Natural Product Inspired Environmentally Friendly Strategy Based on Dopamine Chemistry toward Sustainable Marine Antifouling

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ABSTRACT: The combination of natural active antifouling composition and intelligent coatings has been regarded as a prospective approach to avoid marine biofouling. However, the relatively complex coating structure and the excessive rapid release of antifoulants maintain unresolved issues in their practical application. In this work, a novel environmentally friendly natural antifoulant (Stellera chamaejasme, SC) encapsulated in the polydopamine (PDA) microcapsule (SC@PDA) is prepared by emulsion interfacial polymerization and blended with the acrylate polymer to prepare a sustainable antifouling coating. Herein, the PDA shell acting as an “intelligent capsule” ensures the controlled release of the antifoulant SC, and the corresponding SC loading amount could be high up to 75.40%. As a model antifoulant, the impact of SC on the adsorption activity of the protein bovine serum albumin (BSA) is studied, as well as the settlement of presentative fouling communities (diatom Navicula sp. and red algae Porphyridium sp.) on the constructed coating. The experimental results demonstrate that the natural product SC integrated eco-friendly antifouling coating occupies the superior capacity of impeding the adsorption of both protein BSA and algae. Such antifoulant (SC) integrating with controlled release character is a great advance in terms of marine antifouling applications. It is, therefore, expected that this innovation will provide guiding significance for developing the next generation of antifouling techniques, especially in the field of marine antifouling.

1. INTRODUCTION

Marine biofouling is a kind of biological phenomenon and technical challenge that mankind inevitably encounter when they engage in maritime activities. There are a number of hazards caused by the settlement of marine organisms (bacteria, algae, and mollusks), such as increased ship resistance and fuel consumption, hull corrosion, hull imbalances, and ecosystem destruction.1−4 Therefore, many antifouling technologies have been investigated for avoiding or mitigating the damage induced by marine biological fouling.5−10 For example, antifouling coatings have been developed to prevent the settlement of fouling organisms in large-scale practical application.11−13 Generally, some antifouling coatings are developed through releasing toxic antifoulants (such as Cu2O); however, there are ineluctably risks and disadvantages induced by these antifoulants in the marine ecological environment.14−16 As a consequence, questing for novel, highly efficient, and environmentally friendly antifouling prototypes has become an urgent research hotspot. Besides the surface chemical composition and defined unique interface architecture, which plays a critical role in determining the antifouling capability, natural products have also been brought forward for environmentally friendly antifoulants.17,18 An ideal antifoulant compounds should be qualified with certain characteristics, such as low dose but effective function, inhibiting the biological adhesion without a poison effect, broad effective for all target organisms, and degrading without a negative effect on the marine environment. At present, although some antifouling substances have been found from marine organisms,19 their contents are relatively low and the synthesis of these antifoulants is always difficult to scale up as well, which has greatly impeded their practical application as a consequence. Therefore, it might be a worthwhile attempt to explore and select alternatives from the widely distributed terrestrial plant resources.20 In the field of terrestrial phytochemistry, a lot of biomedical research has been conducted in terms of new and environmentally friendly fungicides.21−29 Based on the enlightenment for the investigation about the phytochemical defense function of terrestrial plants, they might be a good alternative and highly efficient to harmful organisms, safe to nontarget organisms, and easy to decompose without damage to the environment.30 For example, tannins isolated from chestnut and mimosa could inhibit the attachment of larvae of Balanus amphitrite and...
have also been proved to have a good antifouling properties by oxidative self-polymerization (b).

Therefore, in this work, a sustained release microcapsule material (SC@PDA) is designed through combining the natural antifouling component Stellera chamaejasme (SC) with polydopamine (PDA) chemistry. The microcapsule with high antifoulant SC loading exhibits excellent antifouling behavior to the presentative fouling diatom, red algae, and BSA protein. Meanwhile, its more practical application is proved by integrating SC@PDA into the acrylic coating, which also imparts a great influence on the algae fouling behavior. As a result, the application of the active antifouling ingredient SC@PDA and its deuterogenic coating to marine antifouling will provide practical and significant guidance for the environmentally friendly protection strategies.

2. EXPERIMENTAL SECTION

2.1. Materials. SC is the active ingredient extracted from the natural plant in Northwest China. Dopamine hydrochloride (DA, Sigma-Aldrich) is used to form the shell of SA@PDA. Tris-(hydroxymethyl) aminomethane (Tris) and hydrochloric acid are adopted from Beijing Chemical Reagents Company, China. KCl, NaCl, Na2HPO4·12H2O, and NaH2PO4·2H2O are employed to prepare the PBS phosphate buffered solution. Ethanol, n-butyl alcohol, hexadecyltrimethylammonium chloride (CTAC), butyl methacrylate (BMA, 98%), methyl methacrylate (MMA, 99%), butyl acrylate (BA, 98%), 1-vinyl-2-pyrrolidone (NVP, 99%), 2-hydroxyethyl methacrylate (HEMA, 97%), 2,2-azobisobutyronitrile (AIBN), and toluene (99.5%) are purchased from J&K Chemical Ltd. Both the red algae Porphyridium sp. and diatoms Navicula sp. are supported by Freshwater Algae Culture Collection at the Institute of Hydrobiology. All reagents are used as received; deionized water is prepared with an ion-exchange system.

2.2. Preparation of SC@PDA Microcapsules. The microcapsule structures based on the PDA chemistry are fabricated by a feasible emulsion polymerization. As delineated schematically in Figure 1a, the water solution containing 0.75 g of CTAC (1.5% m/v of the water phase) dissolved in 50 mL of Tris-buffer solution (pH = 8.5) and the oil phase containing 0.05 g of SC dissolved in 5.0 mL of n-butyl alcohol are prepared first. Then, the obtained oil phase is poured into the as-prepared water solution with vigorous mechanical stirring to generate a surfactant stabilized oil/water emulsion. Subsequently, 0.05 g of DA is added and simultaneously stirred at 300 rpm for a further 24 h at room temperature. The product is centrifuged (10 000 rpm) and washed at least three times with deionized water, and then dried under vacuum at 45 °C for 12 h. As shown in Figure 1b, antifoulant SC encapsulated in the PDA microcapsules (SC@PDA) is obtained.

2.3. Preparation of the SC@PDA Microcapsule Doped Coating. As SC has the function of inhibiting infection by the sterilization effect, it might have certain utilization in the field of marine antifouling. Herein, SC is taken as a novel kind of sustained-release algaecide and expected to be leaked abidingly to achieve the marine antifouling effect. For their more industrial application, SC@PDA microcapsules are doped into the acrylic polymer. The preparation technology is as follows: a mixed solution containing toluene (20 g) and BA (1 g) in a flame-dried round-bottom flask is heated to 80 °C under argon atmosphere. Then the mixed component containing MMA (3.00 g), BA (1.00 g), BMA (7.00 g), HEMA (4.00 g), NVP (2.00 g), AIBN (0.40 g), and toluene (5.00 g) is added dropwise. The radical polymerization is expected to take place within 6 h and finally polymer solution is obtained. Before the polymer is spun on the dried glass substrates about 100 μm thick, a fixed amount of curing agent 1,6-diisocya-tates and SC@PDA are added and degassed for 15 min. At last, the sample is placed in an oven at 80 °C for 4 h to ensure complete solidification.

2.4. Sustained Release Characterization of SC. The ultraviolet absorption spectrum of SC is tested by a UV–vis spectrophotometer (UV-3200, Shanghai MeiPuDa Company)
at the wavelength 285 nm. In detail, the ethanol/Tris solution (3:7, v/v) is used and a series of SC solutions with different concentrations are prepared. The corresponding character UV absorption for each sample is measured at room temperature, and the standard curve between the UV absorption and the SC concentration is plotted as a consequence.

To determine the mass content of SC encapsulated in the PDA microcapsule, a certain amount of SC@PDA microcapsule sample is mixed with 100 mL of ethanol/Tris solution (3:7 v/v) with magnetic stirring long enough to ensure that the loaded SC is released completely. The UV absorption value of released SC is determined by UV−vis spectroscopy, and the corresponding SC loading fraction can be calculated according to the above standard curve and the following equation

$$SC\text{ loading} = \frac{\text{mass of SC loaded in PDA}}{\text{mass of SC@PDA}} \times 100\%$$

Since the pH of natural seawater is generally constant at 7.5−8.2, therefore, the release behavior of antifoulant SC loaded in the microcapsules is investigated under alkaline condition, including the Tris solution and artificial seawater. Taking the Tris solution as an example, the ethanol/Tris solution (pH = 8.3) mixture containing the defined mass content of SC@PDA is prepared and then placed in room temperature at a constant stirring speed. For the measurement of the SC release process, 4.0 mL of the mixture is collected at the de

shown in Figure 1, the preparation mechanism of SC@PDA microcapsules is as follows: first, oil/water emulsion is obtained under high speed stirring where the organic solvent dissolving SC and the surfactant CTAC dispersed DA Tris solution are used as the oil phase and water phase, respectively. After the self-polymerization of dopamine, CTAC stabilized oil/water latex is capsulated by the PDA shell and the SC@PDA microcapsule is obtained.

FT-IR spectra are conducted to confirm the formation of PDA and the existence of SC, as shown in Figure 2a. For the SC component, the adsorption peaks at 3266.8 and 1631 cm$^{-1}$ are attributed to the stretching vibration of −OH and C═O functional groups of aromatic rings, adsorption peaks at 1509 and 1448 cm$^{-1}$ are the characteristic skeleton vibration of the benzene ring, and the adsorption peaks at 1241.5 and 1322 cm$^{-1}$ are assigned to the in-plane bending vibration of C−O and O−H, respectively. On the other hand, the characteristic adsorption of the C═O functional group at 1721.1 cm$^{-1}$, the benzene ring at 1537.9 and 1535.5 cm$^{-1}$, and the C−N bending vibration near 1242.9 cm$^{-1}$ are prominent after the PDA encapsulation. Meanwhile, compared with SC, the thermo performance of SC@PDA is quite different. Its corresponding thermal decomposition temperature decreases to 178 °C because of the PDA component (Figure 2b). The above characterization indicates that the PDA component is successfully integrated with the antifoulant SC.

To further prove that SC is coated by PDA successfully, transmission electron microscopy (TEM) observation is introduced to determine the change of morphology for PDA samples before and after encapsulating SC. As shown in Figure 3, it is clear to find that the overall morphology of the original PDA capsule has no obvious change in contrast, and its boundary position can hardly be identified as a result. However, a light outer shell about 34 nm can be distinguished near the boundary region of the SC@PDA capsule from Figure 3b. Besides, a more compelling core−shell morphology could be defined as well as the uniform particle size distribution of

3. RESULTS AND DISCUSSION

3.1. Preparation and Characterization of SC@PDA Microcapsules. It is well known that polydopamine (PDA) can be obtained by the oxidative self-polymerization process in a mildly alkaline condition, and their microcapsules can be obtained by emulsion interface polymerization in situ. As
about 250 nm (Figure 3b). Combined with the FT-IR and TG analysis, these experimental results confirm that the PDA outer shell has been effectively coated on SC after the PDA self-polymerization.

3.2. Sustained Release Kinetics of the Antifoulant SC. The release behavior of SC@PDA microcapsules under a slightly alkaline medium is indispensable research for antifouling because seawater is naturally alkaline. Hereon, the release characters of SC from SC@PDA microcapsules in Tris solution (pH = 8.3) and artificial seawater (Figure S1) are investigated (Figure 4). First, the ultraviolet (UV) absorption spectrum of SC is measured, and the adsorption near 285 nm is defined as its specific UV adsorption (inset, Figure 4a). The corresponding UV absorption values for the samples with the gradually increased SC concentration are plotted as the standard curve (in Figure 4a), in which $R^2 = 0.99996$ is obtained. Accordingly, the instantaneous concentration of released SC can be determined accurately by referencing the obtained standard curve, and the release kinetics behavior of SC from SC@PDA microcapsules is shown in Figure 4b. It is easy to find that accumulation of SC in the Tris solution increases continuously in the first 20 h, which means a higher release velocity of active SC in the early stages. After that, the accumulation of SC increases to approach stabilization with time lasted; obviously, its corresponding release velocity of SC decreases over time and gradually verges to zero after 193 h as a result. Besides, similar release behavior in the seawater medium also could be observed (Figure S1). This experimental result indicates that the dynamic release of SC goes through a fast-growing process to achieve balance, and a more stable but low release behavior of active SC will be acquired finally, which might be of benefit to extend its service period for the practical application. In addition, SC loading encapsulated in PDA is calculated from the aforementioned equations; its corresponding amount of SC loaded on the resulting microcapsules is 75.40% (w/w). Therefore, a primitive method to encapsulate SC with high loading capacity is successfully developed.

3.3. Resistance to BSA Adsorption. The kinetics of BSA protein adsorption in situ on gold plaque is acquired by Quartz Crystal Microbalance with dissipation measurements (QCM-D) at 25 °C. Commercially available (QSX-301, QSense) gold-coated quartz chips are used. The change of the resonance frequency, $\Delta f$, is measured for each adsorption/desorption step. The mass of the adhering layer can be calculated using the Sauerbrey relation

$$\Delta m = -\frac{C}{n} \Delta f$$

where $\Delta f$ is the resonance frequency (Hz), $n$ is the fundamental crystal frequency (5 Hz), $C$ is 17.7 ng/(Hz·cm²) for a 5 MHz quartz crystal, and $\Delta m$ is the mass change (ng/cm²). Figure 5 shows the frequency change of BSA protein adsorption/desorption behavior before and after introducing SC. Obviously, in Figure 5a, a rapid decrease in frequency is observed after engaging the BSA-PBS solution, which indicates that the amount of BSA protein adsorbs on the surface of gold-coated quartz chips and the corresponding adhesion mass is 204.39 ng/cm². However, in Figure 5b, after introducing the SC antifoulant, the BSA adsorbed capacity decreases dramatically (122.32 ng/cm²). Besides, although after rinsing with the PBS buffer solution, part of dissociative or physical absorbed BSA is washed off for both the BSA and SC mixed BSA samples, different desorption behavior could be observed because of the different adsorption activity. More specifically, the desorption masses for the BSA solution and BSA-SC solution are 132.73 and 108.15 ng/cm², and the corresponding desorption fractions are about 64.94 and 88.42%, respectively. Combined with the fluorescence quenching effect, it can be concluded that SC has negatively affected the adsorption capacity of BSA, which might be attributed to the fact that strong intermolecular hydrogen bonding can be formed between –NH₂ of BSA and –OH of SC according to their structure so that the interaction between BSA and gold plaque is weakened and the adhesion of BSA on the substrate is reduced.

3.4. Fluorescence Quenching Properties of SC and SC@PDA to Algae. To study the antifouling capability of the natural product SC, the fluorescence quenching behaviors of SC to representative algae (chlorella and duchennes) are verified first. As shown in Figure S2 (Supporting Information). It is obvious that the fluorescence intensity of the two species of algae significantly decreases with the increase of the SC concentration after culturing for 24 h. This experimental result shows that the natural product SC possesses a fluorescent quenching effect on both algae, which means that the algae activity has been inhibited obviously. Meanwhile, it is acquired that a linear relationship between $F_0/F$ and $[Q]$ is observed, which agrees well with the Stern–Volmer equation (Supporting Information). Therefore, it can be determined that the interaction mechanism of the natural product SC to the fouling algae is static fluorescence quenching. Besides, to guarantee a long-term service period of the antifoulant SC, embedding and sustained release strategy are employed to fabricate SC@PDA microcapsules. The corresponding fluorescence quenching behavior of SC@PDA microcapsules to other representative algae is also investigated, as shown in Figure 6. Compared with the blank samples without the addition of SC@PDA, the fluorescence of two species for both Navicula sp. and

![Figure 5](https://example.com/figure5.png)

Figure 5. Changes in frequency of the QCM chip for the BSA solution (a) and the BSA solution mixed with SC (b).
Porphyridium sp. will disappear under the action of SC (Figure 6, inset), which leads to a significant decrease in the fluorescence intensity of algae in the solution added to SC@PDA. In practical terms, the fluorescence intensity of the diatom Navicula sp. descends from 950.47 to 11.69 and declines by 98.77% when the SC@PDA microcapsule concentration is 7 mg/mL (Figure 6a). For the red algae Porphyridium sp., the fluorescence intensity decreases from 376.83 to 35.21 and declines by 90.66% when the SC@PDA microcapsule concentration is 7 mg/mL (Figure 6b). These experimental results show that the biological activity of presentative fouling algae has been negatively affected by the natural product SC via the fluorescence quenching effect, which means the fouling capability of these algae on the submerged interface will be hampered because of the decreased activeness.

### 3.5. Antifouling of SC@PDA Microcapsule Blended Coatings

To further prove that the antifouling agent SC can easily combine with the industrial technique and still possess the resistance to the settlement of organisms, a certain number of SC@PDA microcapsules (5% mass fraction) are doped with the acrylic polymer (Figure 7a). As shown in Figure S3, there are a plenty of spherical particles on the polymer surface compared with the sample without mixing SC@PDA constituent (as blank). The fluorescent images of fouled algae on the original resin and SC@PDA blended resin surfaces are shown in Figure 7. In the case of the red algae Porphyridium sp. (Figure 7b–d), compared with the blank sample, it is obvious to find that there are smaller amounts of algae adhered to the SC@PDA blended surfaces, and the corresponding algae density decreases significantly by 84.15%. Similarly, the fouling density of the diatom Navicula sp. on the as-prepared surface decreases by 79.50% (Figure 7e–g). To sum up, the constructed novel coating integrated with a natural antifoulant is capable of achieving the excellent antifouling effect on account of the release of SC. Therefore, the natural product SC as a beneficial antifouling agent will be of great value for marine antifouling. However, considering its huge demands for industrial application, more in-depth research on the acquisition of SC including its extraction and artificial synthesis technology, is still expected. On the other hand, it is crucial to further explore some alternatives employing SC into the industrial coatings as well, such as physical doping techniques or chemical bonding strategies.

### 4. CONCLUSIONS

In this work, an environmentally friendly antifouling coating is fabricated by blending the PDA microcapsule with acrylic polymer, in which a highly efficient natural active component SC is employed as the major antifouling ingredient. Fluorescence quenching valuation, quartz crystal microbalance analysis, and algae settlement characterization reveal that SC as an efficient active participator features effective low-fouling characteristics against a wide range of foulants, including the BSA protein and the presentative marine algae. Meanwhile, considering the remarkable loading ability for the natural active component (75.40% w/w) of the proposed SC@PDA...
microcapsules, a long-term sustained release behavior of antifouling SC could be maintained; therefore, this environmentally friendly natural active component SC and its derivative material (SC@PDA microcapsules) could be a potential candidate for resisting the durable settlement of protein and algae in the field of marine antifouling.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02114.

Fluorescence quenching behavior of antifoulant SC to chlorrella and duchenosa; optical microscopy images of sample; release character of antifoulant SC from seawater medium (PDF)

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Notes
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■ REFERENCES

(1) Schultz, M. P.; Bendick, J.; Holm, E.; Hertel, W. Economic impact of biofouling on a naval surface ship. Biofouling 2011, 27, 87–98.
(2) Fitridge, I.; Dempster, T.; Guenther, J.; de Nys, R. The impact and control of biofouling in marine aquaculture: a review. Biofouling 2012, 28, 649–669.
(3) Kül, S.; Weintell, C.; Yebra, D.; Dam-Johansen, K. Chemical Product Design: Towards a Perspective through Case Studies. Marine Biofouling Protection: Design of Controlled Release Antifouling Paints; Elsevier BV, 2007; pp 181–238.
(4) Piola, R. F.; Dafforn, K. A.; Johnston, E. L. The influence of antifouling practices on marine invasions. Biofouling 2009, 25, 633–644.
(5) Wu, J.; Zhang, D.; He, X.; Wang, Y.; Xiao, S.; Chen, F.; Fan, P.; Zhong, M.; Tan, J.; Yang, J. “Janus-Featured” Hydrogel with antifouling and bacteria-releasing properties. Ind. Eng. Chem. Res. 2019, 58, 17792–17801.
(6) Yang, W.; Lin, P.; Cheng, D.; Zhang, L.; Wu, Y.; Liu, Y.; Pei, X.; Zhou, F. Contribution of charges in polyvinyl alcohol networks to marine antifouling. ACS Appl. Mater. Interfaces 2017, 9, 18295–18304.
(7) Zhang, R.; Zhang, L.; Tian, N.; Ma, S.; Liu, Y.; Yu, B.; Pei, X.; Zhou, F. The tethered fibrillar hydrogels brushes for underwater antifouling. Adv. Mater. Interfaces 2017, 4, No. 1601039.
(8) Wang, W.; Hao, X.; Chen, S.; Yang, Z.; Wang, C.; Yan, R.; Zhang, X.; Liu, H.; Shao, Q.; Guo, Z. pH-responsive Capsaicina@chitosan nanocapsules for antibiofouling in marine applications. Polymer 2018, 158, 223–230.
(9) Hao, X.; Wang, W.; Yang, Z.; Yue, L.; Sun, H.; Wang, H.; Guo, Z.; Cheng, F.; Chen, S. pH responsive antifouling and antibacterial multilayer films with Self-healing performance. Chem. Eng. J. 2019, 356, 130–141.
(10) Yang, Z.; Ma, C.; Wang, W.; Zhang, M.; Hao, X.; Chen, S. Fabrication of Cu2O-Ag nanocomposites with enhanced durability and bactericidal activity. J. Colloid Interface Sci. 2019, 557, 156–167.
(11) Li, Y.; Chen, R.; Feng, Y.; Sun, X.; Tang, L.; Takahashi, K.; Liu, P.; Wang, J. Synthesis of amphiphilic acrylic boron fluorinated polymers with antifouling behavior. Ind. Eng. Chem. Res. 2019, 58, 8016–8025.
(12) Bellotti, N.; Romagnoli, R. Assessment of zinc salicylate as antifouling product for marine coatings. Ind. Eng. Chem. Res. 2014, 53, 14559–14564.
(13) Liu, H.; Ma, Z.; Yang, W.; Pei, X.; Zhou, F. Facile preparation of structured zwitterionic polymer substrate via sub-surface initiated atom transfer radical polymerization and its synergistic marine antifouling investigation. Eur. Polym. J. 2019, 112, 146–152.
(14) Champ, M. A. Economic and environmental impacts on ports and harbors from the convention to ban harmful marine anti-fouling systems. Mar. Pollut. Bull. 2003, 46, 935–940.
(15) Alzieu, C.; Sanjuan, J.; Deltreil, J.; Borel, M. Tin contamination in arcachon bay: effects on oyster shell anomalies. Mar. Pollut. Bull. 1986, 17, 494–498.
(16) Alzieu, C. Environmental impact of TBT: the French experience. Sci. Total Environ. 2000, 258, 99–102.
(17) Scardino, A.; Hadleston, D.; Feng, Z.; Paul, N. A.; De Nys, R. Biomimetic characterisation of key surface parameters for the
development of fouling resistant materials. *Biofouling* 2009, 25, 83–93.

(18) Scardino, A. J.; de Nys, R. Mini review: biomimetic models and bioinspired surfaces for fouling control. *Biofouling* 2011, 27, 73–86.

(19) Qian, P.; Dobretsov, S.; Dahms, H.-U.; Pawlik, J. Antifouling activity and microbial diversity of two congeneric sponges Callyspongia spp. from Hong Kong and the Bahamas. *Mar. Ecol.: Prog. Ser.* 2006, 324, 151–165.

(20) Feng, D.; Ke, C.; Lu, C.; Li, S. Herbal plants as a promising source of natural antifoulants: evidence from barnacle settlement inhibition. *Biofouling* 2009, 25, 181–190.

(21) Manahan, E. G.; da Costa Halmenschlager, R.; Rosa, R. M.; Henrques, J. A. P.; de Paula Ramos, A. L. L.; Saffi, J. Pharmacological evidences for the extracts and secondary metabolites from plants of the genus Hibiscus. *Food Chem.* 2010, 118, 1–10.

(22) Baliga, M. S.; Bhat, H. P.; Baliga, B. R. V.; Wilson, R.; Palatty, P. L. Phytochemistry, traditional uses and pharmacology of *Eugenia jambolana* Lam. (black plum): a review. *Food Res. Int.* 2011, 44, 1776–1789.

(23) Abbassipour, H.; Mahmoudvand, M.; Rastegar, F.; Basij, M. Insecticidal activity of *Peganum harmala* seed extract against the diamondback moth, *Platella xylostella*. *Bull. Insectol.* 2010, 63, 259–263.

(24) Pinto, M. F.; Fensterseifer, I. C.; Migliolo, L.; Sousa, D. A.; de Capville, G.; Arboleda-Valencia, J. W.; Colgrave, M. L.; Craik, D. J.; Magalhães, B. S.; Dias, S. C. Identification and structural characterization of novel cyclotides with activity against an insect pest of sugar cane. *J. Biol. Chem.* 2012, 287, 134–147.

(25) Kumar, P.; Mishra, S.; Malik, A.; Satya, S. Insecticidal properties of Mentha species: a review. *Ind. Crops Prod.* 2011, 34, 802–817.

(26) Bhardwaj, M.; Bharadwaj, L.; Trigunayat, K.; Trigunayat, M. M. Insecticidal and wormicidal plants from Aravalli hill range of India. *J. Ethnopharmacol.* 2011, 136, 103–110.

(27) Flores-Dávila, M.; González-Villegas, R.; Guerrero-Rodríguez, E.; Mendoza-Villegar, R.; Cárdenas-Elizondo, A.; Cerna-Chávez, E.; Aguirre-Uribe, L. Insecticidal effect of plant extracts on *Bactericera cockerelli* (Hemiptera: Psyllidae) nymphs. *Southwest. Entomol.* 2011, 36, 137–144.

(28) Fan, L. S.; Muhamad, R.; Omar, D.; Rahmani, M. Insecticidal properties of *Piper nigrum* fruit extracts and essential oils against *Spodoptera litura*. *Int. J. Agric. Biol.* 2011, 13, 4.

(29) Huang, S.-Q.; Zhang, Z.-X.; Li, Y.-Z.; Li, Y.-X.; Xu, H.-H. Anti-insect activity of the methanol extracts of fern and gymnosperm. *Agric. Sci. China* 2010, 9, 249–256.

(30) Lin, X.; Changyi, L. Toxicity comparison of extracts from six terrestrial plants to larvae of *Balanus amphitrite*. *J. Plant Resour. Environ.* 2008, 17, 22–27.

(31) Stupak, M. E.; Garcia’, M. T.; Pérez, M. C. Non-toxic alternative compounds for marine antifouling paints. *Int. Biodeterior. Biodegrad.* 2003, 52, 49–52.

(32) Pérez, M.; García, M.; Blustein, G.; Stupak, M. Tannin and tannate from the quebracho tree: an eco-friendly alternative for controlling marine biofouling. *Biofouling* 2007, 23, 151–159.

(33) Zhou, X.; Zhang, Z.; Xu, Y.; Jin, C.; He, H.; Hao, X.; Qian, P.-Y. Flavone and isoflavone derivatives of terrestrial plants as larval settlement inhibitors of the barnacle *Balanus amphitrite*. *Biofouling* 2009, 25, 69–76.

(34) Omae, I. General aspects of tin-free antifouling paints. *Chem. Rev.* 2003, 103, 3431–3448.

(35) Pérez, M.; García, M.; Sánchez, M.; Stupak, M.; Mazuca, M.; Palermo, J. A.; Blustein, G. Effect of secocollide acid isolated from the Patagonian shrub *Nardophyllum bryoides* as active component in antifouling paints. *Int. Biodeterior. Biodegrad.* 2014, 89, 37–44.

(36) Cui, J.; Yan, Y.; Such, G. K.; Liang, K.; Ochs, C. J.; Postma, A.; Caruso, F. Immobilization and intracellular delivery of an anticancer drug using mussel-inspired polydopamine capsules. *Biomacromolecules* 2012, 13, 2225–2228.