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# Self-Healable Materials for Underwater Applications

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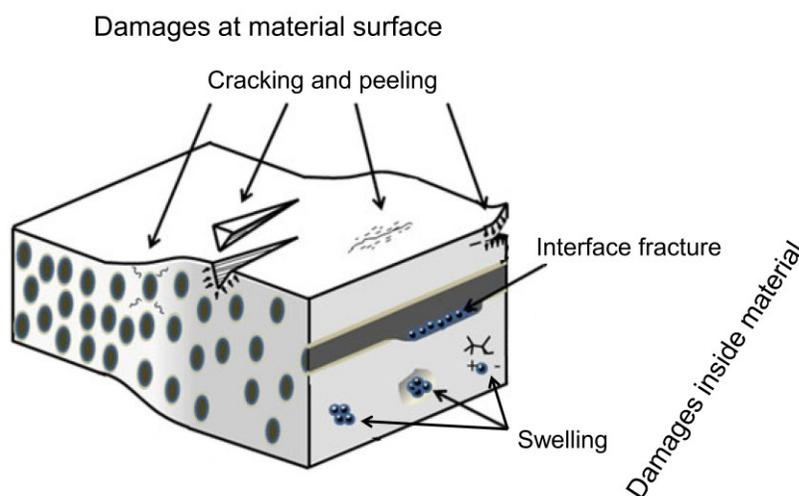
## Abstract

This progress report focuses on the development of new advanced materials with self-healing ability targeting underwater applications. This challenging task requires a particular approach of water-insensitive dynamic chemistries. Among them, the nature-inspired group of catechol-based functional materials are widely utilized due to the proof of the success of the mussel byssus on underwater self-healing and adhesion. Interestingly, self-healing can be manipulated on demand by incorporating active materials such as redox species or magnetic particles into the matrix of the self-healing polymer. Finally, the underwater applications of these self-healing materials, as a proof-of-concept of some electrochemical and electronic devices, are relatively novel at the moment. However, from our perspective, we expect a large impact of these materials on technologies in the near future.

**Keywords:** Self-healing, underwater, polymer, catechol, device, water-insensitive

## 1. Introduction

Designing materials capable of self-repairing or self-healing underwater has been a challenging task for all scientists. The first challenge comes from the hydrophilicity of water molecules and their sorption into the polymer structure, which promote the plasticization of the polymer (Figure 1). This process is associated with a decrease in the glass transition temperature ( $T_g$ ) of the polymer, leading to hydrolytic degradation.<sup>1</sup> **It is worth remembering that** the amount of water absorbed at equilibrium greatly depends on the chemical structure (e.g., hydrophilicity) and morphology (e.g., porosity) of the polymer. The second challenge is the high relative permittivity (or dielectric constant, denoted  $\epsilon$ ) of water ( $\epsilon = 80$  at 20 °C), which weakens the mechanical properties of the polymers and/or polymer-based materials (e.g., polymer composites).<sup>1</sup> This property is simply explained by the electrostatic Coulomb force between two point charges, e.g., the electrostatic interaction between two oppositely charged polymers, the strength of which is inversely proportional to the  $\epsilon$  of the medium.<sup>2</sup> The design of underwater self-healing materials therefore requires a dedicated approach to avoid or neutralize the continuous damaging effect of water. This task is not trivial, and most of the materials that are already known as self-healing under ambient conditions do not necessarily provide the same capabilities underwater. Solving the abovementioned challenging tasks will increase the durability of the polymer or materials in general, which defines the safety of high-end products and will bring about a new range of applications, especially in the field of underwater soft robotics **and tissue engineering.**<sup>3-6</sup>



**Figure 1.** Illustration of possible internal and superficial damage caused by water. (Reproduced with permission.<sup>1</sup> Copyright 2014, Springer). The water molecules can be absorbed by materials through either hydrophilic affinity or pore trapping.

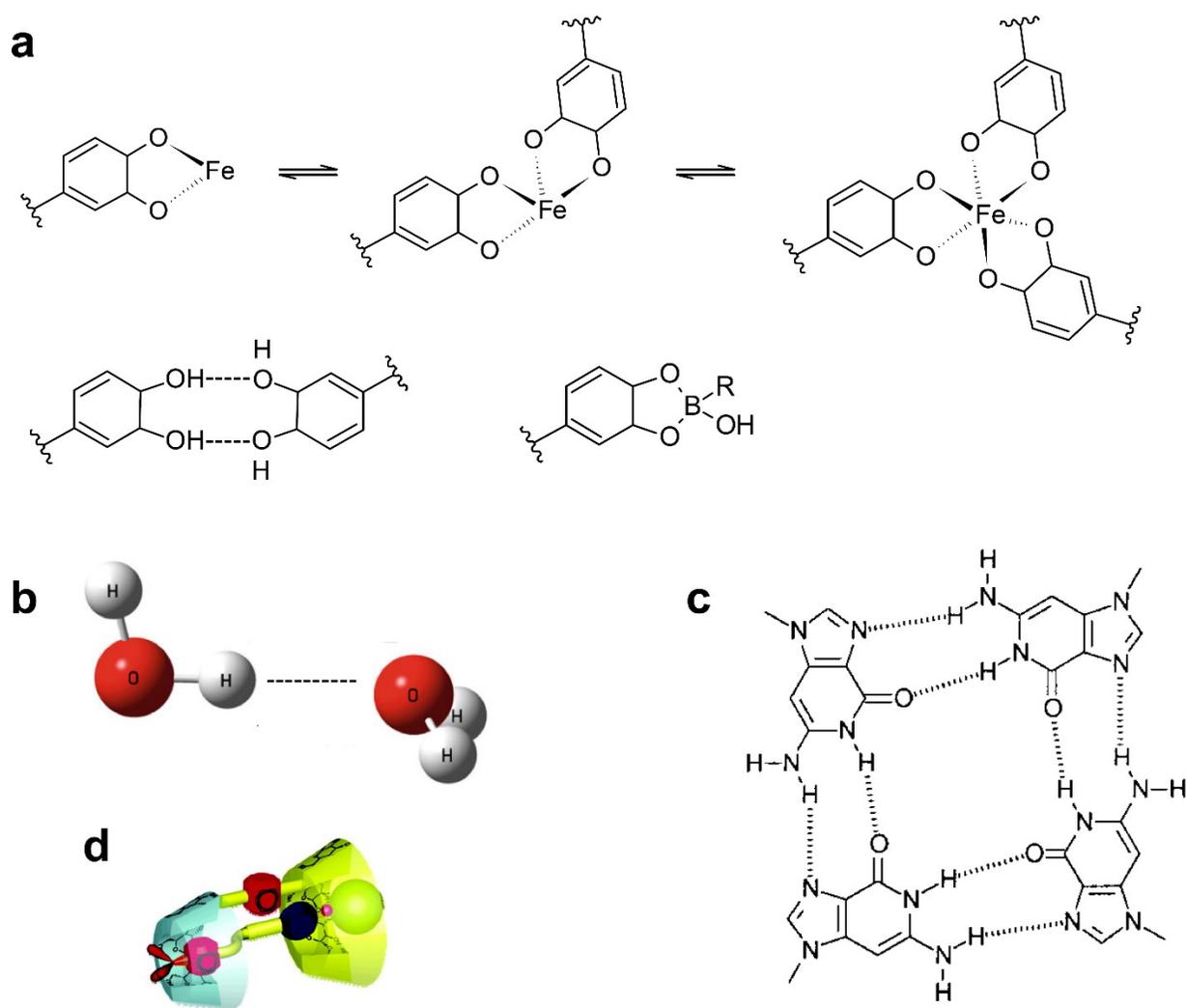
In this report, the underwater challenges are resolved by not only using water-insensitive materials but also endowing them with a very exciting ability – *underwater self-healing*. This feature is inspired by the wound healing process in nature, in which there are many examples, such as animal tongues and internal organs and some invertebrate biomaterials, that exhibit self-healing properties, even underwater.<sup>7-9</sup> This progress report begins by reviewing the state-of-the-art chemistries and design approaches for achieving underwater self-healing capabilities (section 2). The progress report then continues with a demonstration of how these chemistries apply to the fabrication of underwater self-healing materials (most of which are polymeric materials). The promise and challenges in the advances of each aspect of the underwater self-healing capability are presented and discussed. Critical thinking and ideas regarding the orientation of the development of this field in the future are also discussed.

## **2. Chemistries for self-healing underwater**

Self-healing materials emerged from a group of composite-like (such as capsule- or vesicle-based self-healing) and supramolecular (in the case of intrinsically self-healing) materials.<sup>10-12</sup> The former design performs self-healing with the release of healing agents (monomers/precursors and catalyst/enzymes) from fractured capsules/vessels. This composite-like design features the practical advantages of less complicated chemistries and the ability to sustain large damage; however, it seems the less favorable candidate for self-healing devices, particularly for underwater applications. In other words, extrinsic self-healing is infeasible for underwater self-healing because water would deactivate the encapsulated catalysts or inhibit the polymerization of the monomers released from ruptured microcontainers. Moreover, other limiting factors include the slow self-healing and complexity of the composite (in which it is hard to disperse additional active materials). Obviously, the only remaining choice is to endow polymers with an intrinsic self-healing ability, which will ensure high structural dynamicity and provide fast and multi-time self-healing. Accordingly, the last decade has witnessed the advance of the latter design of self-healing polymers, which is based on the intrinsic reversible formation of molecular interactions/bonds between the functional groups designed intrinsically on the polymer backbone.<sup>13-17</sup>

The main reason for the failure of reversible bonds underwater in most of the currently existing self-healing materials arises from the interference of water molecules in the “active sites” – the sites of available functional groups – which are involved in the reversible bonds between the chains of the polymer. In addition, compared to the chemistries that are practical in air, the

choice of chemistries for molecular interactions underwater is relatively limited,<sup>18</sup> as the binding constant between functional groups, which make self-healing possible, has to surpass those between the functional groups and water molecules.<sup>19</sup> Consequently, it is important to look for strong bonding to overcome the interference of water molecules. Herein, we present a number of bonds, including Lewis acid-base (hydrogen and  $\sigma$ -hole) bonds, coordination bonds (catechol chemistry), and hydrophobic interactions, which have been successfully applied in some related studies.



**Figure 2.** (a) A brief summary of catechol chemistry, including catechol-Fe coordination, in which the proportion of mono-, bis-, and tris- (from left to right) coordinated complexes is pH dependent; hydrogen bonding; and reversible covalent B–O bonding.<sup>20</sup> (b) Hydrogen bond formation between two water molecules. (c) Multiple hydrogen bonding formed in a self-assembled tetramer of deoxyguanosine oligomers in an aqueous medium. (Reproduced with permission.<sup>21</sup> Copyright 1991, ACS Publications). (d)

Hydrophobic interaction found between a cyclodextrin (CD) dimer and a tert-butyl group. (Reproduced with permission.<sup>22</sup> Copyright 2006, ACS Publications)

## 2.1 Catechol chemistry

Blue mussel (*Mytilus edulis*, common mussel) has been reported to achieve rapid, tough, and long-lasting adhesion in wet environments where most synthetic glues are unsuccessful.<sup>23-25</sup> By analyzing the attachment system of the mussel, i.e., its byssal thread and **plaque**, scientists concluded that the presence of a high percentage of L-3,4-dihydroxyphenylalanine (DOPA) is the main contributor to the outstanding adhesion of the **plaque** and the self-healing of the thread under seawater.<sup>23, 25-27</sup> The latter self-healing ability is attributed to the chemistries of DOPA, in particular the catechol moiety, which enable a wide variety of reversible chemistries. These exceptionally versatile reaction chemistries of catechols allow on-demand design of the chemical and physical properties of materials. Catechol-containing natural molecules have been used for different applications, including **(i)** preparing stable surface anchors, adhesives, and multifunctional coatings onto almost any material; **(ii)** developing biocompatible materials with multiple clinical advantages; and **(iii)** integrating them into polymer chemical structures as reversible crosslinkers to obtain self-healing materials.<sup>28</sup> Thus, catechol-functionalized polymers have demonstrated their remarkable self-healing ability underwater, especially seawater, through coordination chemistry, hydrogen bonding, and reversible boron ester (B-O) bonding.

Coordination chemistry is emerging as a promising tool to make self-healing materials due to the reversible nature of coordination bonds.<sup>20, 29, 30</sup> For example, the coordination of catechol and Fe(III) (Figure 2a, upper) can lead to the formation of a self-healing hydrogel that is similar to the coating of the byssal threads.<sup>31-33</sup> More interestingly, the chemistry is able to extend easily to include other hard metal ions.<sup>34</sup> The stoichiometry of the metal–catechol bond is highly pH dependent and therefore defines the mechanical properties of the resulting complexed materials. At low (e.g., acidic) pH, mono complexes are formed. As the pH increases, the formation of stable bis and tris complexes appears. Thus, the coordination chemistry of the catechol tends to be used in stable (tris complexes) and reversible (unoxidized catechol) designs for self-healing under neutral and basic conditions.

Based on the same dihydroxyl group, catechols are capable of participating in either hydrogen bonding with each other or other polar molecules<sup>24</sup> and forming reversible covalent B–O bonds with boronic acids and their derivatives<sup>35-37</sup> (Figure 2a, lower). The hydrogen bonds between catechol groups are usually very sensitive to pH conditions, which strongly restricts their

practical application in some fields. The B–O bond can also be seen as a coordination bond with a high degree of covalency.<sup>38-40</sup> Many examples of underwater self-healing polymers based on the B–O reversible bonds have been introduced. The resulting materials are hydrogels prepared by using either boronic acids as crosslinkers or boronic acid-derived polymers to react with catechol-functionalized polymers.<sup>41-43</sup> These hydrogels exhibit self-healing ability in a wide pH range.

## 2.2 Lewis acid-base interactions

Based on the same concept of Lewis acids and bases, which act as electron acceptors and donors, respectively, this class of interactions involves electrostatic attraction between two oppositely charged regions. In addition to the electrostatic forces between ions and/or van der Waals dispersion forces, the Lewis acid-base interaction involves an electron density shift, i.e., charge transfer from the Lewis base to the Lewis acid. Indeed, it was shown that the Lewis acid-base interaction involves various chemical bonds, such as hydrogen, halogen, chalcogen, pnictogen, tetrel, triel, beryllium, and lithium bonds.<sup>44</sup> These bonds can be divided into three major groups: hydrogen bonds,  $\sigma$ -hole bonds (e.g., halogen bonds) and  $\pi$ -hole bonds.<sup>45, 46</sup>  $\sigma$ - and  $\pi$ -holes (the region of positive electrostatic potential or lower electron density) can also be regarded as Lewis acids that theoretically can interact with numerous negatively charged species.<sup>46, 47</sup> Within the scope of this report, we still focus on the types of bonding that are being used for underwater complexation, i.e., multiple hydrogen bonds and halogen bonds.

### 2.2.1 Multiple hydrogen bonding

Figure 2b shows an example of the water dimer linked through a hydrogen bond. The hydrogen bond  $A-H\cdots B$  can be understood as “an attractive interaction between a hydrogen atom from a molecule or a molecular fragment  $A-H$  in which  $A$  is more electronegative than  $H$ , and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation”, as recommended by IUPAC.<sup>48</sup> According to the concept of Lewis acid-base interactions, the  $A-H$  proton-donating bond is part of the Lewis acid subunit, while  $B$  marks the Lewis base center possessing at least one free electron pair. The  $H\cdots B$  interaction is an analog of the interaction of the Lewis acid and base centers, respectively. The  $H$ -atom hemisphere is characterized by a positive electrostatic potential, while the  $B$ -center is characterized by a negative electrostatic potential. Hydrogen bonding exhibits directionality (i.e., hydrogen bonds define the *growth* direction of a supramolecular polymer)<sup>49, 50</sup> and versatility (viz. diversity of design and manipulation of hydrogen bonds)<sup>51</sup>.

However, even strong hydrogen bonds are often weakened by water molecules. Therefore, the design of multiple hydrogen bonding is a practical way of stabilizing complexes or complexed polymers underwater by increasing the number of hydrogen bonds. This concept has therefore been used for designing intrinsic self-healing polymers.<sup>13, 51, 52</sup> Brunsveld et al.<sup>51</sup> demonstrated that the stability constant of complexes is proportional to the number of hydrogen bonds. Figure 2c is an example of a self-assembled tetramer of deoxyguanosine oligomers that is stable underwater.<sup>21</sup>

### 2.2.2 Halogen bonding

According to the IUPAC definition, “a halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity”<sup>53</sup>. This section focuses specifically on the C-F group of polyvinylidene fluoride (PVDF) that was utilized to obtain a self-healing polymer.<sup>54</sup> Herein, the C-F moiety serves both as a halogen bond donor and as an acceptor. Owing to fluorine having the highest electronegativity among all elements, the C-F bond is highly polarized with the electron density substantially on fluorine, resulting in a very high dipole–dipole binding constant of the C-F bonds between polymer chains.<sup>55, 56</sup> The polymer chains of PVDF bind each other through electrostatic dipole–dipole interactions between C-F dipoles. Thus, water molecules barely interfere with these interactions, which are characteristic of fluorinated-based polymers of high hydrophobicity and chemical stability underwater.<sup>57-59</sup>

### 2.3 Hydrophobic interaction

Dispersing a hydrophobic molecule or a polymer into water (a hydrophilic medium) causes the formation of a water cage around the solute through hydrogen bonding (see section 2.2.1).<sup>2</sup> On the one hand, the process is exothermic and corresponds to the negative values of the enthalpy of transfer of the hydrophobic molecule (from a nonpolar solvent) to water ( $\Delta_{\text{transfer}}H$ ). On the other hand, the process decreases the entropy of the system and leads to negative values of  $\Delta_{\text{transfer}}S$  due to a proportional increase in the very large number of water cages around each molecule. However, when these hydrophobic molecules interact with each other and then form complexes (e.g., the CD dimer and *tert*-butyl group in Figure 2d), fewer water cages are required, and the unbound water molecules leave the hydrophobic molecules. This effect leads to a decrease in the organization of the water and thus a net *increase* in the entropy of the system. The increase in entropy is the origin of the hydrophobic interaction. This interaction tends to support self-healing in hydrophobic-derived polymers.<sup>60, 61</sup> The hydrogels using multiple hydrophobic moieties tend to

form microphase-separated domains inside the hydrogel to decrease their interaction with water. Also, such separated domains are known to contribute to an improvement in mechanical properties.<sup>62</sup> Furthermore, the reversibility of hydrophobic interactions inside the domains can dissipate energy upon exposure to environmental damage and then reform again.

### **3. Underwater self-healing polymers and their applications**

As discussed in section 2, the polymer can be healable or self-healable when a water boundary layer (the interferent for the reformation of the dynamic bonds) is removed at cracked surfaces to strengthen the molecular interactions. If the polymer is too hydrophilic, it absorbs huge amounts of water (polymer network swelling), which in turn decreases the mechanical strength, leading to an increased sensitivity to structural damage. In addition, the presence of water molecules inside the polymeric network eventually accelerates its degradation. Therefore, the high crosslinking density and hydrophobicity of the polymer network are the central factors that are considered in the design of self-healing polymers/materials for underwater applications. Experiments for the fabrication of new materials to overcome these challenges are reported in the following subsections.

#### **3.1 Underwater self-healing polymers**

Catechol-derived polymers have been the main class of polymers with underwater self-healing ability.<sup>63-65</sup> The predominant use of these polymers is attributed to one or a combination of the following advantages: **(i)** functionalization of the catechol group on the polymer backbone is relatively simple; **(ii)** catechol-based polymers are often biocompatible; and **(iii)** their chemistry is diverse in terms of synthetic routes and properties (Figure 2a).<sup>66-68</sup> As discussed in section 2.1, the reversible B-O bond is the key to achieving both underwater stability and self-healing in this category of polymers, where the crosslinkers (e.g., phenylboronic acid (PBA) or phenyldiboronic acid (PDBA)) facilitate the healing process<sup>42, 43, 69</sup> via re-esterification of the B-O bonds upon the reconnection of the cut surfaces. The healing mechanism is related to the presence of free catechol and boronic acid groups at the surface, which are ready to undergo esterification and heal the cut. These free functional groups appear when the polymer is swollen underwater, and therefore, the equilibrium of the reaction slightly shifts towards hydrolysis. Thus, the absorbed water enhances the dynamics of esterification between the catechol and boronic acid moieties.

Many examples of catechol-functionalized polymers have been reported. These examples include poly(dopamine acrylamide-co-n-butyl acrylate) [p(DA-co-BA)]<sup>19, 20</sup> and catechol-grafted hyperbranched polyurethane (HBPU).<sup>42, 70, 71</sup> **But we will start with the most straightforward study**

in which polydopamine (pDA) is used as the healing matrix in an anti-corrosion coating consisted of benzotriazole-load mesoporous silica nanoparticles.<sup>72</sup> Benzotriazole herein is a well-known inhibitor of steel corrosion and its engagement in the coating assisted by self-healing ability of the coating. The self-healing mechanism was explained by the coordination chemistry between catechols of pDA and Fe from rust upon damages.

p(DA-co-BA) is a catechol-based polymer that can form both hydrogen and coordination bonding, leading to nonswellable and self-healable hydrogels.<sup>43, 73</sup> p(DA-co-BA) is complexed with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in seawater.<sup>73</sup> The complexation causes a mechanical transition of the viscous p(DA-co-BA) in seawater and transforms it into hard material with a toughness of  $\sim 5$  MPa. The healing efficiency of the hydrogel is as high as 80% (calculated from toughness values). Interestingly, the swelling of the hydrogel in seawater is lower than that in deionized water due to the difference in osmotic pressure. Coordinating p(DA-co-BA) with PDBA (mole ratio of 2 catechol to 1 PDBA) and combining it with triethylamine (TEA) enable nonswellable ( $< 2$  wt% of swelling) and highly self-healable (healing efficiency of 91% under artificial seawater) properties for a period of over 1 month.<sup>43</sup> The high stability of the polymer in seawater is due to the PDBA crosslinkers forming sterically hindered tetrahedral B-O moieties. The role of seawater for self-healing is highlighted in this research as the healing efficiency of the samples was  $< 2\%$  when they were kept under normal air conditions (humidity  $< 20\%$ ). Characterization with atomic force microscopy (AFM) and transmission electron microscopy (TEM) showed that the PDBA crosslinker is well dispersed in the hydrophobic p(DA-co-BA) network, preventing the interaction with water. For comparison, replacing PDBA with  $\text{Ca}^{2+}$  (a component of artificial seawater) leads to the presence of byproduct aggregates of  $\sim 100$  nm.

Xia et al. studied various catechol chemistries on different polymer structures, including HBPU, and examined interactions that are beyond the B-O ones<sup>42</sup> including metal-ion coordination<sup>70</sup> and hydrogen bonding<sup>71</sup>. The hyperbranched structure of HBPU enables easy movement of the macromolecules in water, which is an important kinetic factor of self-healing.<sup>64</sup> The authors have shown that specific chemical modification can manipulate the self-healing of a hydrogel in different pH (from basic to acidic) environments while resulting in stable complexes underwater.<sup>42, 70, 71</sup> To prepare pH-dependent self-healing hydrogels, the  $\text{pK}_a$  (acid dissociation constant) of the catechol chemistries must be considered. One approach is based on the incorporation of quaternary ammonium cations (formed by the reaction of the  $-\text{COOH}$  group in the polymer with TEA or 4-dimethylaminopyridine, DMAP) into the polymer backbone.<sup>42</sup> In this approach, the quaternary ammonium cations interact with the B-O bonds to reduce the  $\text{pK}_a$ . As a result, the polymer self-healed at high pH ( $=9$ ), whereas the polymer that contained no quaternary

ammonium cations could not, confirming the important role of quaternary ammonium cations in self-healing hydrogels. The stability of the polymer at high pH is also demonstrated through rheological data, in which the  $G'$  (storage shear modulus) and  $G''$  (loss shear modulus) values for the hydrogels prepared at pH 9 and those made at pH 7 are comparable. The polymer network is highly dynamic and thus contributes to the self-healing process at the damaged surface. The mechanism is attributed to the reshuffling and rearrangement of the polymer networks via the dynamic reversible coordination of B-O bonds. The underwater healing efficiencies of the hydrogels recorded at pH 9 and 7 were 92 and 77%, respectively. Additionally, the hydrogels also showed stronger (2-fold) adhesion underwater than hydrogels without the quaternary ammonium cations.

Another way to obtain the self-healing ability under basic condition is by the formation of tris- and bis-coordination bonds between DOPA-HBPU and  $\text{Fe}^{3+}$ . The complexed hydrogel was found to be self-healing in artificial seawater at pH 9.<sup>70</sup> The existence of the tris- and bis-complexes is characterized by the Mössbauer parameters of anhydrous  $\text{Fe}[\text{DOPA}]_3$ . Therefore, seawater of pH 8.3 can be used to trigger the dynamic reversibility of the catechol- $\text{Fe}^{3+}$  coordination bonds contained in the hydrogel. The complexed polymer has an extremely high failure strain (~2900%) and a moderate tensile strength (~2.5 MPa). When the hydrogel is damaged in the alkaline seawater, the mobile HBPU networks reshuffled across the crack interface, and the dynamic catechol- $\text{Fe}^{3+}$  bond rebinds the damaged site. This process achieves a healing efficiency of up to 92.5%. In this case, the self-healing of a cracked polymer is also defined by the mobility of the  $\text{Fe}^{3+}$  ions in the network of the catechol- $\text{Fe}^{3+}$  crosslinks; i.e.,  $\text{Fe}^{3+}$  ions tend to diffuse to free (uncomplexed) catechol groups found at the cracked surface.

As catechol chemistry (above) is relatively unstable at low pH (e.g., the stability constant of a PBA-catechol complex decreases from  $3300 \text{ M}^{-1}$  at pH 8.5 to  $31 \text{ M}^{-1}$  at pH 5.8),<sup>74</sup> the self-healing under acidic conditions requires different chemistry, i.e., hydrophilic thiomalic acid and hydrophobic acrylonitrile-butadiene-styrene (ABS) copolymer groups incorporated on the same HBPU backbone.<sup>71</sup> At an acidic pH, hydrogen bonds are formed between the protonated thiomalic acid units, as the  $\text{p}K_a$  of thiomalic acid is ~3.4.<sup>75</sup> On the other hand, the ABS chains build up reversible crosslinks, while the hydrophobicity within the polymer networks prevents them from swelling (as low as 25% at pH 4). When the polymer is damaged underwater, this amphiphilic design helps close the crack through hydrogen bonding and then consolidated the polymer with its hydrophobicity. Compared to that of other HBPU developed at neutral or pH 9 conditions, the healing efficiency of this polymer is lower – 87%. This is perhaps because of the weaker hydrogen bonding in this system than the coordination or boronate ester bonding system. In the effort of

looking for inexpensive materials and practical design, an ultrafast self-healing hydrogel composed of a double network (hydrogen bonds and dynamic B-O bonds) was formulated with poly(vinyl alcohol) (PVA), agarose, and borax.<sup>76</sup> With 1 wt% agarose in PVA, the gel exhibits an excellent self-healing property underwater. The gel achieved a maximum original stress of 19.5 kPa and recovered up to 70% in 60 s after underwater healing. The polymer exhibits several advantages, such as the low toxicity of its components and sufficient softness, making it a potential candidate for further applications in underwater devices. Thus, it is also important to herein review the state-of-the-art self-healing materials used for electrochemical and electronic devices.

With the increasing trend of utilizing natural molecules for building desirable complex and functional systems, Zhang and coworkers have recently introduced a self-healing and adhesive supramolecular polymer based on a naturally occurring small molecule, thiocetic acid.<sup>77</sup> The novelty of their design arises from the combination of natural molecules and facile preparation methods to obtain complex materials. The autonomous self-healing capability of this polymer was based on the existence of three different types of dynamic chemical bonds: dynamic covalent disulfide bonds, noncovalent H-bonds, and Fe(III)-carboxylate coordinative bonds. This unique design of the polymeric structure endowed it with a very efficient (up to 80% in 1 min, measured from elastic modulus) healing ability under ambient conditions as well as under water.

### 3.2 Electrochemical self-healing devices

Many electrochemical devices (e.g., electrochemical sensors, supercapacitors, wearable devices)<sup>78-85</sup> operate in a liquid medium, and a number of them work in water or multicomponent water (such as seawater or sweat). These devices include chemo- or biosensors and electrolyzers. The signal or power collected from those devices is structure dependent; i.e., the signal can be lost or can become noisier upon damage. Therefore, much effort has been made to develop self-healing materials or films with electroactive properties. Thus, electroactive species including ferrocene (Fc)<sup>86</sup> or catalyst nanoparticles<sup>87</sup> must be functionalized or dispersed in the polymer network.

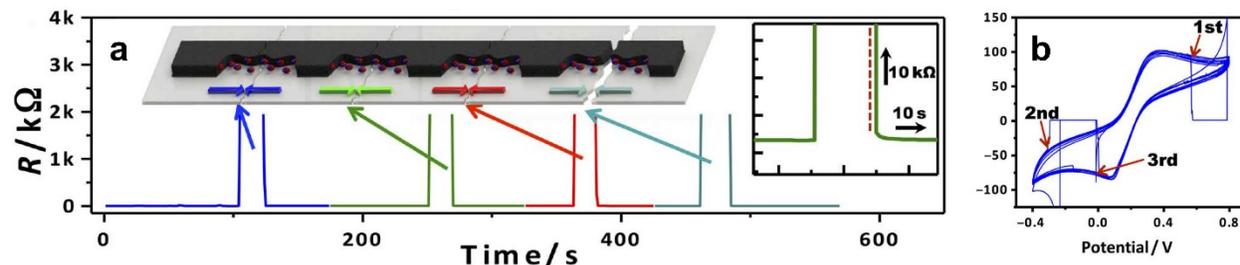
A self-healing hydrogel was prepared through host-guest chemistry between the  $\beta$ -cyclodextrin ( $\beta$ -CD) and ferrocene (Fc) moieties of newly developed polymers, viz. poly(N,N-dimethylacrylamide-r-glycidol methacrylate- $\beta$ -CD) [p(DMA-r-GMA-CD)] and poly(N,N-dimethylacrylamide-r-2-hydroxyethylmethacrylate-Fc) [p(DMA-r-HEMA-Fc)].<sup>86</sup> The host-guest chemistry (or inclusion chemistry)<sup>88-90</sup> occurs between the  $\beta$ -CD host (the molecular entity processing *convergent* binding sites) and the Fc guest (the molecular entity processing *divergent*

binding sites).<sup>91</sup> It is believed that hydrophobic interactions drives the complexation between the cavity of  $\beta$ -CD and Fc. In contrast to other self-healing polymers based on  $\beta$ -CD,<sup>92</sup> the electroactive Fc moiety in p(DMA-r-HEMA-Fc) manipulated the reversibility of the gel-sol transition of the hydrogel, i.e., the binding constant of the host-guest interaction, through its oxidation states.<sup>93</sup> The hydrogel had good self-healing ability, as demonstrated by rheology; i.e. both  $G'$  and  $G''$  recovered to their initial levels under small strain ( $\gamma = 0.1\%$ ). The self-healing ability, mild conditions for preparation, and expected relative biocompatibility endowed the hydrogel with potential applications in electrochemical devices such as molecular switches.<sup>90, 94</sup> However, the premise of using  $\beta$ -CD for complexing with Fc in this work is unexplained, even though there are several reports on the host-guest chemistry between  $\alpha$ -CD (the cavity size of which is smaller than that of  $\beta$ -CD) and Fc.<sup>95, 96</sup>

In an effort to stabilize sensors for detecting sodium, which is linked with hypertension and high blood pressure,<sup>97-100</sup> a self-healing electrochemical sensor was proposed.<sup>101</sup> To this end, the researchers used capsules containing liquid-phase hexyl acetate as the healing agent. The capsules were dispersed in a polymer-based ink and then processed into a film. If the polymer film is ruptured upon damage, the hexyl acetate is released to heal the crack, together with redistribution of the conductive (carbon or Ag/AgCl) particles and restoration of the conductive pathway. The self-healing film was coated onto a flexible polyethylene terephthalate (PET) substrate to serve as the working electrode of the electrochemical sensor. The electrochemical signal was recorded through the redox reaction of a ferricyanide probe (10 mM) in 1 M phosphate buffer (pH 7). As a result, the damage and healing process can be tracked by the electrochemical signals, herein the anodic and cathodic current of a cyclic voltammogram. Even though this approach has been successful in producing self-healing conductive ink,<sup>102, 103</sup> its main drawback, similar to other capsule-based self-healing materials, is being a single-time self-healer; i.e., if another cut occurs at the same location, the healing process will be inefficient or fail. Moreover, this technique cannot be applied under flow conditions because the carrier solution dilutes the healing agents.

Offering distinct advantages over common capsule-based and intrinsically self-healing systems, the use of permanent magnetic Nd<sub>2</sub>Fe<sub>14</sub>B microparticle (NMP)-loaded graphitic inks for constructing an inexpensive printed electrochemical device with a rapid (~50 ms) and remarkable self-healing capability was reported.<sup>104</sup> The incorporation of NMPs into the printable ink imparted the self-healing ability to the printed conducting trace due to the permanent and surrounding-insensitive magnetic properties of the NMPs. The recovery of the trace occurred upon repeated large (3 mm) damage, even at the same location (Figure 3a). The real-life applicability of the new

self-healing concept is demonstrated on the autonomous repair of all-printed electrochemical sensors (Figure 3b), indicating its considerable promise for widespread practical applications and long-lasting printed electronic devices.



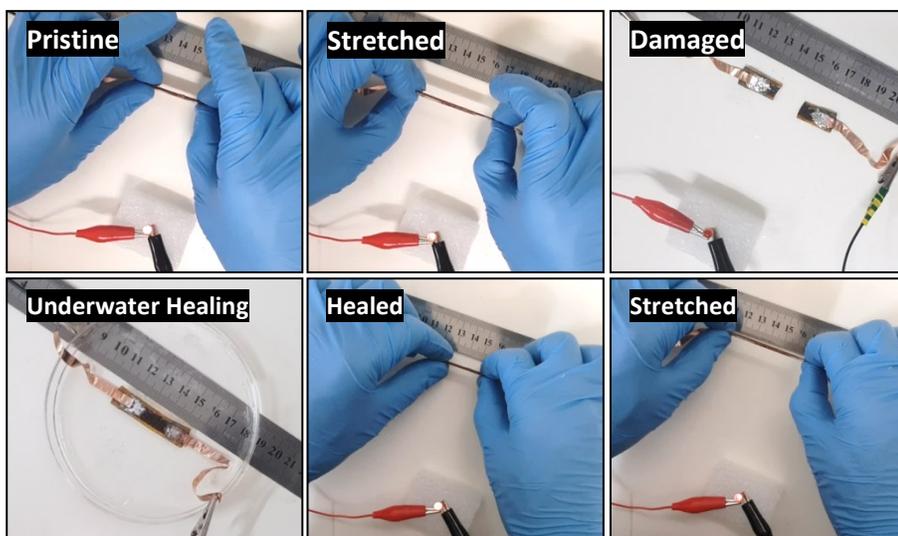
**Figure 3.** (a) Electrical conductivity–based studies analyzing the self-healing ability of a self-healing printed trace damaged at multiple locations (damage width, 1 mm). Inset for the respective panels shows zoomed-in plots, illustrating the conductivity recovery of the self-healing traces upon damage. The dotted red line represents the time when the self-healing process is allowed to take place. (b) CV plot illustrating the real-time recovery of three repeated 3-mm-wide breaks. Individual CVs showing the point at which the electrode is damaged and the point at which self-healing is initiated for the first, second, and third consecutive 3-mm-wide damage at the same location. (Reproduced with permission.<sup>104</sup> Copyright 2016, AAAS).

Not only are polymeric materials designed to be healable, but the catalyst films of a non-zero gap alkaline electrolyzer can also become healable. As a proof-of-concept, the healing of the catalyst film was induced by the in situ self-assembly of catalyst particles (with NiFe layered double hydroxide and Ni<sub>3</sub>B nanopowders for the anode and cathode, respectively) during electrolysis.<sup>87</sup> The catalyst particles were periodically added to the electrolyte, forming a suspension that is pumped through the electrolyzer. Particles with negatively charged surfaces stick onto the anode, while positively charged particles adhere to the cathode. The self-assembled catalyst films are healable as long as sufficient catalyst particles are present in the electrolyte; i.e., this is not the “self-healing” material but rather the “healing” material (as the healing process is triggered only by the supply of the catalyst particles). Steady cell voltages were maintained for at least three weeks during continuous electrolysis at 50–100 mA cm<sup>-2</sup>.

### 3.3 Electronic self-healing devices

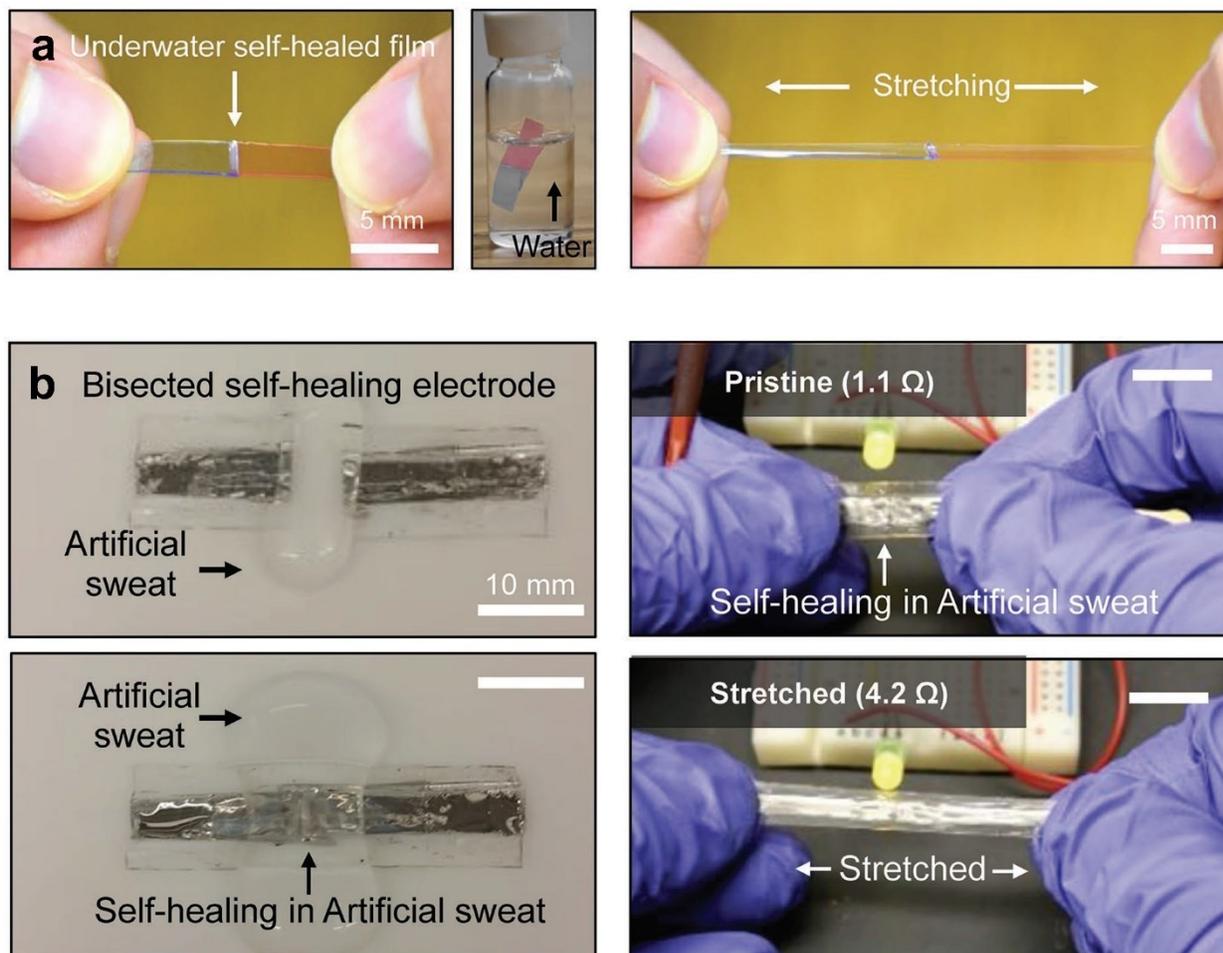
Similar to electrochemical devices, electronics also require self-healing to endure their working lifetime, and this capability is in even more demanding for circuitry devices, in which an unhealed circuit causes breakdown of the whole device.<sup>105, 106</sup>

In recent years, considerable attention has been focused on disulfide-containing poly(urea-urethane) structures for the preparation of self-healing polymers due to the combination of covalent (disulfide) and noncovalent (hydrogen) dynamic bonds.<sup>14, 107</sup> However, in most of the reported materials, underwater applications are out of reach, mainly due to the swelling of such polymers, which in turn will degrade their mechanical properties as well as their self-healing ability. This swelling behavior originates mainly from the chemical properties of the main repeating unit. For instance, in the reported polypropylene glycol-based poly(urea-urethane),<sup>108-111</sup> the main repeating unit is propylene glycol, which is hydrophilic and thus absorbs large amounts of water. Following this logic, Khatib et al. (unpublished data) suggested building a new poly urea-urethane based on a very hydrophobic repeating unit. To this end, polybutadiene was chosen as a prepolymer for the synthesis. The resulting polymer achieved a fairly high hydrophobicity, which led to significantly little swelling. The repelling of water molecules due to the high hydrophobicity of the backbone endowed this polymer with the ability to recover structural damage underwater with very high efficiency. In addition, because of its great mechanical properties, it would be a great fit for the preparation of soft and stretchable electronics, including electronic skins (e-skins) and soft robotics. E-skin herein is the biomimetic version of human/animal skin used for multiparametric sensing.<sup>112</sup> An example of self-healing electrodes based on a composite of carbon nanotubes (CNTs) and our newly developed polymer are presented in Figure 4. The presented electrode was used to drive a light-emitting diode (LED). At the beginning, the intensity obtained with pristine (undamaged) electrodes was very high even with 100% strain. The electrode was then cut and allowed to heal for 24 h under seawater. Afterwards, the stretchability and conductivity were recovered, allowing very similar intensities to those obtained with the pristine conductive composites.



**Figure 4.** Demonstration of the stretchability and healing process for an underwater self-healing CNT-based conductive composite with an LED. (Photo credit: M. Khatib)

The urea moiety is also included in a polydimethylsiloxane (PDMS) elastomer that is capable of self-healing in water or sweat.<sup>113</sup> The elastomer is rationally designed with 4,4'-methylenebis(phenyl urea) (MPU) and isophorone bisurea (IU) units in order to form multiple hydrogen bonding interactions (see section 2.2). Self-healing occurred in artificial sweat (Figure 5), which is unlikely to be observed in other self-healing materials based on hydrogen bonding. This supramolecular network allows the polymer to stretch up to 3000%; in particular, the polymer is relatively notch-insensitive; i.e., the stretchability of a notched sample is still as high as 1200%. Together with the high toughness of  $12000 \text{ J m}^{-2}$ , these results indicate that this self-healing material can be processed underwater to achieve self-healing e-skins. Nevertheless, the researchers in this report did not examine the stability of their new polymer in underwater conditions, which is very important for proper functionality in real applications. This noncrosslinked polymer, which is based on PDMS and urea linkages, is expected to swell underwater, leading to increased degradation of the polymer, especially the urea linkages. Therefore, it would be very important to test the stability of this polymer before its use in underwater applications.



**Figure 5.** (a) Self-healing of the urea-modified PDMS film can even take place underwater. The film was bisected to two pieces, which were stained with pink and blue ink from colored pens and put together underwater for self-healing (left). After 24 h, the film was successfully stretched (right). (b) A self-healing electrode with conductive lines was cut into two pieces (top). They were placed together in artificial sweat (bottom). The artificial sweat solution is a potassium phosphate dibasic solution (1.0 M). (Reproduced with permission.<sup>113</sup> Copyright 2018, John Wiley & Sons)

Underwater self-healing can also be achieved by the dipole–dipole interaction that forms between the highly polar and hydrophobic poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) molecules.<sup>54</sup> The polymer with a high content of hexafluoropropylene (HFP) (~40%), which contains  $\text{CF}_3$  groups, is expected to have stronger dipole–dipole interactions than unmodified PVDF. Importantly, a plasticizer (e.g., dibutyl phthalate (DBP)) with a content of ~15% helps increase the flexibility of the polymer network (or decrease  $T_g$  of the polymer), resulting in self-healing even under very harsh aqueous conditions such as highly acidic media and highly basic solutions. The polymer is also transparent, stretchable, and stable underwater for months

without significant degeneration of its mechanical properties. Unfortunately, the underwater healing efficiency of this polymer is relatively low, 30% after 24 h.

#### 4. Perspectives

The number of studies on the special topic of “self-healing underwater” is fairly modest and still lagging behind the massive number of publications on intrinsic self-healing polymers, the first paper on which was published by Chen et al.<sup>114</sup> in 2002. In fact, it took more than 10 years to overcome the *underwater* challenges and introduce the first example of underwater self-healing materials.<sup>86</sup> So far, the solutions are relatively diverse, including coordination chemistry, multiple hydrogen bonding, hydrophobic interactions, and even reversible disulfide and B-O bonding, with approximately half of the underwater self-healing materials developed with catechol-based chemistry. However, this chemistry is quite underestimated, as there has not yet been any application of it in self-healing devices. The reason perhaps is a lack of communication between chemists, physicists, and engineers in this field. We therefore believe that interdisciplinary projects focusing on the development of underwater self-healing devices will lead to exceptional achievements compared to the current situation. In addition, we anticipate that the main underwater applications of practical materials or devices with self-healing ability would include the following:

- a) self-healing materials for wound healing that help to avoid re-surgery to fix or remove the failed (and unhealable) materials. For instance, a proof-of-concept experiment using a self-healing hydrogel to successfully repair the central nervous system of zebrafish;<sup>115</sup>
- b) self-healing artificial organs that have features that are quite similar to those of self-healing biomaterials but require more complicated fabrication techniques, such as 3D bioprinting<sup>116, 117</sup>;
- c) self-healing sensors or robots for aqueous environments, which are mentioned throughout this report. There is not yet a device for real-world applications; however, research on this field is extremely important for healthcare and deep-sea discovery that no repair system can easily reach.

The first two applications are actually connected to medical and clinical research, where the applied materials must be biocompatible and biodegradable. Therefore, the self-healing materials should be based on natural polymers such as cellulose-based polymers as well as biocompatible self-healing chemistries.<sup>118, 119</sup> By contrast, the self-healing materials for the last of the three applications demand a different developmental approach. **On the one hand, materials for deep-sea discovery must be robust to survive at high pressure underwater; interestingly,**

recent research on self-healing of steel under seawater is successful by using microcapsules containing epoxy resin and hardener.<sup>120</sup> On the other hand, materials for self-healing sensors (e.g., e-skin) under sweat conditions require high flexibility and multiparametric responses. Cao et al.<sup>121</sup> demonstrated that a traditional rigid printed circuit board (PCB) can be healable underwater (of different pH) as it is fabricated from materials composed of a fluorocarbon elastomer and a fluorine-rich ionic liquid. In conclusion, we are convinced that with the development of underwater self-healing materials and devices, these applications could have a great impact on science, technology, and society.

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