

# Mussel-Inspired Underwater Adhesives- from Adhesion Mechanisms to Engineering Applications: A Critical Review

Yanfei Ma<sup>1,2</sup>, Bozhen Zhang<sup>1</sup>, Imri Frenkel<sup>1</sup>, Zhizhi Zhang<sup>2</sup>, Xiaowei Pei<sup>2</sup>,  
Feng Zhou<sup>2\*</sup> and Ximin He<sup>1†</sup>

<sup>1</sup>*Department of Materials Science and Engineering, University of California Los Angeles,  
Los Angeles, CA, USA*

<sup>2</sup>*State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics,  
Chinese Academy of Sciences, Lanzhou, China*

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**Abstract** Recent progress in the adhesion mechanism of mussels has led to great excitement in the field of adhesive materials. Although great progress has been made in the mussel adhesion mechanism and underwater adhesives, there are still many unknowns and challenges in this area. Thus, it is highly important to review the recent progress in mechanisms of mussel adhesion and mussel-inspired adhesives and predict trends for the future. In this review, we (1) summarize the research progress in fundamental interaction mechanisms in natural mussels; (2) discuss the application of the mussel interaction mechanism in the biomimetic mussel adhesive materials, from permanent/high-strength adhesives to temporary/smart adhesives; (3) briefly state the potential applications of the mussel-inspired adhesives in multiple fields, such as engineering applications, smart robotics and biomedicine; (4) summarize the future perspectives and unsolved challenges of mussel adhesion mechanisms and mussel-inspired adhesive materials. We envision that this review will provide an insightful perspective in understanding the mussel adhesion mechanism and directions to further explore, and promote the development of novel biomimetic mussel adhesive materials.

**Keywords** Byssus, mussel foot proteins, wet adhesion, adhesive, DOPA

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\*Corresponding author: zhouf@licp.cas.cn

†Corresponding author: ximinhe@ucla.edu

## 17.1 Introduction

As a marine organism, a mussel is able to adhere to various substrate surfaces, such as rocks, ship hulls, cables, etc., by using a proteinaceous holdfast or byssus to form a firm bond on the substrates which even can resist the impact of waves and erosion of seawater [1–4]. Such strong and stable adhesion is mainly attributed to the six mussel foot proteins (Mfps): Mfp-1 to Mfp-6. Each of these is distributed in a specific part of *Mytilus byssus* and performs its own functions. For example, Mfp-5 and Mfp-3 mainly exist at the interface and are responsible for adhesion based on various interfacial interactions dominated by 3,4-Dihydroxy-L-phenylalanine (DOPA, a catecholic amino acid in mussel adhesive proteins), such as hydrogen bonding, hydrophobic interactions,  $\pi$ - $\pi$  stacking, electrostatic interactions, and ion coordination [5–8]. Mfp-2 is mainly located inside the byssus, whose main contribution is enhancing the cohesion with a bridging effect generated by metal ions ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ) between Mfp-2 films as well as between Mfp-2 and other Mfps [9] (details are provided in Section 17.2).

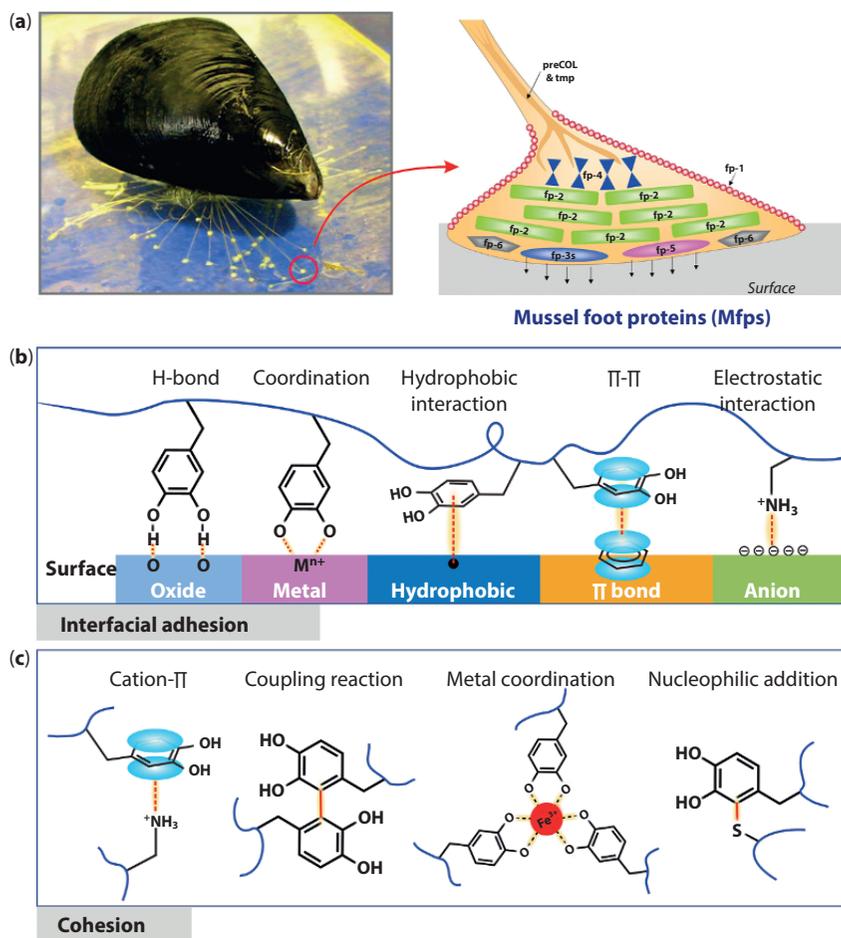
Wet adhesion is highly desired in specific applications such as water pipeline leakage repairing, wound dressing [10, 11], bioelectronic devices and biosensors [12–14]. However, the interface water molecules greatly weaken the contact adhesion, and thus significantly limit application of adhesive materials in various fields. Recently, a large number of wet adhesive technologies and materials have been developed. Generally, the mechanism of interfacial adhesion based on chemical interactions can be divided into covalent bonds and non-covalent bonds, of which the latter have a wider range of applications in adhesive materials because of their better flexibility and diversity. Compared with other organisms, mussels can produce a large number of non-covalent bonds during the adhesion process, because Mfps contain many specific functional groups, such as catechol, phosphate, carboxylate, amino groups and hydrophobic groups. By studying the adhesion mechanism of Mfps, a large number of biomimetic materials that can be used in different fields have been developed [15, 16]. Compared to traditional adhesives, the mussel-inspired adhesive materials have many advantages. Firstly, catechol-based adhesive materials can be adapted to a variety of substrates based on a number of interactions with the substrates [15, 17–19]. Secondly, catechol-based dynamic bonds can be used to design some intriguing smart adhesive materials whose interface adhesion strength can be switched between high and low values via destroying and restoring adhesive groups [20, 21]. Thirdly, the excellent adhesion of DOPA groups endows dopamine-based adhesive materials with high adhesion strength [22–26]. In addition, the challenges of producing consistent adhesives in the human body mirror the challenges encountered in the marine environment, in particular the presence of salt solutions, fluid flow, fouling, degradation, etc. Therefore, research on the adhesion mechanism of mussels and the development of mussel-inspired materials have spurred numerous new paradigms for the design and engineering of medical adhesive materials [27–31].

Over the past decade, significant progress has been made in many fields based on the known adhesion mechanism of mussels, not only in the primitive field (e.g. underwater adhesives) but also in interdisciplinary fields (e.g. electronic skin, biomedical engineering), where long-standing problems have been solved. However, to date, the mussel adhesion mechanism has not been fully elucidated and there are still many challenges (such as weak adhesion stability and environmental adaptability) in the area of underwater adhesives. Thus, it is highly important to review the recent progress in the adhesion mechanism of mussels and mussel-inspired adhesives and make prediction of the future trend. Here, we first briefly introduce the adhesion mechanism of mussels, and then summarize the research progress in mussel-inspired underwater adhesives including both permanent/high-strength adhesives and temporary/smart adhesives. Finally, we propose some current technical challenges and possible solutions as well as the future opportunities.

## 17.2 Adhesion Mechanisms of Mussel and the Catechol Chemistry

*Mytilus byssus* is composed of different mussel foot proteins including Mfp-1, Mfp-2, Mfp-3, Mfp-4, Mfp-5, and Mfp-6, which are responsible for its adhesion [5]. Each type of mussel foot proteins plays an important and characteristic role in mussel adhesion. Mfp-1 is a cuticle protein that endows the *Mytilus* byssal cuticle with high stiffness and high extensibility based on the interaction between  $\text{Fe}^{3+}$  and DOPA in Mfp-1 [32–34]. Mfp-2, the most abundant protein in the plaque, can interact with itself in the presence of iron or calcium ions to enhance the cohesion of the *Mytilus byssus* [9]. Mfp-3 and Mfp-5 are two adhesive proteins which contain up to 10~30 mol% DOPA that is mainly responsible for the strong adhesion of mussels [35]. Mfp-4 can bind with  $\text{Cu}^{2+}$  in high capacity and is located at the junction of the Mfp-2 and the byssal thread. Therefore, it is speculated that the function of Mfp-4 is to connect the byssal thread and the adhesive plaque via copper complexes [36]. Mfp-6 contains a large number of thiol functional groups. It is currently believed to have two functions: the first is to reduce dopaquinone to maintain the catechol functional group (adhesion group) and increase the cross-linking between different Mfps, and the second is to maintain the redox balance during the formation of the *Mytilus byssus* [8, 35, 37, 38]. Each mussel foot protein contains different types or proportions of constituent amino acids and plays a different role in the mussel adhesion based on different interactions [5]. A common feature is that all 6 proteins contain DOPA residues.

High-performance natural adhesive proteins should have not only high interfacial adhesion, but also high cohesion. There are abundant functional groups in mussel foot proteins, which have the potential to form a variety of interactions, such as hydrogen bonding, metal coordination, hydrophobic interaction, cation/anion/ $\pi$ - $\pi$  interaction and so on. Therefore, mussels can simultaneously possess high interfacial adhesion and cohesion, based on the interaction between proteins,



**Figure 17.1** Adhesion mechanisms of the mussel foot proteins. (a) Schematic diagram of the distribution of Mfp-1 to Mfp-6 [9]. (b) Interfacial adhesion. (c) Cohesion.

as well as between proteins and substrates (Figure 17.1). All interactions together endow the *Mytilus byssus* with strong underwater adhesion.

### 17.2.1 Hydrogen Bonding and Metal Coordination

Hydrogen bonding is a weak intermolecular interaction, or intramolecular if the geometry of a large molecule permits it, formed between the hydrogen atoms of one molecule and the atoms with large electronegativity and small radius (O, F, N, etc.) of another molecule, using hydrogen as a medium. DOPA contains catechol

hydroxyl groups, which can easily form hydrogen bonds with some inorganic oxide surfaces, such as mica [39, 40]. In addition, the H-bonding can also be formed on the surface of metal oxides such as titania [41, 42], alumina [43] and iron oxide [44]. Specifically, on the surface of a metal oxide, the catechol (DOPA) bonding is not always hydrogen bonding, rather it is pH dependent. With the increase of pH, the bonding gradually transforms from bidentate hydrogen bonding to bidentate coordination bonding [45].

In addition to the formation of interface adhesion based on the coordination between catechol group and certain metal or metal oxide, mussel foot proteins can also increase their own cohesion through interaction with free metal ions. Zeng *et al.*, demonstrated that the DOPA-metal interactions provide a cohesive bridge between adjacent Mfp-1 molecules. The bridge strength is up to  $4.3 \text{ mJ/m}^2$  in a buffer solution with the ionic strength close to seawater [34]. Monahan and Wilker systematically studied the influence of different metal ions on the degree of cross-linking of mussel foot proteins, and the results showed that  $\text{Fe}^{3+}$  exhibits the strongest coordination ability [46].

### 17.2.2 Hydrophobic Interaction

There are a lot of hydrophobic amino acids in mussel foot proteins, such as DOPA, tryptophan, isoleucine, and phenylalanine residues which may contribute to the formation of the hydrophobic interaction (another important water-mediated interaction) on hydrophobic surfaces [47]. Han and co-workers found that different mussel foot proteins have different abilities to remove the hydration layers from surfaces, which is a necessary step for adhesion, leading to more contact of adhesion molecules to form a stronger interface adhesion. Mussel foot protein-surface intimacy under force-free conditions relies on constituent hydrophobic side chains. These hydrophobic side chains act as initial facilitators, or vanguards, which can weaken the hydration forces at the surface and enhance the effective contact area of the interface [48].

### 17.2.3 Cation/Anion/ $\pi$ - $\pi$ Interactions

**Cation- $\pi$  interaction:** In mussel foot proteins, there are many aromatic residues and cationic residues, such as tryptophan, tyrosine, phenylalanine (aromatic functional groups), lysine and arginine (cationic functional groups), where the cationic functional group can easily form a cation- $\pi$  interaction with the electron-rich functional group (aromatic), which helps to enhance the cohesion between proteins. Although a cation- $\pi$  interaction tends to be much weaker in aqueous media than in the gas phase, it is stronger than the conventional electrostatic interaction (quite strong in nonpolar media) in the aqueous phase because it dissolves more easily [49, 50]. In order to evaluate the interaction, Lu *et al.* used surface forces apparatus (SFA), a micromechanics measuring instrument, to probe directly the mechanical

nature of cation ( $\text{NH}_3\text{R}^+$ )- $\pi$  (i.e., indole, phenol, and benzene) interactions in an aqueous solution. The results showed that the cation- $\pi$  interactions depend on the type of aromatic side group (indole > benzene  $\approx$  phenol) and can be affected by the introduction of other cations ( $\text{NH}_4^+ \approx \text{K}^+ > \text{Na}^+ > \text{Li}^+$ ) [49].

**Anion- $\pi$  interaction:** In addition to being rich in many cations and aromatic groups, mussel foot proteins also have a large number of anionic groups, such as glutamic acid and phosphoserine. Therefore, the anion- $\pi$  interaction may also be operative in the proteins and contribute to their high adhesion strength. Most recently, Zeng and co-workers demonstrated the existence and quantified the nanomechanics of anion (phosphate, sulfate and nitrate group)- $\pi$  (catechol group) interaction in marine bioadhesives using the SFA for the first time. This interaction is very strongly affected by charge density, polarity, and hydration effect. The interaction strength of anions with the  $\pi$ -conjugated moieties follows this trend: phosphate ester >  $\text{HPO}_4^{2-}$  >  $\text{SO}_4^{2-}$  >  $\text{NO}_3^-$  [51].

**$\pi$ - $\pi$  interaction:** The  $\pi$ - $\pi$  interaction based on aromatic groups in Mfps plays a very important role in mussel adhesion. Lu *et al.* found that oxidation of the 3,4-dihydroxyphenylalanine (DOPA) group in Mfp-1 will not reduce the cohesion of Mfp-1 protein, but the addition of chemicals with aromatic groups to Mfp-1 protein will increase the cohesion, which suggests that the cohesion of Mfp-1 protein is not mainly mediated by hydrogen bonds, but by the interaction based on aromatic groups, such as  $\pi$ - $\pi$  or cation- $\pi$  interaction [52].

### 17.2.4 The Flexibility of the Molecular Chain

In summary, there are a variety of interactions within Mfps and between Mfps and different substrate surfaces in the *Mytilus byssus*, which endows it with super strong underwater adhesion ability. Sufficient contact is the basis for these interactions. For macromolecules, the effect of chain flexibility on the contact during the adhesion process is very significant, especially on rough surfaces. The flexible, random coil conformation of macromolecules can easily adapt to different roughness and surface chemistries [53–55]. Chain flexibility generally decreases with increasing molecular weight in polymers [56]. Among the Mfps, Mfp-1 has the highest molecular weight (92.0 kDa), followed by Mfp-5 (9.5 kDa), and Mfp-3 has the lowest molecular weight (5.3 kDa). Therefore, compared with Mfp-3 (70 mol%) and Mfp-5 (61.1 mol%), Mfp-1 has the lowest flexibility (50.4 mol%), leading to the weakest adhesion strength under the same contact time [5].

## 17.3 Catechol-Functionalized Adhesive Materials

With the strong adhesion resulting from multiple interactions of catechol groups and different substrate surfaces, a large number of adhesive materials based on catechol chemistry have been reported. Based on catechol-functionalized adhesives' distinctive nature of strong underwater adhesion, many researchers in this

field focus on materials aiming for permanent strong underwater adhesion [16]. In addition, in order to achieve smart on-demand adhesion, diverse stimuli-responsiveness has also been introduced into many catechol-functionalized adhesives. Applications of these adhesive materials in hemostatic and wound sealing have also been demonstrated by a multitude of works [16, 57]. This section introduces the study of catechol-based adhesives with both permanent adhesion and stimuli-sensitive adhesion (e.g. pH, electrical signals, temperature, and light) [58].

### 17.3.1 Permanent/High-Strength Adhesives

Considerable works have been done to design and fabricate catechol-based permanent adhesive materials. Most of the efforts have focused on designing the compositions of synthetic polymers and designed proteins, tuning non-composition factors, and promoting the availability of catechol-bearing materials.

Directly polymerizing catechol-bearing monomers and bonding catechol groups to existing polymers are common methods to fabricate mussel-inspired adhesives. For instance, Kaneko and co-workers used bio-derived catechol-carrying caffeic acid and coumaric acid to synthesize catechol-functionalized adhesive resin [59]. Wilker and co-workers used polystyrene as a backbone and catechol as an adhesive group to produce poly(vinyl catechol-co-styrene), which has a better adhesive performance in saline than in deionized water [26]. Wan and co-workers used polyvinylpyrrolidone (PVP) as backbone and utilized straightforward alkyne-azide cycloaddition click chemistry to graft catechol groups on it, forming a catechol-functionalized PVP which shows better adhesion under water than under dry conditions [60]. Xu and co-workers used poly( $\gamma$ -glutamic acid) as backbone and fabricated a catechol-based adhesive for wound closure [61]. There are many other works that aim to design catechol-functionalized materials by using different polymer backbones and functional groups for biodegradability and high mechanical properties. For example, Wilker and co-workers introduced a catechol group into poly(lactic acid), a common biodegradable polymer, to create a biodegradable catechol-based adhesive [62]. Messersmith and co-workers used benzoxazine, a high strength thermoset engineering polymer, as the matrix and prepared structural catechol-based adhesives [24]. Advanced structural design of polymer chains has also been used to tune the properties of catechol-functionalized polymers. Wang and co-workers introduced a hyperbranched design that used dopamine and a triacrylate monomer to fabricate a biodegradable high-performance adhesive [63]. These works have demonstrated that it is possible to fabricate catechol-functionalized adhesives with different properties by simply selecting specific matrix polymers and tuning for performance.

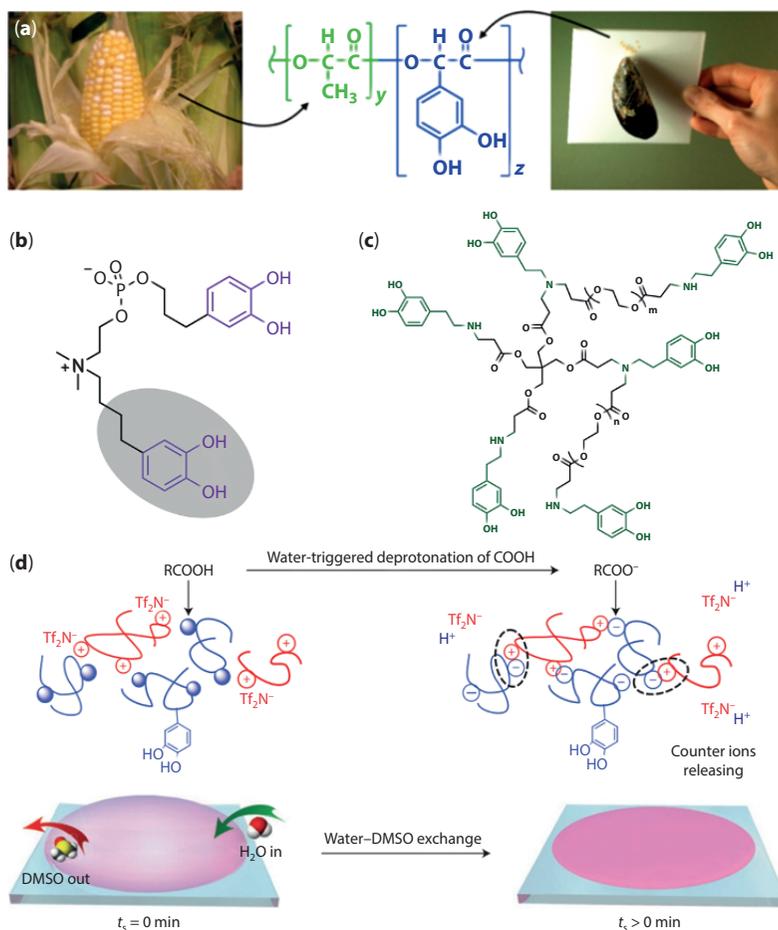
In addition to using synthetic polymers as backbones of the adhesives, many researchers have also engineered mussel-derived proteins to produce the required adhesives. Using the genetic fusion method, Lu and co-workers fused Mfps with another adhesion-related protein, CsgA protein, which is the major subunit of *E-coli*

amyloid curli fibres [64]. The as-prepared, bio-derived, protein-based, underwater adhesive could self-assemble into fibres, where the adhesive Mfps are located external to the CsgA cores. The researchers also conducted molecular dynamics simulations to analyze the assembly process. Besides using the existing proteins directly, some works have aimed to mimic the protein with synthetic polymers. Waite and co-workers analyzed the functional groups distribution of Mfp-5, the protein highly related to mussel's high adhesion, and synthesized a small molecule with similar percentage of catechol groups, positively-charged groups and negatively-charged groups [23] (Figure 17.2b). The molecules were then coacervated to form an adhesive. Though this kind of adhesive is more similar to the natural mussel adhesive, its performance is relatively low.

Some works focused more on promoting potential industrial applications of catechol-based adhesives. High cost and complex fabrication are both obstacles, keeping catechol-functionalized adhesives from practical applications. Schmidt and co-workers used corn zein protein and catechol-bearing tannic acid, which are both bio-derived, to fabricate more cost-efficient and environmentally sustainable adhesives [65] (Figure 17.2a). Mu and Wan selected two cheap and commercially available materials, poly(vinyl alcohol) and 3,4-dihydroxybenzaldehyde, and fabricated an adhesive through simple acid-catalyzed diacetal formation [66]. These innovations shed light on reducing the cost and complexity of producing catechol-based adhesives, which is necessary for industrial applications.

In conjunction with selecting specific chemical compositions for better adhesion or particular functionalities, some works paid more attention to non-composition designs. Among them, tuning the interaction between polymer chains is a relatively common strategy. For example, Wilker and co-workers enhanced adhesion by using additional dissipation. The energy-absorbing hydrogen bonds were introduced by adding diol ethylene glycol into carboxyl-bearing catechol-based adhesive, which further enhanced its toughness and performance [25]. Wan and co-workers systematically studied catechol-functionalized adhesives with different polarities and found that species with higher polarity had higher adhesive performance [67]. This can be explained by higher intermolecular interactions between high polarity moieties, which serve as an energy absorber and thus enhance adhesion. Special structural designs have also been combined with catechol-based adhesives. Gecko-inspired nanofabricated pillar arrays have been widely studied because of their high adhesion resulting from the intermolecular interaction amplified by their densified pillars [68]. Messersmith and co-workers combined the gecko-inspired structure with mussel-inspired adhesive coating and obtained a catechol-functionalized adhesive with underwater adhesion force increased by 14.6 fold compared to bare pillars [69].

Water-triggered adhesion is another promising property for adhesives used in underwater conditions, which makes it more convenient to store and handle the adhesives. Some researchers focused on introducing this property into catechol-functionalized materials. Waite and co-workers utilized solvent-exchange-induced



**Figure 17.2** Permanent/high-strength adhesives. (a) A degradable adhesive synthesized by combining a plant-based polymer with adhesion chemistry from mussel [62]. (b) High-performance mussel-inspired zwitterionic adhesive [23]. (c) A hyperbranched polymer adhesive [71]. (d) Wet adhesion mediated by solvent exchange [70].

polyelectrolyte complexation to turn a non-adhesive dimethyl sulfoxide (DMSO) solution of catechol-functionalized poly(acrylic acid) (PAA) and quaternized chitosan into an adhesive fluidic complex coacervate when injected into water [70]. In this process (Figure 17.2d), water deprotonated PAA which was neutral in DMSO, making it negatively charged. This negative polymer then formed a coacervate with the positively charged quaternized chitosan through electrostatic interaction, ultimately forming a fluidic adhesive. Here, the solvent exchange played a crucial role

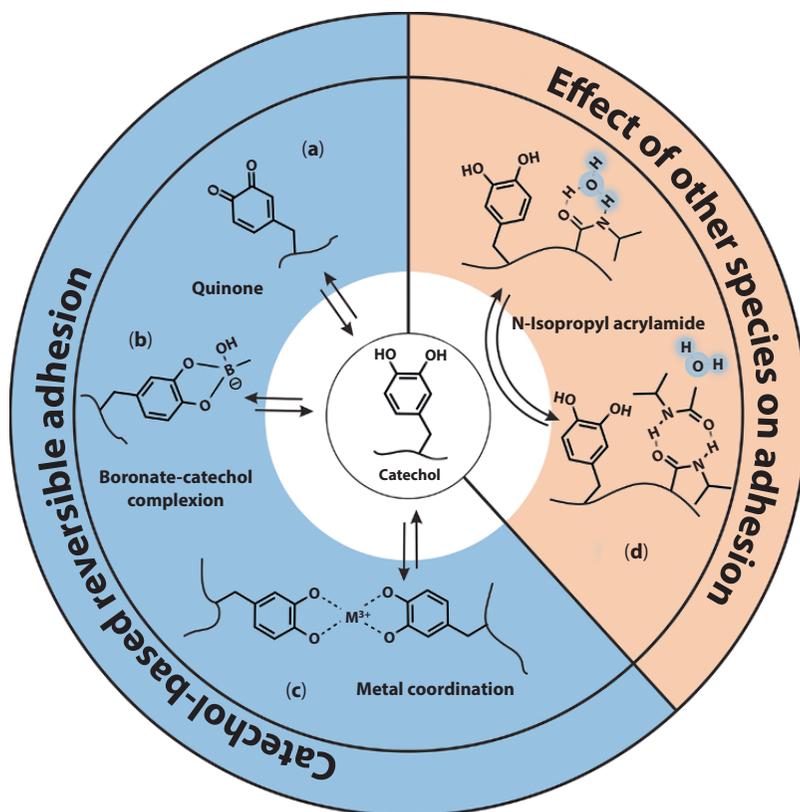
in the initiation of adhesion. Similarly, Liu and co-workers used the aggregation of hydrophobic moieties in water to realize the triggering [71]. They fabricated a hyperbranched polymer adhesive (Figure 17.2c) with hydrophobic backbone (pentaerythritol tetraacrylate) and hydrophilic catechol side branches. When the adhesive contacted water, the backbone aggregated and formed a coacervate, exposing more catechol groups to the target surface. These works illustrate methods that make catechol-based adhesives easier to store and handle when not in use.

### 17.3.2 *Temporary/Smart Adhesives*

When forcibly detached, permanent adhesives always leave uneven layer, which makes them not very optimal for applications which may only require adhesion temporarily. Moreover, peeling off strong permanent adhesives produces a huge peeling force, which consequently can cause pain when used on living patients. To address these problems, temporary adhesives which can achieve on-demand detachment are required. The main strategy for obtaining this kind of materials is to introduce stimuli-responsiveness into the catechol-based adhesives so that they can switch between bonding and non-bonding state after receiving a certain stimulus. So far, a variety of stimuli have been used to obtain smart switchable adhesives, such as chemical signal (pH), electric field, heat, and light [58]. Related works are introduced in the following subsections.

#### 17.3.2.1 **pH-Responsive Adhesives**

Catechol groups themselves are inherently sensitive to the changes in pH. When in a basic environment, the catechol groups are highly sensitive to oxidants, like oxygen in air, tending to oxidize into quinone which is not adhesive [72]. Taking advantage of this property, one can thus inactivate catechol-based adhesives by raising pH. However, this change in adhesion is irreversible, so it is always regarded as a drawback rather than a positive attribute. To control the pH responsiveness of catechol groups and obtain reversible adhesion, Lee and co-workers introduced a protection to preserve catechol's reactivity in alkaline environment [20]. They synthesized a copolymer with both catechol moiety and phenylboronic acid moiety. In alkaline environment (pH = 9), boronic acid groups form a complex with catechol groups, preventing them from oxidizing. When acidifying the environment (pH = 3), the complex disassembles and adhesion is recovered (Figure 17.3b). With this method, the pH responsiveness of catechol groups is retained and becomes reversible. The critical pH value can also be adjusted by varying the composition of the copolymer. In subsequent research, the same research group introduced anionic acrylic acid moieties into the original polymer to synthesize a responsive adhesive which can return to its adhesive state at a higher pH (7.5), making the adhesive usable in the neutral environment [73]. Actually, DOPA-mediated underwater adhesion of



**Figure 17.3** Temporary/smart adhesion mechanisms. Catechol whose phenolic hydroxyl groups are transformed by (a) oxidation, (b) complexation and (c) coordination, are assigned to blue-colored shade [20, 21, 34]. (d) Effect of other species on the wet adhesion of catechol is assigned to orange-colored shade [17, 18].

mussel proteins to the metal or metallic oxide substrates can be regulated through reversible metal coordination at different pH (Figure 17.3c).

Additionally, there is also a strategy to achieve this same function by utilizing the controllable folding of mussel-derived proteins. Börner and co-workers polymerized designed catechol-carrying peptides with the tyrosinase-activated method and embedded certain defects in its region critical for  $\beta$ -sheet formation. These defects prevented  $\beta$ -sheet formation under certain pH conditions [74]. The cohesion and adhesion of as-prepared adhesives are poor in acidic environment (pH 5.5), but rise sharply due to structural rearrangement when pH increases to 6.8. This method is more complex but allows more acute responsivity.

### 17.3.2.2 Electrically Responsive Adhesives

Compared with chemical signals such as pH, electrical signals are a more convenient stimulus because they can be transmitted remotely through electrical conductors. And with the intrinsic oxidability, catechol-carrying species are inherently sensitive to electrical signals due to the potential electrochemical reactions. Electricity could be used to trigger catechol's oxidation into non-adhesive quinone, thus abolishing its adhesion [21]. This method is simple but irreversible, so it is fit for one-time detachment-required applications (Figure 17.3a).

### 17.3.2.3 Thermally Responsive Adhesives

Both pH and electrical stimuli as mentioned require contact with the material to take effect, which is still not as convenient as remote stimuli such as heat and light. This subsection mainly focuses on thermally responsive catechol-based adhesives. Thermally responsive polymers have been investigated for a long time, providing a strategy to directly combine catechol with existing thermally responsive materials such as poly(*N*-isopropyl acrylamide) (PNIPAAm). For example, Wang and co-workers utilized host-guest interaction to design a thermally responsive catechol-functionalized underwater adhesive [18]. They combined cyclodextrin and PNIPAAm as host, thermally responsive moieties, and conjugated adamantane and DOPA were guest and adhesive moieties, in which cyclodextrin and adamantane connected the two different chains through host-guest interaction. When temperature is under the lower critical solution temperature (LCST) ( $\sim 35^\circ\text{C}$ ), the PNIPAAm chain is in swollen state which shields the interfacial interaction between DOPA and target surface, making the material non-adhesive. When temperature exceeds LCST, PNIPAAm chains located above DOPA chains through host-guest interaction will collapse and agglomerate, exposing the adhesive moieties and making the adhesive material adhere again (Figure 17.3d).

Furthermore, the sol-gel transition of PNIPAAm has also been used to design thermally responsive adhesives. Zhou and co-workers grafted catechol and PNIPAAm moieties to chitosan backbone and synthesized a thermally responsive wet adhesive [75]. Due to the sol-gel transition of PNIPAAm, the material can change reversibly between lubrication state and adhesive state when its temperature goes above and below LCST ( $\sim 35^\circ\text{C}$ ). This design can also be combined concurrently with other strategies for adhesion enhancement. In another publication from this group, catechol-NIPAAm copolymer was coated on a gecko-inspired structure to form a thermally responsive pillar array with a similar switchable behavior depending on temperature [17].

### 17.3.2.4 Photo-Responsive Adhesives

Compared with heating alone, light is a more suitable signal for remote transmission. With the help of photo-thermal additives, photo-responsivity can be added to thermally responsive adhesives conveniently.  $\text{Fe}_3\text{O}_4$  nanoparticles

are a common additive for this use, and were used in the two works mentioned in subsection 17.3.2.3 [17, 75]. These particles made it possible to use remote near-infrared irradiation to heat the adhesive and trigger its thermally induced transformation. This photothermal technique could be used to extend the application of various thermally responsive adhesives and fabricate optically responsive adhesives conveniently.

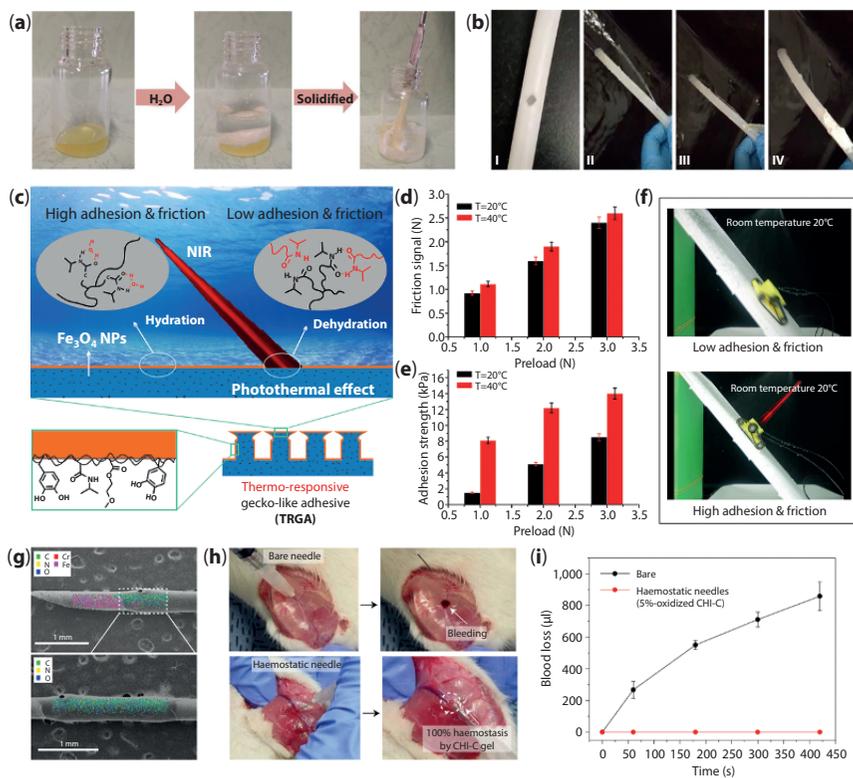
Photochemical reactions could also be used to fabricate photo-responsive adhesives. Wang and co-workers utilized dimerization of anthracene, a Diels-Alder reaction, to obtain a photo- and thermal-responsive catechol-functionalized adhesive. When exposed to light, anthracene dimerizes and the polymer chains are cross-linked, which “turns on” the adhesion. When the adhesive is heated to over 70 °C, the material returns to its non-adhesive state. This process can cycle reversibly [76].

### 17.3.3 Applications

Due to the outstanding underwater adhesion performance of catechol-functionalized adhesives, many potential applications have been demonstrated. So far, biomedical applications such as hemostasis and wound sealing have been the main focus in this field. Recently, other applications in fields such as engineering sealing, underwater repair, and robotics have also been attracting researchers’ attention. This subsection focuses on how permanent and temporary catechol-based adhesives could be applied.

Firstly, adhesives capable of working in physiological (wet) environments are highly required in biomedical fields. Currently, the most used methods for hemostasis and wound closure in surgery are still invasive methods, such as sutures and staples, which may cause infections and further trauma [77]. Replacing these with non-invasive surgical adhesives could make hemostasis safer and simpler. However, the present commercial surgical adhesives like fibrin glue and albumin adhesive suffer from poor adhesion. Catechol-based strong underwater adhesives can be used to address these problems. Several catechol-functionalized biocompatible materials have been employed as biomedical sealants, such as bio-derived chitosan [30, 75, 78], poly(amino acid) [61] and so on. These materials can function as liquid glue, solid patches, or needle coatings suitable for a number of surgical conditions. For biomedical application, water-triggered or thermally responsive properties are also useful, which can help the materials turn to an adhesive state upon contacting the surface of skin or other organs. Zhou and co-workers used a thermally responsive catechol-based adhesive coating to fabricate a smart hemostatic needle [75] (Figure 17.4g). When the needle is inserted, the coating is a lubricant, helping with the insertion. After the needle is removed, the coating is left on the pinhole in its adhesive state, sealing the wound created by the needle (Figure 17.4h and 17.4i).

Moreover, strong catechol-functionalized adhesives can also be used in engineering applications. With designed chemical structures and processing, they can



**Figure 17.4** Potential applications of the mussel-inspired adhesives. Engineering Applications: (a) Water-triggered coacervation of hyperbranched polymer adhesives (HBPA). (b) Mend the hole of silicone tube with HBPA [71]. Smart robotics: (c) Remote control over thermo-responsive gecko-like adhesive (TRGA) (d) Friction and (e) adhesion of TRGA surface under different temperature conditions. (f) Realizing controllable movement of the mobile device on a wet tilted glass plate, slipping without near-infrared (NIR) irradiation (top) or climbing upon NIR irradiation (bottom) [17]. Biomedicine: (g) SEM image (top) of the catechol-conjugated chitosan coated (CHI-C-coated) needle and EDS analysis (bottom) of surface chemical components. (h) Hemostasis was assessed upon intramuscular injections of Sprague Dawley rats injected with bare needles (top) and CHI-C-coated needles (bottom). (i) Blood loss as a function of time following injections with bare needles and CHI-C-coated hemostatic needles [30].

have different desired engineering properties. For example, by using thermoset polymers as the backbone, one can produce a high-strength structural adhesive [24]. Alternatively, choosing polymers based on desirable fluidic properties allows to obtain adhesion conformable to rough surfaces, which can then be used to fix fractured rubber and other materials [76]. In addition to these classic engineering

applications, catechol-based adhesives are also eligible for underwater repair due to their outstanding underwater adhesion [71] (Figure 17.4c-f), which is highly required but extremely difficult using currently available common adhesives. The diversity and tunability of catechol-based adhesives broaden the fields to which they may be applied, and their excellent underwater adhesion performance makes them competent candidates for myriad niche areas.

Catechol-functionalized adhesives can also function as coatings to modify a targeted surface. With the promising adhesion property, these coatings alter the behavior of coated surfaces when they come in contact with other surfaces. This has been applied to robotics to manipulate the locomotion of intelligent robots [17, 79]. A thermally responsive adhesive was coated on the track of a mobile device, which helps it to climb a wet, tilted, glass plate that it would otherwise be unable to climb without such adhesion (Figure 17.4f). With the development of underwater robots and other devices necessitating underwater contact, catechol-functionalized adhesive coatings are expected to have an increasingly vital role in this field.

## 17.4 Summary and Outlook

In the past, much attention has been paid to mussel-related catechol-based adhesion, including the adhesion mechanism of Mfps and adhesive materials utilizing the catechol chemistry. The distribution, composition, and contribution of mussel foot proteins in *Mytilus byssus* have been thoroughly investigated, deepening the understanding of the mechanism and interactions giving rise to its strong underwater adhesion performance. Based on the adhesive property of the catechol group, many synthetic adhesive materials have been designed and fabricated, including strong permanent adhesives with diverse polymer backbones and smart stimuli-responsive adhesives taking advantage of the oxidation of catechol or other responsive moieties. However, though there has been much research done in this field, there are still many remaining challenges and opportunities, which are further discussed in this section.

Though much attention has been paid to chemical compositions (like backbones) of catechol-based adhesives, little attention has been paid to non-composition aspects such as processing and structural design. The composition and functional groups of Mfps are critical to their adhesion, but the distribution of different Mfps and their microstructure also play a synergistic role. As is known, many biogenic materials' outstanding properties originate from their fine hierarchical structures, such as in nacre [80]. Therefore, it is predicted that further investigating the natural structure of *Mytilus byssus* could inspire more work on adhesion related to microstructure-induced high performance. Moreover, existing property-enhancing geometrical designs and processing methods could also be introduced into mussel-inspired adhesives. Gecko-inspired pillar arrays have demonstrated an ability to be combined with catechol-contained coating [17, 69].

And grooved structural designs that enhance adhesion by facilitating the drainage of water have been reported in non-catechol adhesive research [81]. These works are encouraging for emerging structural designs. Novel structure-controlling processing methods, such as self-assembly and micro-templating, could also be introduced to tune the catechol-based adhesives.

Furthermore, stimuli-responsive adhesion is another promising and meaningful subfield. This subfield was brought forward a few years ago and has gained increasing attention. Many topics including proper signal and responsive material selection, and accelerating the responses are still underdeveloped areas. In addition to switchable adhesives, these smart adhesive materials could also be useful in applications like soft robotics and smart encapsulation. Furthermore, borrowing concepts from other related fields is another emerging trend. Catechol-based adhesives is a subfield of hydrogel adhesives, which is also a novel field receiving increasing attention. Many concepts and designing strategies are universal to both fields so that it is reasonable to use methods in that field to enhance the performance of catechol adhesives. For example, reversible bond-induced dissipation used to enhance the energy absorption ability of adhesives is a hot topic in this field [82], which could be introduced to catechol-based adhesives [25].

Mussel-inspired adhesives have been an exciting field in academic research for years, but there is almost no commercialization. The main obstacles preventing these from commercialization include high cost of catechol-containing species and lack of rigorous control over practically important parameters, such as curing rate, biocompatibility, chemical stability and so on. Therefore, application-oriented research promoting the industrial translation of catechol-based adhesives is another important direction for this field. Finding less costly raw materials and improving the scalability of fabrication are useful for enhancing the availability of catechol-functionalized products. In addition, it is important to study and develop novel curing mechanism and enhance the stability of catechol in diverse environments (such as adding reductant [83]) to improve the properties of practical adhesives. There is still plenty of space for further mechanism investigation, material design and commercialization promotion.

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