting of PEI/QPEI, showing significantly reduced contact angle to 72.4° and 65.1° , respectively. The PEI layer inherits hydrophilic functional group $-\text{NH}_2$, appealing to water molecules

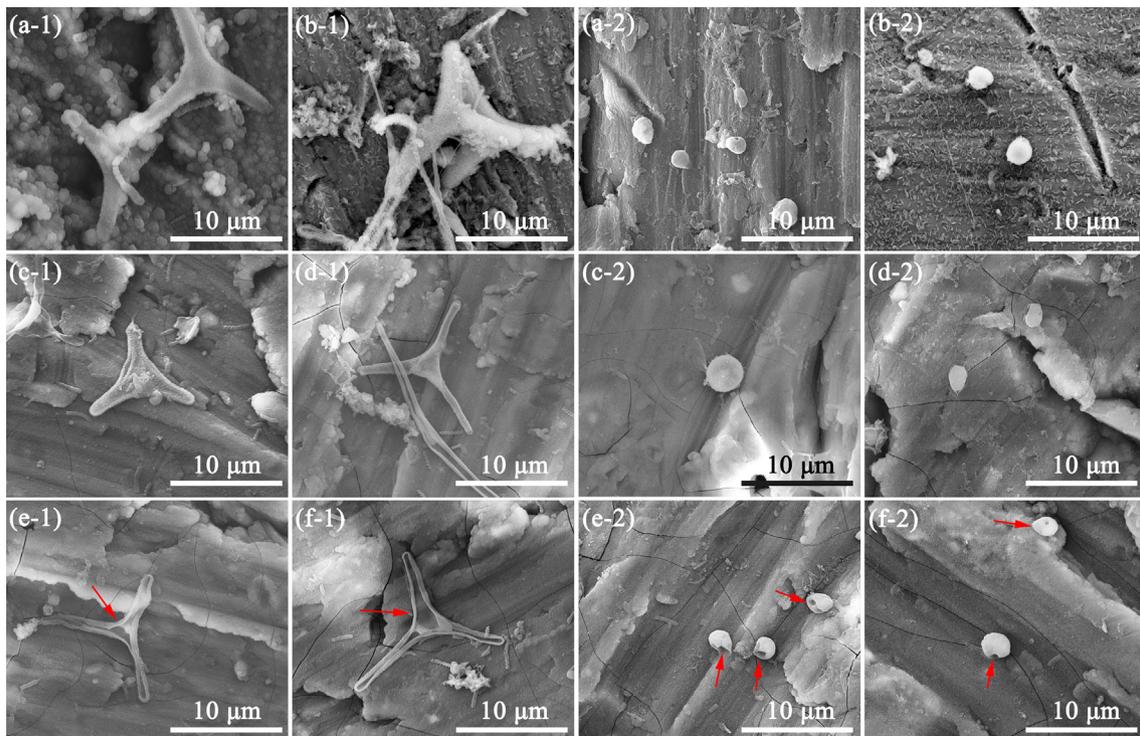


Fig. 8. SEM images showing adhesion of *Phaeodactylum tricornutum* (-1) and *Chlorella pyrenoidosa* (-2) on the Al plate (a), the boiling-water treated Al plate (b), the PEI treated Al plate (c), the PEI/boiling-water treated Al plate (d), the QPEI treated Al plate (e), and the QPEI/boiling-water treated Al plate (f). The red arrows point to typical dead algae (in e-1, e-2, f-1, and f-2).

to approaching the surface by hydrogen bonding. After quaternization, all the treated samples show hydrophilic feature with the water contact angle of 61.5° and 47.2°, respectively. The QPEI groups are hydrophilic due to their ionic nature [19]. The highly hydrophilic surface could easily produce a hydration layer which effectively prevents direct contact of microorganisms with the surfaces. This raises difficulties for microorganisms to achieve favorable adherence, since the microorganisms must overcome certain energy barrier to break through the hydration layer [5,44]. When the distance between bacterium and material surface is less than 3 nm, short-range interactions such as chemical bonding, ionic and dipole interactions and hydrophobic interactions likely play a dominant role in determining the adherence of the microorganisms [45]. It was reported that diatoms prefer to adhere onto hydrophobic surfaces instead of hydrophilic surface, and they adhere weakly to hydrophilic surfaces [46,47]. In this case, the newly constructed hydrophilic surfaces show remarkable capability to decline the adhesion of the diatoms.

Apart from the hydrophilicity, the grafting with quaternary ammonium salt also provides a high positive electrical charge density which facilitates killing a wide range of microorganisms [19]. Morphological characterization of the adhered algae further reveals damaged structure of the microorganisms as accomplished by the contacting quaternary ammonium salt (Fig. 8). These worn structures are only seen for the algae adhered on QPEI treated surfaces (Fig. 8e-1 and f-1). Both *Phaeodactylum tricornutum* and *Chlorella pyrenoidosa* adhered on QPEI treated surfaces exhibit abnormal shape and distinctive damage regime induced by quaternary ammonium salt. It has been claimed that positively charged nitrogen in quaternary ammonium groups electrostatically interacts with negatively charged proteins/polysaccharides in cellular member, causing perturbations [15]. This consequently causes the cells to lose osmoregulation and other physiological functions [15]. The abundant quaternary ammonium groups in the QPEI layers damage both *Phaeodactylum tricornutum* and *Chlorella pyrenoidosa* cells by disrupting their cellular membranes with obvious curls and holes (Fig. 8). It was claimed that these stable surface functionalized layers possess long-lasting contact-based antimicrobial property [15]. The quaternization functionalization would be a promising route for providing marine structures with antifouling performances.

4. Conclusions

Surface functionalization of PEI and QPEI onto aluminum substrata and boiling-water treated Al plate was accomplished and the layer provides the plates with excellent antifouling performances against adhesion of typical algae *Phaeodactylum tricornutum* and *Chlorella pyrenoidosa*. Compared with the pure Al surface, the grafted PEI/QPEI layer declines the adhesion of ~95% of *Phaeodactylum tricornutum* adhesion and ~98% of *Chlorella pyrenoidosa*. The grafting of the antimicrobial substances also remarkably enhances the hydrophilicity of the substrata to inhibit algal adhesion. The results would give insight into construction of nanostructured topologies and easy grafting of antibacterial organics on metal structures for antifouling applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.apsusc.2018.01.109>.

References

- [1] M. Tasso, S.L. Conlan, A.S. Clare, C. Werner, Active Enzyme nanocoatings affect settlement of *Balanus amphitrite* Barnacle Cyprids, *Adv. Funct. Mater.* 22 (2012) 39–47.
- [2] F. Wan, Q. Ye, B. Yu, X.W. Pei, F. Zhou, Multiscale hairy surfaces for nearly perfect marine antibiofouling, *J. Mater. Chem. B* 1 (2013) 3599–3606.
- [3] X. Zhu, D. Janczewski, S. Guo, S.S. Lee, F.J. Parra Velandia, S.L. Teo, T. He, S.R. Puniredd, G.J. Vancso, Polyion multilayers with precise surface charge control for antifouling, *ACS Appl. Mater. Interfaces* 7 (2015) 852–861.
- [4] B.R. Knowles, P. Wagner, S. Maclaughlin, M.J. Higgins, P.J. Molino, Silica nanoparticles functionalized with zwitterionic sulfobetaine siloxane for application as a versatile antifouling coating system, *ACS Appl. Mater. Interfaces* 9 (2017) 18584–18594.
- [5] X. He, Y. Liu, J. Huang, X. Chen, K. Ren, H. Li, Adsorption of alginate and albumin on aluminum coatings inhibits adhesion of *Escherichia coli* and enhances the anti-corrosion performances of the coatings, *Appl. Surf. Sci.* 332 (2015) 89–96.
- [6] A. Rosenhahn, S. Schilp, H.J. Kreuzer, M. Grunze, The role of “inert” surface chemistry in marine biofouling prevention, *PCCP* 12 (2010) 4275–4286.
- [7] S.M. Olsen, L.T. Pedersen, M.H. Laursen, S. Kiil, K. Dam-Johansen, Enzyme-based antifouling coatings: a review, *Biofouling* 23 (2007) 369–383.
- [8] F. Natalio, R. Andre, A.F. Hartog, B. Stoll, K.P. Jochum, R. Wever, W. Tremel, Vanadium pentoxide nanoparticles mimic vanadium haloperoxidases and thwart biofilm formation, *Nat. Nanotechnol.* 7 (2012) 530–535.
- [9] I. Banerjee, R.C. Pangule, R.S. Kane, Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms, *Adv. Mater.* 23 (2011) 690–718.
- [10] S.L. Gaw, S. Sarkar, S. Nir, Y. Schnell, D. Mandler, Z.J. Xu, P.S. Lee, M. Reches, Electrochemical approach for effective antifouling and antimicrobial surfaces, *ACS Appl. Mater. Interfaces* 9 (2017) 26503–26509.
- [11] R.F. Piola, K.A. Dafforn, E.L. Johnston, The influence of antifouling practices on marine invasions, *Biofouling* 25 (2009) 633–644.
- [12] D.M. Yebra, S. Kiil, C.E. Weinell, K. Dam-Johansen, Effects of marine microbial biofilms on the biocide release rate from antifouling paints – a model-based analysis, *Prog. Org. Coat.* 57 (2006) 56–66.
- [13] E. Almeida, T.C. Diamantino, O. de Sousa, Marine paints: The particular case of antifouling paints, *Prog. Org. Coat.* 59 (2007) 2–20.
- [14] H.U. Dahms, X. Ying, C. Pfeiffer, Antifouling potential of cyanobacteria: a mini-review, *Biofouling* 22 (2006) 317–327.
- [15] J. Hasan, R.J. Crawford, E.P. Ivanova, Antibacterial surfaces: the quest for a new generation of biomaterials, *Trends Biotechnol.* 31 (2013) 295–304.
- [16] D. Jiang, Z. Liu, J. Han, X. Wu, A tough nanocomposite hydrogel for antifouling application with quaternized hyperbranched PEI nanoparticles crosslinking, *RSC Adv.* 6 (2016) 60530–60536.
- [17] B. Gao, X. Zhang, Y. Zhu, Studies on the preparation and antibacterial properties of quaternized polyethyleneimine, *J. Biomater. Sci. Polym. Ed.* 18 (2007) 531–544.
- [18] P. Majumdar, E. Lee, N. Patel, K. Ward, S.J. Stafslie, J. Daniels, B.J. Chisholm, P. Boudjouk, M.E. Callow, J.A. Callow, Combinatorial materials research applied to the development of new surface coatings IX: an investigation of novel antifouling/fouling-release coatings containing quaternary ammonium salt groups, *Biofouling* 24 (2008) 185–200.
- [19] C.M. Grozea, G.C. Walker, Approaches in designing non-toxic polymer surfaces to deter marine biofouling, *Soft Matter* 5 (2009) 4088–4100.
- [20] J. Gao, E.M. White, Q. Liu, J. Locklin, Evidence for the phospholipid sponge effect as the biocidal mechanism in surface-bound polyquaternary ammonium coatings with variable cross-linking density, *ACS Appl. Mater. Interfaces* 9 (2017) 7745–7751.
- [21] H. Shi, L. Xue, A. Gao, Y. Fu, Q. Zhou, L. Zhu, Fouling-resistant and adhesion-resistant surface modification of dual layer PVDF hollow fiber membrane by dopamine and quaternary polyethyleneimine, *J. Membrane Sci.* 498 (2016) 39–47.
- [22] R. Piola, C. Grandison, Assessments of quaternary ammonium compounds (QAC) for in-water treatment of mussel fouling in vessel internals and sea chests using an experimental seawater pipework system, *Biofouling* 33 (2017) 59–74.
- [23] A. Cavallaro, A. Mierczynska, M. Barton, P. Majewski, K. Vasilev, Influence of immobilized quaternary ammonium group surface density on antimicrobial efficacy and cytotoxicity, *Biofouling* 32 (2016) 13–24.
- [24] P. Majumdar, E. Lee, N. Patel, S.J. Stafslie, J. Daniels, B.J. Chisholm, Development of environmentally friendly, antifouling coatings based on tethered quaternary ammonium salts in a crosslinked polydimethylsiloxane matrix, *J. Coat. Technol. Res.* 5 (2008) 405–417.
- [25] Y.W. Liu, C. Leng, B. Chisholm, S. Stafslie, P. Majumdar, Z. Chen, Surface structures of PDMS incorporated with quaternary ammonium salts designed for antibiofouling and fouling release applications, *Langmuir* 29 (2013) 2897–2905.

- [26] C.J. Waschinski, J. Zimmermann, U. Salz, R. Hutzler, G. Sadowski, J.C. Tiller, Design of contact-active antimicrobial acrylate-based materials using biocidal macromers, *Adv. Mater.* 20 (2008) 104–108.
- [27] L. Asri, M. Crismaru, S. Roest, Y. Chen, O. Ivashenko, P. Rudolf, J.C. Tiller, H.C. van der Mei, T.J.A. Loontjens, H.J. Busscher, A shape-adaptive, antibacterial-coating of immobilized quaternary-ammonium compounds tethered on hyperbranched polyurea and its mechanism of action, *Adv. Funct. Mater.* 24 (2014) 346–355.
- [28] S. Peng, X. Yang, D. Tian, W. Deng, Chemically stable and mechanically durable superamphiphobic aluminum surface with a micro/nanoscale binary structure, *ACS Appl. Mater. Interfaces* 6 (2014) 15188–15197.
- [29] X. He, Y. Liu, Y. Gong, C. Zhou, H. Li, Autoclaving-induced in-situ grown alumina on arc-sprayed aluminum coatings: multiscaled topography facilitates antifouling performances, *Surf. Coat. Technol.* 309 (2017) 295–300.
- [30] S. Ren, S. Yang, Y. Zhao, T. Yu, X. Xiao, Preparation and characterization of an ultrahydrophobic surface based on a stearic acid self-assembled monolayer over polyethyleneimine thin films, *Surf. Sci.* 546 (2003) 64–74.
- [31] L. Feng, H. Zhang, Z. Wang, Y. Liu, Superhydrophobic aluminum alloy surface: fabrication, structure, and corrosion resistance, *Colloids Surf. A* 441 (2014) 319–325.
- [32] L. Feng, H. Li, Y. Song, Y. Wang, Formation process of a strong water-repellent alumina surface by the sol-gel method, *Appl. Surf. Sci.* 256 (2010) 3191–3196.
- [33] R. Sili, Y. Shengrong, Z. Yapu, Nano-tribological study on a super-hydrophobic film formed on rough aluminium substrates, *Acta. Mech. Sinica.* 20 (2004) 159–164.
- [34] S. Ma, Q. Ye, X. Pei, D. Wang, F. Zhou, Antifouling on gecko's feet inspired fibrillar surfaces: evolving from land to marine and from liquid repellency to algae resistance, *Adv. Mater. Interfaces* 2 (2015) 1500257.
- [35] J. Landoulsi, K.E. Cooksey, V. Dupres, Review – interactions between diatoms and stainless steel: focus on biofouling and biocorrosion, *Biofouling* 27 (2011) 1105–1124.
- [36] K.C. Anyaogu, A.V. Fedorov, D.C. Neckers, Synthesis, characterization, and antifouling potential of functionalized copper nanoparticles, *Langmuir* 24 (2008) 4340–4346.
- [37] N. Poulsen, N. Kroeger, M.J. Harrington, E. Brunner, S. Paasch, M.T. Buhmann, Isolation and biochemical characterization of underwater adhesives from diatoms, *Biofouling* 30 (2014) 513–523.
- [38] W.J. Yang, T. Cai, K.G. Neoh, E.T. Kang, S.L. Teo, D. Rittschof, Barnacle cement as surface anchor for “clicking” of antifouling and antimicrobial polymer brushes on stainless steel, *Biomacromolecules* 14 (2013) 2041–2051.
- [39] S.J. Yuan, S.O. Pehkonen, Y.P. Ting, K.G. Neoh, E.T. Kang, Inorganic-organic hybrid coatings on stainless steel by layer-by-layer deposition and surface-initiated atom-transfer-radical polymerization for combating biocorrosion, *ACS Appl. Mater. Interfaces* 1 (2009) 640–652.
- [40] X.D. Zhang, X.K. Chen, J.J. Yang, H.R. Jia, Y.H. Li, Z. Chen, F.G. Wu, Quaternized silicon nanoparticles with polarity-sensitive fluorescence for selectively imaging and killing gram-positive bacteria, *Adv. Funct. Mater.* 26 (2016) 5958–5970.
- [41] J. Peyre, V. Humblot, C. Methivier, J.-M. Berjeaud, C.-M. Pradier, Co-grafting of amino poly(ethylene glycol) and Magainin I on a TiO₂ surface: Tests of antifouling and antibacterial activities, *J. Phys. Chem. B* 116 (2012) 13839–13847.
- [42] M. Katsikogianni, Y. Missirlis, Concise review of mechanisms of bacterial adhesion to biomaterials and of techniques used in estimating bacteria-material interactions, *Eur. Cells Mater.* 8 (2004) 37–57.
- [43] X. He, J. Wang, L. Abdoli, H. Li, Mg²⁺/Ca²⁺ promotes the adhesion of marine bacteria and algae and enhances following biofilm formation in artificial seawater, *Colloids Surf. B* 146 (2016) 289–295.
- [44] C. Zhao, K. Patel, L.M. Aichinger, Z.Q. Liu, R.D. Hu, H. Chen, X.S. Li, L.Y. Li, G. Zhang, Y. Chang, J. Zheng, Antifouling and biodegradable poly(N-hydroxyethyl acrylamide) (polyHEAA)-based nanogels, *RSC Adv.* 3 (2013) 19991–20000.
- [45] Y.H. An, R.J. Friedman, Concise review of mechanisms of bacterial adhesion to biomaterial surfaces, *J. Biomed. Mater. Res.* 43 (1998) 338–348.
- [46] A. Statz, J. Finlay, J. Dalsin, M. Callow, J.A. Callow, P.B. Messersmith, Algal antifouling and fouling-release properties of metal surfaces coated with a polymer inspired by marine mussels, *Biofouling* 22 (2006) 391–399.
- [47] S. Krishnan, R. Ayothi, A. Hexemer, J.A. Finlay, K.E. Sohn, R. Perry, C.K. Ober, E.J. Kramer, M.E. Callow, J.A. Callow, D.A. Fischer, Anti-biofouling properties of comblike block copolymers with amphiphilic side chains, *Langmuir* 22 (2006) 5075–5086.