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Bio-Inspired Hairy Crab Claw Polymer Surface with Excellent Self-Cleaning Wettability in Muddy or Oil-Contaminated Water

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KEYWORDS: bio-inspired interface; hierarchical nanostructure; self-cleaning; superoleophobic surface; 3D cross-linked structure

ABSTRACT

The hairy crab *Eriocheir sinensis* lives in muddy freshwaters, such as ponds and paddy fields. The crab's claw features dense patches of setae and exhibits an excellent self-cleaning surface in muddy waters. This study examined the micro-nano structure and wettability properties of the crab claw. The results showed that the claw consists of 3D cross-linked fibers with a hierarchical micro-nano structure, and the main chemical composition of these fibers was determined chitosan molecules. The claw also has special superoleophobic and self-cleaning properties in muddy water. Inspired by the structure of the crab claw, 3D-layered micro/nano-structures with poly(vinyl alcohol)/chitosan/poly(*N*-isopropylacrylamide) were prepared by electrospinning and *in situ* polymerization. This novel bio-inspired polymer surface exhibits superhydrophilicity in the air, superoleophobicity underwater (with an oil contact angle of 163°), and excellent self-cleaning potential in muddy water.

INTRODUCTION

Self-cleaning underwater superoleophobic surfaces have received remarkable attention due to their fundamental value in research and their potential applications in antifouling, oil/water separation, microfluidics, aquatic smart devices, crude oil pipelines, and the self-cleaning ability of marine equipment[1-6]. These materials have been obtained by combining the chemical composition with hierarchical micro/nanostructure surfaces through various methods, such as layer-by-layer self-assembly and photolithography, electrochemical deposition, and electrochemical polymerization[7-10]. Inspired by the features of some marine organisms, such as fish scales, clam shells and shark skin, several underwater superoleophobic surface materials with novel structures have been recently reported, which provides us an alternative strategy for preparing this type of material[11-14]. Subsequently, various underwater superoleophobic surfaces, such as hydrophilic polymer hydrogel[15], carbon nanotube[16,17], graphene[18], conducting polymers[19,20], metal oxide[21,22] and other organic/inorganic hybrids have been fabricated[23-25]. In general, bio-inspired materials with a superoleophobic surface underwater are mainly used in the context of marine environmental problems. However, many similar issues exist for freshwaters, such as the muddying of rivers due to soil loss, oil spills during transport, and oily wastewater. Although antifouling prevention, oily wastewater remediation, and growth organism in freshwaters are faced every day, it remains a challenge to fabricate underwater superoleophobic surfaces for use in contaminated freshwaters.

The natural world provides inspiration for engineering new, functional surface materials. The hairy crab *Eriocheir sinensis* spends most of its life in freshwater, including rice paddies, muddy rivers and lake habitats. The hairy cheliped of this species maintain a clean surface when the crab climbs out of muddy or oil-contaminated water. This interesting phenomenon of the claw's surface inspired us to study the micro-nano structure and chemical composition of the hairy crab cheliped to explain this special wettability property. In this study, a novel bio-inspired hairy crab cheliped polymer surface has been well developed, and the material is expected to have practical applications. The method of fabrication combined the electrospinning of chitosan (CS) and polyvinyl alcohol (PVA) with *in situ* photopolymerization of *N*-isopropylacrylamide (NIPAAm) and *N,N'*-methylenebisacrylamide (MBAAm). The cross-linked three-dimensional (3D) bio-inspired composite fiber arrays exhibit un-pderwater superoleophobicity with low adhesive force, as shown by an oil contact angle (OCA) of 163 ± 1.2° for 1,2-dichloroethane in water, and an oil sliding angle (OSA) of about 3°. Furthermore, the prepared bio-inspired polymer surface presents self-cleaning properties in an oil/water mixture as well as in muddy water. The biomimetic approach to creating this artificial material is expected to be helpful in fashioning self-cleaning surfaces and oil-repellent coatings for use in either contaminated freshwater or on land.

EXPERIMENTAL SECTION

Materials

Hairy crabs were obtained from Yangcheng Lake, Jiang Su Province, China. Chitosan (CS) (~80–95% deacetylated) was purchased from Sinopharm Chemical Reagent Co. Ltd. Polyvinyl alcohol (PVA) (degree of polymerization: 1 750 ± 50) was obtained from Beijing Yili Fine Chemical Co. Ltd, and *N*-isopropylacrylamide (NIPAAm) (99%) was obtained from Aldrich. Both *N,N'*-methylenebisacrylamide (MBAAm) and 2,2-diethoxyacetophenone (DEOP) were acquired from TCI (Shanghai) Development Co. Ltd. All other reagents were analytical grade and therefore used as received, without further purification.

Fabrication of the bio-inspired hairy crab cheliped polymer surface

In a typical process, 5 g PVA was first mixed with 100 mL deionized water by strong magnetic stirring at 100°C. CS (2 wt%) was dissolved in an aqueous solution of 50 wt% acetic acid and 0.1 wt% NaCl. Next, a PVA/CS mixed solution was obtained by combing 5 wt% PVA and 2 wt% CS at a volume ratio of 8:2. Mixed solution was loaded into a 5-mL plastic syringe equipped with a stainless-steel needle, which was connected to a high-voltage power supply (FL32174, Gamma); the PVA/CS solution was provided at a fixed rate of 0.3 mL min^{-1}. A working voltage of 20 kV was applied, and the fibers were collected on an aluminum foil plate placed 20 cm below the tip of the needle. After electrospinning, a homogeneous monomer solution with 1 mol L^{-1} NIPAAm, MBAAm (0.1 wt% based on NIPAAm), and DEOP (0.1 wt%) was sprayed onto the PVA/CS fibrous surface. The bio-inspired hairy crab cheliped polymer surface was finally obtained by *in situ* polymerization after 8 hours under ultraviolet light (λ = 365 nm, ZF-1 UV-light，Hangzhou Qiwei Instrument Co., Ltd).

Characterizations

Morphologies of the hairy crab cheliped and the bio-inspired surface were examined under a Quanta FEG-250 environmental scanning electron microscope (SEM) at an accelerating voltage of 10 kV. Static contact angle (CA) measurements were conducted using a DataPhysics OCA20 instrument (DataPhysics, Germany). The 2 μL oil droplets (1,2-dichloroethane) were carefully dropped onto materials that were then immersed in water; the average value of five measurements performed at different positions on the same sample was adopted as the contact angle. A CCD (couple-charged device) camera was used to record the sliding behavior. Photographs were taken with a Canon 60D digital camera.

RESULTS AND DISCUSSION

In nature, the surface of the hairy crab cheliped retains a clean bristly surface when the animal climbs out of muddy or oil-contaminated water. To reveal the detailed micro-nano structure of a typical hairy crab cheliped, environmental scanning electron microscopy was performed (**Figure 1b-c**). **Figure 1b** shows that a typical cheliped is composed of two types of fibers with different sizes; slender fibers with an average diameter of 1.98 ± 0.64 μm are located between thick fibers with an average diameter of 22.00 ± 4.99 μm (**Figure 1c)**, creating cross-linked structures on the surface of the cheliped. The thick fibers have numerous non-uniform convex structures on their surface. Additionally, the main chemical components of the crab setae were studied by Fourier-transform infrared (FT-IR) spectroscopy (**Figure S1a**). The typical peaks located at 1642 cm^{-1} and 1540 cm^{-1} could be assigned to characteristic amide I and amide II absorption bands, respectively[26,27]. The broad peak in the region of 3000–3500 cm^{-1} is ascribed to O-H stretching and N-H stretching vibrations[28-30]. Infrared (IR) spectroscopy indicated that hydrophilic chitosan (CS) is the main ingredient of the setae. To test the seemingly excellent self-cleaning performance of the hairy crab cheliped, samples were submerged in oily and muddy water. **Figure 1d-k** shows the anti-oil-fouling behavior of the cheliped in water; even after being stained with oil, the cheliped had a capacity to clean itself when immersed in water. These results demonstrate that the hairy crab cheliped with its cross-linked structures has a self-cleaning capability in muddy or oil-contaminated water, and thus possesses a superoleophobic property.

Previous studies have shown that hydrophilic composites help to hold water in a hierarchical structure and thereby improve the underwater superoleophobicity of materials[31-32]. With regard to the cheliped of hairy crabs, the water contact angle (WCA) in air was about 0° (**Figure 2a**), thus presenting a superhydrophilic property in air. The oil droplets (1,2-dichloroethane) maintained a spherical shape in water, and the oil contact angle (OCA) was as high as 161.7±1.2° (**Figure 2b**), indicating underwater superoleophobicity. **Figure 2c-f** shows a 2-μL oil droplet touching and leaving the surface of a hairy crab cheliped; to examine the dynamic wetting behavior of oil on the crab's surface, a CCD camera was applied to record the process. The droplet maintained its spherical shape throughout the process, which indicated low oil adhesion between the hairy crab cheliped and the oil droplet. Therefore, the anti-oil-fouling property of the hairy crab cheliped was easily observed by this test, which provided inspiration for designing a novel surface material based on the structure and chemical composites.

Inspired by the underwater superoleophobicity of hairy crab, a simple approach based on electrospinning combined with *in situ* polymerization was designed to fabricate a superoleophobic and low-adhesive polymer underwater surface. IR spectroscopy determined that CS is the main component of the hairy crab cheliped, therefore CS was chosen as one of the raw materials for electrospinning. However, spherical beads or a fibrous system may be obtained by electrospinning a CS solution[33]. In addition, the electrospinning efficiency is low due to vastly different chain conformations, hydrodynamic responses, and repulsive forces in a CS solution[34]. Therefore, PVA was reasonably introduced into the raw materials to reduce the repulsive force and increase the fibers' spinning efficiency[35]. By controlling the Rayleigh instability of the bending polymer solution, spindle-shaped CS/PVA nanofibers were obtained. The aqueous solution containing the monomer (NIPAAm), cross-linker (MBAAm), and photo-initiator (DEOP) was then sprayed on the surface of the CS/PVA non-woven nanofabrics. The *in situ* polymerization resulted in cross-linking structures among the CS/PVA nanofibers.

A schematic illustration of the design of the special underwater superoleophobic surface is shown in **Figure 3a-b.** The morphologies of the CS/PVA non-woven fabrics and the bio-inspired hairy crab cheliped surface are shown in **Figure 3c-e**. A SEM image shows thin fibers with an average diameter of 66 ± 1.4 nm coexisting with spindles with an average diameter of 518 ± 130 nm (**Figure 3c**). After *in situ* polymerization, the complex structure was covered with various holes having an average diameter of 351 ± 154 nm at the surface. NIPAAm was polymerized between the spindles and the fibers, forming a connective structure and creating a porous cross-linking 3D network (**Figure 3d-e**). Water could penetrate into the 3D network and form a stable water layer, contributing to the oleophobic and low-oil-adhesive properties of the surface material.

The bio-inspired hairy cheliped film was also studied by FT-IR spectra, as shown in **Figure S1b**. The broad absorption band located at 3297 cm^{-1} was assigned to the superposition of stretching vibration of O-H and N-H from PVA. The typical peak for CS assigned to amide II could be found at 1562 cm^{-1}.[30] The FT-IR spectra of the CS/PVA surface modified with PNIPAAm is shown in **Figure S1c**. The band at 3296 cm^{-1} denotes the stretching vibration of O-H[35]. PNIPAAm is characterized by amide I and amide II bands at 1649 cm^{-1} and 1548 cm^{-1}, respectively[36]. The SEM images and FT-IR spectra reveal that the bio-inspired hairy crab cheliped film was well developed.

Achieving stability of the underwater superoleophobicity of the bio-inspired cheliped surface material is important for its application. The average OCAs of the bio-inspired surface were tested over 30 days. The surface realized superoleophobicity with OCAs above 160° (**Figure 4f**) and remained stable for at least 30 days (**Figure 5**). **Table 1** summaries some typical underwater superoleophobic materials reported in recent years[37-41]. These results prove that the prepared bio-inspired hairy crab cheliped surface has a stable fantastic underwater superoleophobic property, and the stable 3D structures among the fibrous CS/PVA film contributed to stability of its wettability.

Underwater oil self-cleaning property has paramount importance for application of the bio-inspired hairy crab cheliped surface material[41-48]. To investigate its underwater wettability, a CCD camera was employed to observe oil sliding behavior underwater. As shown in **Figure 6a**, an 2-μL oil droplet (1,2-dichloroethane) was placed on the surface of the bio-inspired film. When the surface was tilted to a 3° angle, the oil droplet immediately slid off the material at a speed of 3.96×10^{-5} m s^{-1}. By contrast, the oil droplet did not roll off but stuck to the CS/PVA surface without PNIPAAm modification although the material was likewise tilted to a 3° angle (**Figure 6b**). When an oil droplet was placed on the bio-inspired surface, a substantial amount of water could be trapped within the cross-linked network and form a water layer between the oil droplet and the solid surface, creating a stable repellent force even when the surface was tilted at a greater angle. For the fibrous CS/PVA surface, water could not be stably trapped in the structure, resulting in a higher degree of oil hysteresis and oil adhesion. To test and compare the self-cleaning properties of the surfaces, digital photographs were taken to record the process of oil droplets contacting the bio-inspired film, the original aluminum, and the CS/PVA surface. Oil on the surface of the bio-inspired material could be cleaned thoroughly in water (**Figure 7a-e**). In contrast, both the original aluminum foil and CS/PVA surfaces maintained oil when placed in water, establishing that the oil adhesive force was lower for the bio-inspired hairy crab cheliped material than for the CS/PVA and aluminum surfaces (**Figures S4-S5**). Compared with the original aluminum foil and the CS/PVA surfaces, the bio-inspired material's surface showed excellent repellence to underwater oil. The underwater anti-oil-fouling behavior of the bio-inspired surface matched that of a crab cheliped itself. **Figure 7f-i** shows a 2-μL oil droplet touching and leaving the surface of the bio-inspired material; during the entire process, the oil droplet maintained a nearly spherical shape and was easily transferred, indicating a low-adhesive force between the prepared surface and the oil droplet underwater. These results suggest that the bio-inspired 3D cross-linked surface structure indeed has low oil adhesion. Therefore, an excellent underwater superoleophobic and low-oil-adhesive artificial surface was achieved by combining electrospinning and *in situ* photopolymerization to mimic the cross-linking structure of the hairy crab cheliped.

By *in situ* polymerization of NIPAAm and MBAAm on the CS/PVA fibrous surface, a 3D cross-linked structure was successfully fabricated. The phenomenon of underwater superoleophobic and low-oil-adhesive properties of the novel bio-inspired hairy crab cheliped material prove that water can be held in the cross-linked structure, thus providing an easy-sliding surface for oil. **Figure 8** shows the water layers with different stability, for the interlayer between the oil droplets and the CS/PVA fibrous surface and for the bio-inspired hairy crab cheliped material surface. An oil droplet could become trapped in the film due to much more space unlike the spindle-like fibrous CS/PVA film (**Figure 8a**); underwater it transitioned from the Wenzel's to the Cassies's state. The prepared bio-inspired surface with 3D cross-linked structures has more micro-nano structures on its surface, which is a typical underwater Cassies's state (**Figure 8b**). For the underwater Cassie's case, the apparent OCA, $\theta_{ow}*$, is described by the underwater Cassie's equation (1)[49]

$$\cos\theta_{OW}^{*} = f\cos\theta_{OW} + f - 1 \quad (1)$$

where f is the area fraction of the oil/solid interface, θ_{ow} is the underwater Young's OCA, which is defined as the CA of a small oil droplet on a flat solid surface underwater. In our solid/water/oil three phase system, θ_{ow} of an oil droplet in underwater Young state meets Equation (2)[49-50]

$$\cos\theta_{OW} = \frac{\gamma_{OV}\cos\theta_{O} - \gamma_{WV}\cos\theta_{W}}{\gamma_{OW}} \quad (2)$$

where γ_{OV}, γ_{WV}, and γ_{OW} are the interfacial tensions of oil/vapor, water/vapor, and oil/water interfaces, respectively. θ_O is the intrinsic CA of an oil droplet on such flat solid surface in air and θ_W is the intrinsic CA of a water droplet on the flat substrate. The smaller SA of this material indicates that the bio-inspired hairy crab cheliped material surface has excellent self-cleaning performance.

CONCLUSIONS

In summary, a bio-inspired hairy crab cheliped polymer film was obtained by the electrospinning of chitosan and polyvinyl alcohol and *in situ* polymerization of N-isopropylacrylamide. The bio-inspired polymer film has 3D cross-linking fibers with hierarchical micro-nano structures. Bio-inspired by the hairy crab cheliped surface, and with an underwater Cassie's state that can form a stable water interlayer, it provides a repellent force against oil droplets, constituting a self-cleaning property. This study provides a simple and low-cost strategy to fabricate a novel underwater self-cleaning superoleophobic surface. The bio-inspired hairy crab cheliped polymer film has promising applications to environmental issues in freshwaters.

Table 1. Comparison of some typical underwater superoleophobicity materials with present work

Materials	Oil Contact Angle（OCA）	Ref
Polyacrylamide hydrogel-coated Mesh	155.3±1.8 º	37
MHMS-based surface Material	160.8 º	38
Organohydrogel networks	149.6-163.8 º	39
Nanofibrous membrane	~162 º	40
Cupric Phosphate nanosheets wrapped inorganic membranes	158 º	41
Bio-inspired CS/PVA/PNIPAAm film	163±1.2°	This work

FIGURES

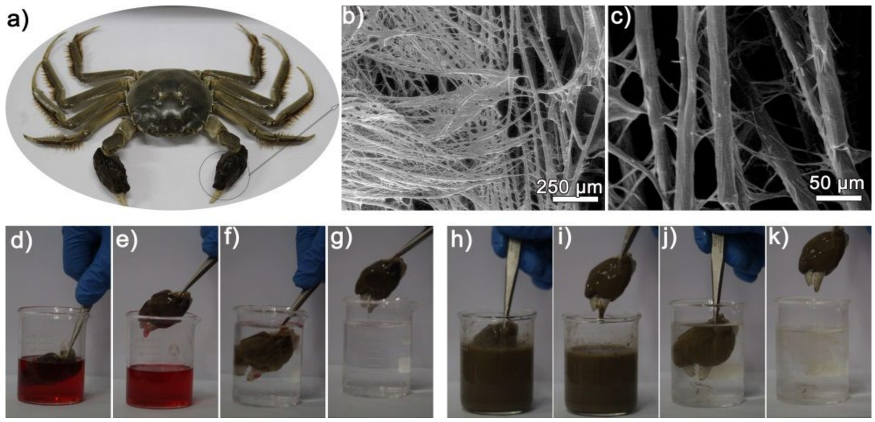

Figure 1. a) Photograph of a hairy crab *Eriocheir sinensis*; b-c) SEM images of the setae on the crab cheliped, under different magnifications; d-k) a sequences of images depicting the underwater anti-oil-fouling test with a hairy crab cheliped, showing that an oil-stained claw has the capacity to clean itself after being placed in water.

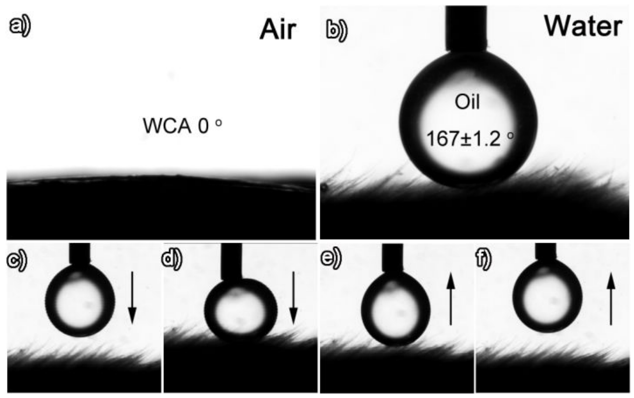

Figure 2. Wettability of the hairy crab cheliped. a) The water contact angle (WCA) in air, and b) the oil contact angle (OCA) in water; c-f) underwater micrographs of an oil droplet as it approaches and leaves the surface.

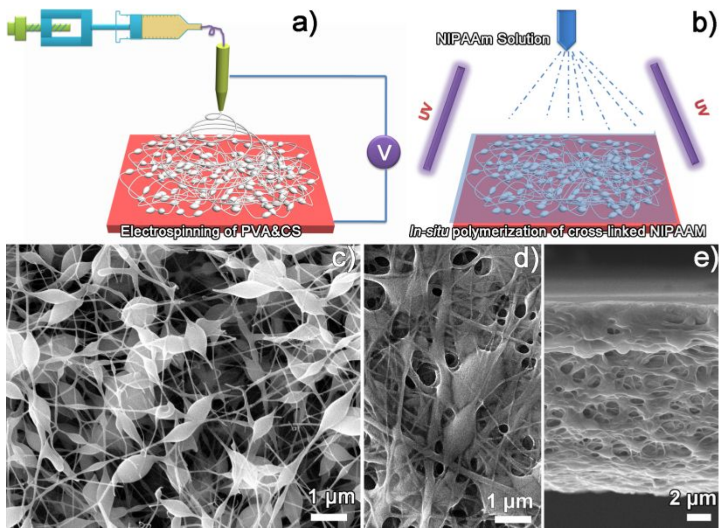

Figure 3. a) and b) Schematic presentation showing preparation of the underwater superoleophobic surfaces inspired by the hairy crab cheliped. c) SEM image of the CS/PVA spindle-like film. SEM images of the surface d) and cross-section e) the bio-inspired hair crab cheliped surface after spraying NIPAAm and MBAAm and *in situ* photo-polymerization on the PVA/CS spindle-like film.

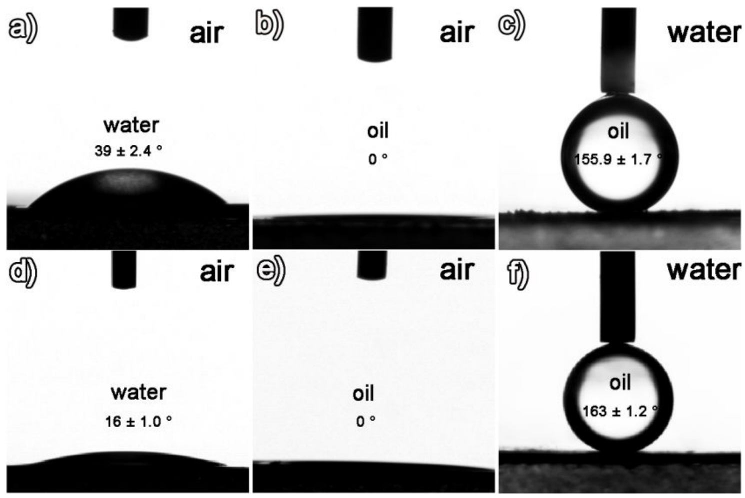

Figure 4. Wetting properties of the PVA/CS and bio-inspired hairy crab cheliped surfaces. a-c) depict the water contact angle (WCA) and oil contact angle (OCA) in air, and the OCA in water for the PVA/CS surface; d-f) depict the WCA and OCA in air, and the OCA in water for the bio-inspired material.

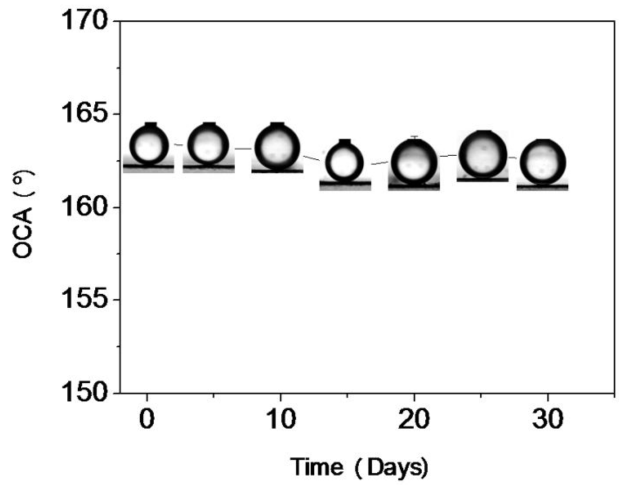

Figure 5. Stability of the underwater oil contact angle (OCA) on the bio-inspired superoleophobic hairy crab cheliped surface material.

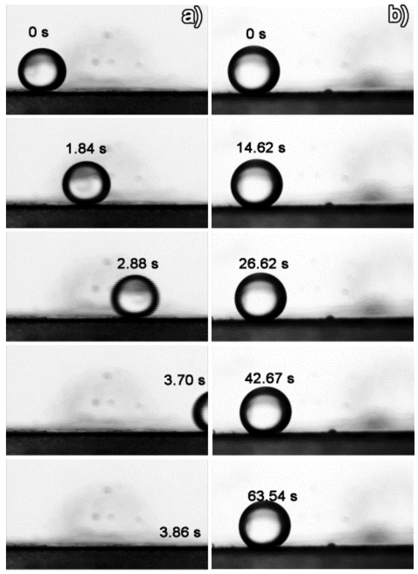

Figure 6. a) 2-μL oil droplet easily slide off the bio-inspired hairy crab cheliped material surface at an angle of 3°; b) no sliding was observed on the PVA/CS surface when the surface was likewise tilted to 3°.

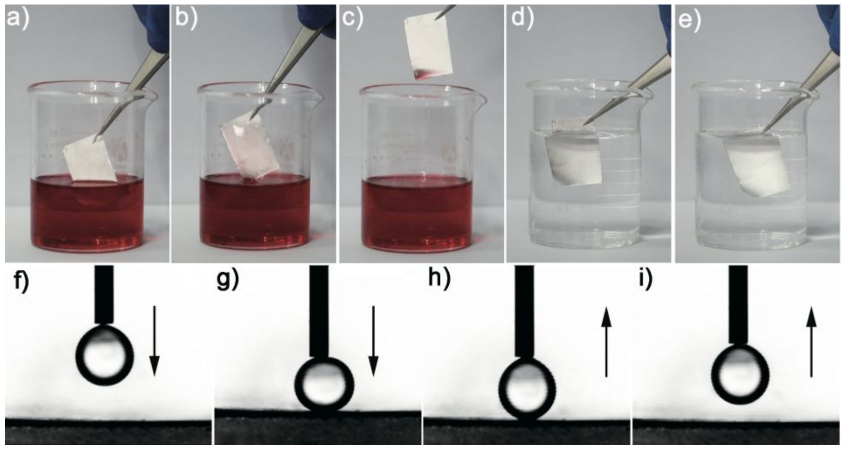

Figure 7. a-e) Underwater anti-oil-fouling performance of the bio-inspired hairy crab cheliped material surface; the sequences of images show that the PVA/CS/PNIPAAm surface, stained by oil, were self-cleaning when placed in water. f-i) Diagrams of the dynamic measurement of underwater oil-adhesion on the membrane.

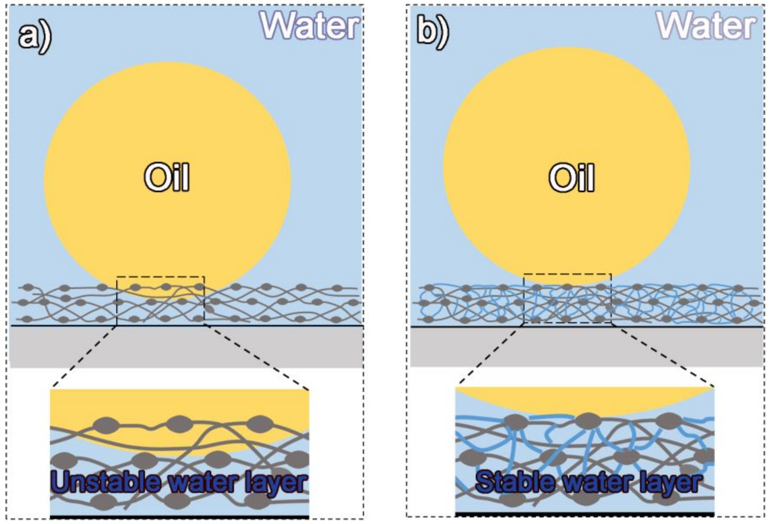

Figure 8. Schematic illustrations of the underwater oil wetting and adhesion mechanism on the PVA/CS surface and the PNIPAAm-modified surface. a) The fibrous structure could not form a stable water layer, resulting in a larger oil/solid contact area and high oil hysteresis; b) the cross-linked network induced a stable water layer by trapping water in the interspaces, thus leading to superoleophobicity and low oil adhesion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

The Infrared spectroscopy of the hairy crab cheliped surface, the PVA/CS surface, and the PNIPAAm-modified surface. Diagrams of the contact angle on the PNIPAAm surface. Diagrams of the contact angles on the aluminum surface. Photographs of the underwater property of the aluminum foil surface; Photographs of the underwater property of the PVA/CS surface

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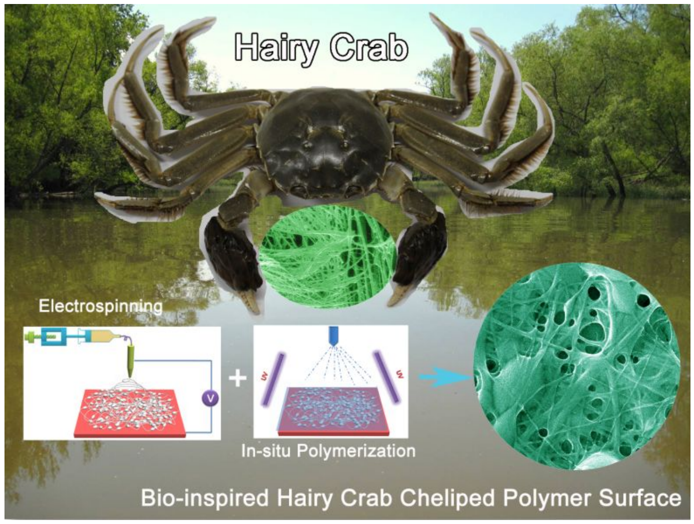
Hairy Crab
Electrospinning
In-situ Polymerization
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