

Versatile, Tannic Acid-Mediated Surface PEGylation for Marine Antifouling Applications

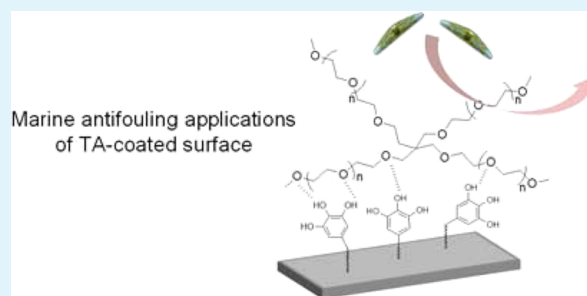
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Supporting Information

ABSTRACT: In this study, we report a facile and versatile approach to the formation of marine antifouling surface coatings. The approach consists of a combined coating of polydopamine (pDA) and tannic acid (TA) and subsequent immobilization of polyethylene glycol (PEG) on solid substrates. TA coating of a pDA-coated surface was carried out using iron(III) coordination chemistry, and PEG was immobilized on the TA-coated surface via hydrogen bond formation. Stainless steel and nylon were successfully modified by this approach, and the resulting substrates were used for marine antifouling applications, in which diatom adhesion was significantly inhibited. Advantageously, this approach allowed marine antifouling coatings to be prepared by a simple immersion process under environmentally friendly conditions.

KEYWORDS: marine antifouling, surface modification, tannic acid, iron(III), polyethylene glycol, diatom adhesion



1. INTRODUCTION

The development of marine antifouling coatings is of importance because severe adhesion of marine organisms onto synthetic surfaces causes increased fuel consumption in marine vessels and malfunctioning of aquaculture instruments.¹ To inhibit the adhesion of marine organisms onto solid substrates, paints containing biocides have generally been used, and as a result, marine fouling was effectively reduced.² However, an environmental issue emerged when the adverse effect of biocides was revealed,³ and the development of environmentally friendly marine antifouling coatings is needed.

Much effort has been made to find new methods for marine antifouling coatings, with a focus on changing the surface chemical composition of solid substrates^{4–13} because the adhesion of marine organisms is known to be highly related to the surface properties of a substrate.^{14–17} In particular, considering that some marine organisms adhere to solid substrates using protein-containing glues,^{18–20} protein-adsorption-resistant materials have been employed to prevent adhesion of marine organisms. For example, Schilp et al. formed hexa(ethylene glycol) (EG₆)-containing self-assembled monolayers (SAMs) on gold, and showed that OH-terminated EG₆-SAMs are highly resistant to diatom adhesion.⁸ In addition to oligo(ethylene glycol) compounds, the marine antifouling properties of poly(ethylene glycol) (PEG) were also investigated by Statz et al., who synthesized L-3,4-dihydroxyphenylalanine (DOPA)-conjugated PEG, and applied this polymer as a coating on titanium surfaces.⁹ The adhesion behavior of diatoms and *Ulva* spores on the PEG-coated surface was analyzed, and excellent antifouling and fouling release properties were identified.

Similar to the PEG coatings, superhydrophilic polymer coatings have also revealed marine antifouling abilities, as well as inhibition of protein adsorption. For instance, Zheng et al. fabricated a sulfobetaine methacrylate (SBMA)-grafted glass surface via surface-initiated atom transfer radical polymerization, and showed that diatoms are unable to adhere to the SBMA-grafted surface.¹⁰ Recently, superhydrophilic polymer coatings were further advanced by combining these coatings with control of the surface topography.^{11,12} Wan et al. grafted 3-sulfopropyl methacrylate (SPMA) on the surface of leaf-like microstructures¹¹ and natural fur,¹² and found that these surfaces inhibit the adhesion of marine microorganisms very effectively. Although PEG- or superhydrophilic polymer-coated surfaces have been successfully implemented in marine antifouling applications, all examples have the critical drawback that they can only be applied to limited types of materials,^{8–12} i.e., they exhibit a lack of versatility, and advancement in coating methods is required.

Very recently, polyphenol-based surface coatings were developed.^{21–24} Ejima et al. reported the surface coating ability of the mixture of tannic acid (TA) and Fe^{III} for the first time,²¹ and Sileika et al. reported that a TA coating can be achieved under high salt conditions (~0.6 M), even in the absence of Fe^{III}.²² Owing to the ease of use and environmental friendliness of the TA coating developed by Sileika et al., various applications were investigated, such as control of bacterial and mammalian cell adhesion, and radical scavenging.²² In spite of the promising applicability, there are still some limitations to

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TA coatings prepared under high salt conditions. The coating does not show versatility, and specific PEG compounds (thiol- or amine-conjugated PEG) are required to control cell adhesion.²² Meanwhile, our group reported a TA coating that consists of a material-independent polydopamine (pDA) coating and Fe^{III}-mediated TA deposition (pDA/TA coating).²³ Given the versatility of our coating method, we speculated that combining the pDA/TA coating with the antifouling properties of PEG would yield versatile marine antifouling coatings. In fact, TA is known to be a good PEG-binding agent in food science.^{25,26} Herein, we report that the pDA/TA coating can serve as an effective platform for marine antifouling surface coating preparation. Utilizing the high binding capability of TA for PEG (via hydrogen bonding), thiol- and amine-free PEG was easily immobilized on the pDA/TA-coated surface. Furthermore, the versatility of the coating enabled diverse marine antifouling coatings to be prepared.

2. MATERIALS AND METHODS

2.1. Materials. Dopamine hydrochloride (98%, Aldrich), Trizma base (99%, Sigma), Trizma HCl (99%, Sigma), iron(III) chloride hexahydrate (FeCl₃·6H₂O, 97%, Sigma-Aldrich), tannic acid (TA, Sigma-Aldrich), fibrinogen (from human plasma, Sigma), four-arm polyethylene glycol methoxy (2k MW, SunBio), stainless steel (Fe/Cr₁₈/Ni₁₀/Mo₃; thickness, 0.25 mm; disc diam., 10 mm, Goodfellow), nylon (thickness, 0.5 mm; size, 50 × 50 mm, Goodfellow), hydrochloric acid (HCl, Junsei), absolute ethanol (Merck), and acetone (99%, Daejung Chemicals & Metals) were used as received.

2.2. Polydopamine (pDA) Coating. Solid substrates were cleaned in acetone or ethanol with sonication prior to use. pDA coating was carried out by immersing substrates in a buffer solution (2 mg of dopamine hydrochloride per 1 mL of 10 mM Tris, pH 8.5) at room temperature for 1 h.²⁷ The coated substrates were rinsed with deionized water and dried under a stream of nitrogen gas.

2.3. Tannic Acid (TA) Deposition. To deposit TA, the pDA-coated substrates were transferred to ethanolic solutions of FeCl₃ (10 mM) and TA (10 mM). The following cycle was generally used for TA deposition on the pDA-coated surface: (1) FeCl₃ for 1 s, (2) rinsing with ethanol, (3) TA for 1 s, and (4) rinsing with ethanol. Further experiments were carried out after 5 repetitive treatments with FeCl₃ and TA.

2.4. PEGylation. PEG was grafted to the pDA-coated and pDA/TA-coated surfaces by incubating the solid substrates in an acidic solution of PEG (1 mg/mL, 0.01 M HCl) for 10 min. The resulting substrates were rinsed with deionized water and dried under a stream of nitrogen gas.

2.5. Protein Adsorption. For the protein adsorption study, nontreated, pDA-, pDA/PEG-, pDA/TA-, and pDA/TA/PEG-coated surfaces were incubated in a PBS buffer solution of fibrinogen (0.1 mg/mL). After 1 h, the substrates were washed with distilled water and dried under a stream of nitrogen gas.

2.6. Diatom Adhesion. *Amphora coffeaeformis* was received from the Korea Marine Microalgae Culture Center (KMMCC) and grown in 100 mL of f/2 culture medium at 18 °C for 10 days. The cell suspension (13 mL) was added to Petri dishes containing the solid substrates, and after 1 day at room temperature, the substrates were washed in seawater to remove cells that had not attached to the solid substrates. The attached cells were characterized and counted by optical microscopy (Nikon, LV100ND).

2.7. Characterization. X-ray photoelectron spectroscopy (XPS) was carried out using a MultiLab 2000 (Thermo VG Scientific) with a Mg K α X-ray source and ultrahigh vacuum ($\sim 10^{-10}$ mbar). The thickness of the organic layers on the solid substrates was measured using a M-2000D ellipsometer (J.A. Woollam Co.). Static water contact angle measurements were carried out using a Phoenix-300 TOUCH goniometer (Surface Electro Optics Co., Ltd.). Fourier-transform infrared spectroscopy (FT-IR) was carried out in single-reflection mode using a dry N₂-purged Thermo Nicolet Nexus FT-IR

spectrophotometer equipped with the smart SAGA (smart apertured grazing angle) accessory. The *p*-polarized light was incident at 80° relative to the surface normal of the substrate, and a narrow band mercury–cadmium–telluride (MCT) detector cooled with liquid nitrogen was used to detect the reflected light.

3. RESULTS AND DISCUSSION

The preparation of the marine antifouling surface coating was carried out using a three-step procedure: (1) pDA coating, (2) Fe^{III}-mediated TA deposition (Fe^{III}-TA), and (3) PEGylation resulting in pDA-, pDA/TA-, and pDA/TA/PEG-coated surfaces, respectively (Figure 1). Recently, Caruso and co-

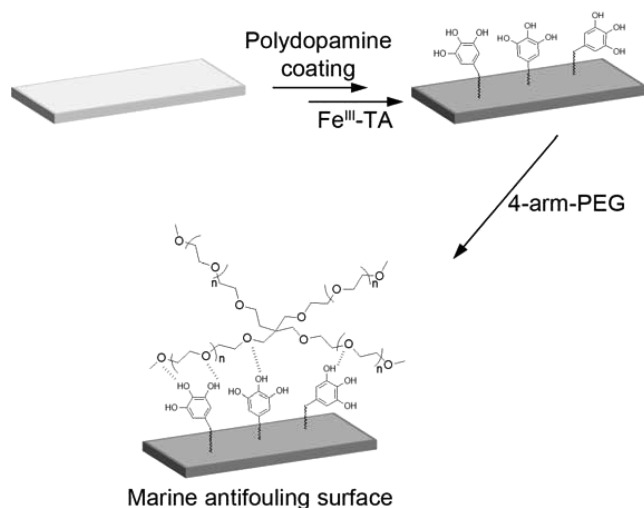


Figure 1. Schematic illustration of the preparation of the marine antifouling surface coating.

workers successfully deposited TA layers on solid substrates²¹ and also reported that the grafting precursor layers, polyethylenimine, enhanced the adhesion of TA on the substrates.²⁴ However, applications of the approach would be limited because the adhesion mechanism of the first TA layer on solid substrates has not been fully understood, yet. This drawback encouraged us to develop a well-defined strategy for depositing TA on the substrates. We reported the pDA-assisted TA deposition on solid substrates, where the first TA layer was interacted with the pDA-coated surface by Fe^{III} coordination reaction between the pDA catechol moieties and TA.²³ Herein, we demonstrated the formation of TA layers on solid substrates using the pDA-assisted strategy. PEGylation of the pDA/TA-coated surface was carried out by immersing the surface into a solution containing PEG. From the various types of available PEG molecules, we chose to use the four-arm PEG because the branched structure of this molecule was expected to be advantageous for hydrogen bond formation. The modifications of the surface by pDA, TA, and PEG were directly characterized by XPS and FT-IR.

For the XPS and FT-IR analyses, Si and Au substrates were used, respectively. In the XPS analysis, the pDA-coated surfaces showed C 1s, N 1s, O 1s, and Si 2p peaks, of which the C 1s and N 1s peaks corresponded to pDA (Figure 2a). After treatment with Fe^{III}-TA, new Fe 2p peaks were apparent (Figure 2b), and those peaks were decreased after PEGylation, with a concurrent increase in the peak intensities of C 1s and O 1s, corresponding to PEG (Figure 2c). The quantitative analysis of the surface chemical composition is shown in Table 1. The

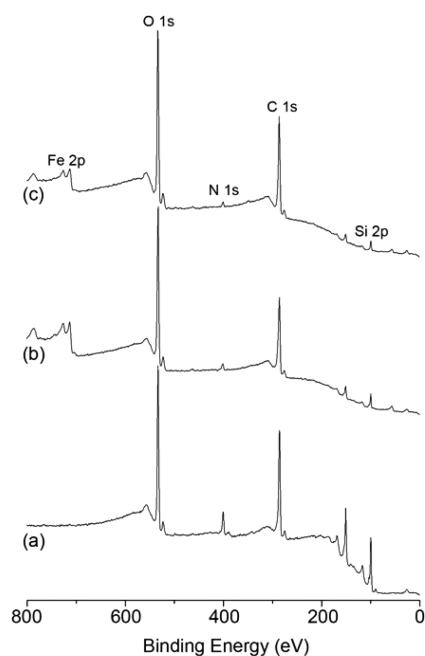


Figure 2. X-ray photoelectron spectra of (a) pDA-coated, (b) pDA/TA-coated, and (c) pDA/TA/PEG-coated Si surfaces.

Table 1. Atomic Composition (%) of pDA-, pDA/TA-, and pDA/TA/PEG-Coated Si Surfaces

	C 1s	N 1s	O 1s	Fe 2p	Si 2p
pDA	50.68	5.96	22.34	0	21.02
pDA/TA	53.33	2.46	32.92	3.71	7.58
pDA/TA/PEG	58.68	1.8	33.48	1.86	4.19

sequential decrease of the N 1s and Si 2p peaks and increase of the C 1s and O 1s peaks indicated the successful deposition of TA and PEG on the pDA-coated surface. The C/O ratio for the pDA/TA-coated surface was calculated to be 1.62, which is in good agreement with the theoretical C/O ratio for TA ($C_7H_{52}O_{46}$, C/O = 1.65). An XPS narrow scan of the C 1s region also supported the presence of TA and PEG on the pDA-coated surface. The intensities of the peaks at 288.6 eV (C=O) and 286.3 eV (C—O) were significantly increased after TA deposition and PEGylation, respectively (Figure S1, Supporting Information). These peaks are due to the abundant amount of ester and ether groups in TA and PEG, and these results indicated the successful introduction of TA and PEG onto the surface. FT-IR spectra also revealed the successful modification of the pDA-coated surface by TA and PEG. The pDA-coated surface afforded several characteristic peaks, including ring stretching in benzene ($1500\text{--}1600\text{ cm}^{-1}$), NH_2 deformation (1620 cm^{-1}), C—O and C—N stretching ($1000\text{--}1120\text{ cm}^{-1}$), and NH and OH stretching ($3000\text{--}3500\text{ cm}^{-1}$) (Figure 3a).²⁸ Upon TA deposition, a significant increase in the peak intensity in the $900\text{--}1140\text{ cm}^{-1}$ region (C—O stretching) was observed, originating from the surface-deposited TA (Figure 3b). Furthermore, peaks originating from ring stretching in benzene ($1500\text{--}1600\text{ cm}^{-1}$) were observed owing to the benzene moieties of TA.²⁹ In the pDA/TA/PEG-coated sample, an increase in the peaks for CH antisymmetric and symmetric stretching ($2830\text{--}3000\text{ cm}^{-1}$) and a decrease in the peaks for ring stretching in benzene were detected (Figure 3c). All these observations indicated that TA

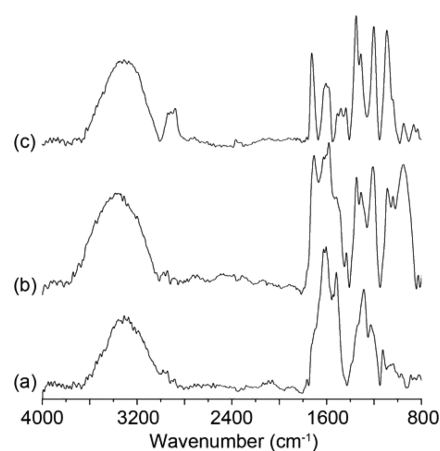


Figure 3. FT-IR spectra of (a) pDA-coated, (b) pDA/TA-coated, and (c) pDA/TA/PEG-coated Au surfaces.

deposition and PEGylation occurred successfully on the pDA-coated surface.

Prior to use of the pDA/TA/PEG-coated surface for marine antifouling applications, a protein adsorption experiment was carried out. PEG is well-known to effectively inhibit nonspecific protein adsorption,³⁰ and therefore, the functional properties of a surface-grafted PEG can be verified by simple protein adsorption tests. In this study, fibrinogen, which is known to be a sticky protein, was used,³¹ and the amount of adsorbed protein was characterized by spectroscopic ellipsometry. A noticeable protein adsorption was not observed after immersion of the pDA/TA/PEG-coated surfaces in a PBS solution of fibrinogen (0.1 mg/mL , pH 7.4), whereas protein layers of more than 2.7 nm thickness were adsorbed on the nontreated, pDA-, and pDA/TA-coated surfaces (Figure 4). As

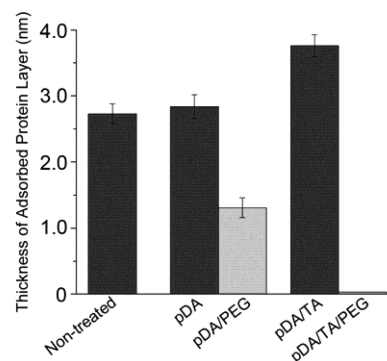


Figure 4. Protein adsorption on the different coatings (substrate: Si). Each point is the mean from 15 measurements on 3 replicate samples. The error bars display the 95% confidence limits.

a control, PEGylation was also carried out on the pDA-coated surface without deposited TA, and the resulting surface had a 1.3 nm thick adsorbed protein layer. These results implied that the combined coating of pDA and TA (i.e., pDA/TA coating) is an effective platform for the PEGylation. Based on the fact that surface-grafted PEG functioned well against protein adsorption, marine antifouling experiments were carried out.

For the marine antifouling experiments, stainless steel was used as a model substrate because stainless steel is the major element of the bodies of marine vessels, on which marine organisms heavily adhere. To characterize the marine

antifouling properties of the coated surfaces, the adhesion behavior of marine diatoms was studied. As a model diatom, *A. coffeaeformis*, which has been frequently utilized in laboratory assays, was selected,^{13,17} cultured in *f/2* medium for 10 days, and used for the adhesion assay (concentration of chlorophyll *a* = 1.1 $\mu\text{g}/\text{mL}$). Figure 5 shows the attached diatom density on

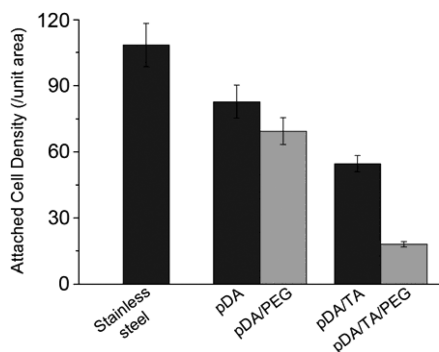


Figure 5. Diatom adhesion on the different coatings (substrate, stainless steel; unit area, 0.11 mm^2). Each point is the mean from 60 counts on 3 replicate samples. The error bars display the 95% confidence limits.

different coatings after being cultured for 1 day. The diatom densities on the coated surfaces were lower than on the nontreated stainless steel surface. Quantitatively, the pDA, pDA/TA, and pDA/TA/PEG coatings reduced diatom adhesion by 23.6%, 49.7%, and 83.4%, respectively, compared with the nontreated stainless steel. It was interesting that the pDA and pDA/TA coatings (without PEGylation) were also resistant against diatom adhesion. The results were thought to originate from the increased hydrophilicity of the surfaces. It is known that diatom adhesion can be reduced by enhancement of surface hydrophilicity.^{8,14,15} Considering that the surface hydrophilicity of stainless steel was sequentially increased by the pDA and pDA/TA coatings, the improved hydrophilicity resulted in the reduction of diatom adhesion on the surfaces. The water contact angle of stainless steel was changed from 53.4° to 32.4° and 28.4° after introduction of the pDA and pDA/TA coatings, respectively (Figure S2, Supporting Information). In particular, the pDA/TA/PEG-coated surfaces showed the most effective antifouling performance, in which less than 20 diatoms/unit area (0.11 mm^2) were attached to the surfaces. As a control, the diatom adhesion test was conducted on the pDA/PEG-coated surface without deposited TA, in order to investigate the effect of TA layers on the PEGylation. As shown in Figure 5, a significant improvement of antifouling performance was not observed on the pDA/PEG-coated surfaces. This result indicated that the TA layers play an important role in efficient surface PEGylation.

To evaluate the long-term marine antifouling performance of the coating, the pDA/TA/PEG-coated surfaces were pretreated with filtered seawater. After immersion for 3, 6, and 10 days in seawater, the pDA/TA/PEG-coated surfaces were taken out and the 1 day diatom adhesion assay was then carried out. The attached diatom density was quantified, and the results are shown in Figure 6. After 3 days, the resistance against diatom adhesion was similar to that of the as-prepared PEG-coated surfaces. However, after 6 and 10 days of immersion in seawater, the attached diatom density on the PEG-coated surfaces was considerably increased (6 days: 30 diatoms/unit

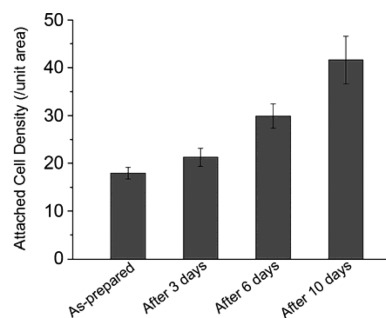


Figure 6. Stability of the pDA/TA/PEG coating in seawater (substrate: stainless steel, unit area: 0.11 mm^2). Each point is the mean from 60 counts on 3 replicate samples. The error bars display the 95% confidence limits.

area, 10 days: 42 diatoms/unit area), indicating that the antifouling performance of the PEG-coated surfaces was reduced in seawater. The long-term instability of the pDA/TA/PEG coating on exposure to seawater may be explained by the dissociation of hydrogen bonds between TA and PEG. Gradual cleavage of the hydrogen bonds would cause a decrease in the fouling resistance with time, followed by an increase in diatom adhesion.

The advantage of our PEGylation approach is that diverse materials can be modified. In order to investigate the versatility of the pDA/TA/PEG coating, we choose an additional substrate, nylon, which is frequently utilized for the preparation of aquaculture instruments, applied our approach to modify the surfaces, and carried out marine antifouling experiments. Figure S3 (Supporting Information) shows that PEGylation was also successfully achieved on the nylon surfaces, by virtue of the pDA/TA coating. After PEGylation, the attached diatom density on the nylon substrates was significantly reduced from 51 to 22 diatoms/unit area. These results clearly indicate the versatility of the pDA/TA/PEG coating for marine antifouling applications.

4. CONCLUSIONS

In summary, a facile approach to the preparation of marine antifouling surface coatings was developed using TA and PEG. TA is known to be a good PEG-binding agent, and was successfully deposited on the solid substrates via a metal coordination reaction. Subsequent PEGylation was achieved by hydrogen bond formation. This approach has several advantages; the whole process proceeds under mild reaction conditions without complicated steps or instruments. Remarkably, only simple immersion of the substrate into the reagent-containing solutions was required to prepare the marine antifouling surface coatings. Moreover, the versatility of the investigated method was confirmed by applying this method to both polymer and metal alloy substrates. Unlike the nontreated surfaces, diatom adhesion was significantly inhibited on the modified surfaces. Given the environmentally friendly processing conditions and the practical applicability of this method, we believe that this method provides an important alternative approach to the previously developed antifouling coatings for marine vessels.

■ ASSOCIATED CONTENT

Supporting Information

High-resolution XPS spectra (C 1s), water contact angle images, and diatom adhesion on nylon surfaces (Figures S1–

S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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