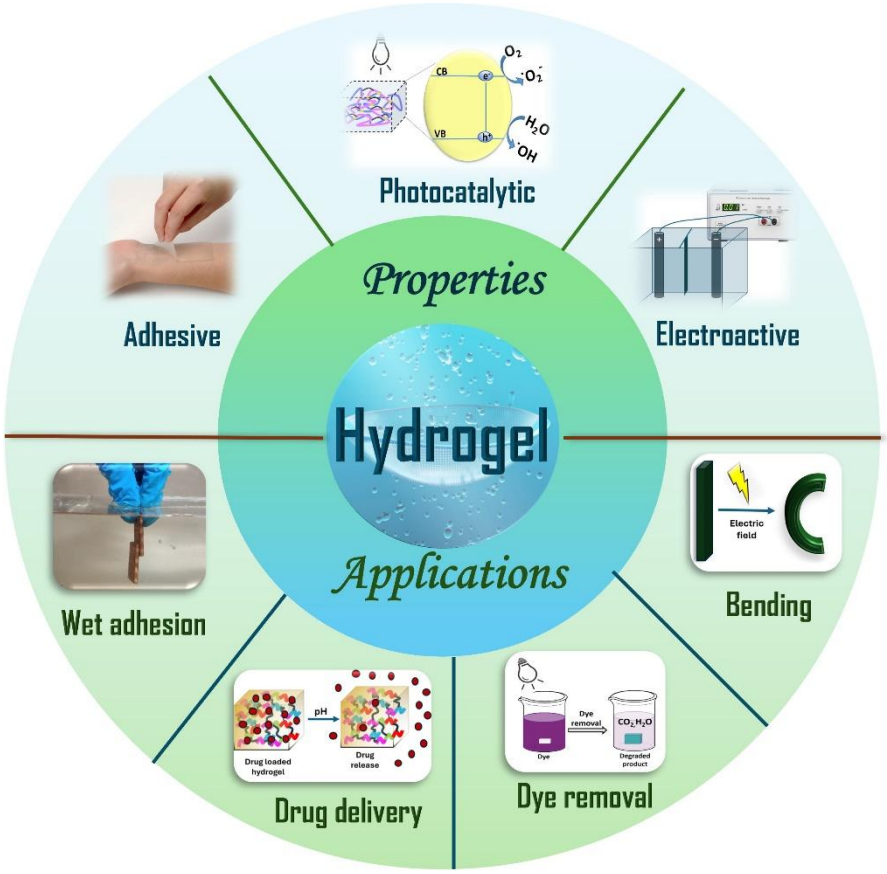
Chapter 1

A general introduction to hydrogel, its properties, and applications in various fields



This chapter outlines the rationale behind the current thesis work. It also provides a comprehensive introduction detailing their fundamental properties and explores their widespread applications as adhesives, photocatalysts, and electroactive materials.

1.1 Introduction

Ever since the discovery of polymeric materials, their application has been gradually increasing and within no time it has become an inescapable part of modern society. Researchers worldwide have been working on advanced functional polymers because of their fast-growing demands in life-changing technologies. One such polymeric material is “hydrogel", considered one of the most versatile biomaterials in material chemistry. Polymeric hydrogel is a soft and wet material saturated with water and is sometimes called ‘aqua gel’ [1]. It is broadly defined as a three-dimensional (3D) network of polymeric compounds cross-linked together by different monomeric units. For the last many years, the exploitation of hydrogel in our daily lives has reached a great height. The porous structure and hydrophilicity of the hydrogel allow them to absorb large amounts of water. The hydrophilicity of the hydrogel is mainly due to the presence of hydrophilic functional groups such as hydroxyl groups, carboxylic groups, amine, and sulfate groups [2-5]. This water sorption can be attributed to the capillary, osmotic, and hydration forces. On absorbing water, the hydrogel undergoes swelling and absorbs water or other aqueous solutions several times its dry weight without dissolution. The hydrogel can undergo reversible swelling and deswelling and retain a huge amount of water for a long period [6]. The swelling property of the hydrogel depends on the type of monomers used, swelling media, and cross-linking within the hydrogel. The structural integrity of the swollen hydrogel remains intact due to the cross-linking within the polymeric structure [7]. The cross-linking within the hydrogel can be chemical, physical, or a combination of both, and by controlling the cross-linking density, various physical and chemical properties of hydrogel can be tuned. Again, hydrogels can absorb water, biological fluids, and various electrolytic solutions, enabling their feasible application in biomedicine, bioelectronics, sensing, etc. The high-water content in the hydrogel imparts exceptional qualities such as softness and flexibility into the hydrogel matrix. The combination of these properties and high porosity renders hydrogel to mimic natural tissue and has found numerous applications in biomedical areas more often than any other biomaterial [8]. These hydrogels have been synthesized by incorporating specific functionalities into the conventional polymer material [9]. The cost-effective and versatile nature of multifunctional hydrogel leads to their application in almost every field such as in biomedical areas, environmental remediation, automotive, energy devices, etc. To fulfill the demands of modern society, researchers around the world have

shown great interest in synthesizing such hydrogels [10]. Moreover, in recent years, the applicability of hydrogel in agriculture [11], cosmetics [12], food industry [13], tissue engineering [14], etc. has been rising enormously. Hydrogels can be synthesized from any water-soluble monomer having a natural or synthetic origin. In addition, they can also be synthesized from a prepolymer or existing hydrophilic polymer [15]. They can be fabricated with various organic or inorganic materials to form a hybrid structure with improved functionalities. Hydrogel can be molded into different shapes and sizes such as thin films, cylindrical structures, slabs, microparticles, coatings, etc. rendering their easy applications in many areas [16,17]. In addition, the tunable properties such as its functionality, biocompatibility, biodegradability, and softness as well as excellent mechanical and optical properties make them a promising material for different applications like bioimaging, diagnosis, sensing, etc. Moreover, one of the exceptional properties of hydrogel is its ability to respond to external stimuli such as pH [18], temperature [19], light [20], electric field [21], magnetic field [22], salt concentration [23], etc. making it suitable for utilization as a 'smart' material thereby often termed as "smart hydrogel". On subjected to external stimuli, hydrogel demonstrates changes in swelling or other properties depending on the type of stimuli provided. However, most hydrogels revert to their original configuration upon withdrawing the stimuli [24,25]. The effects of various stimuli on hydrogel properties will be discussed in section 1.2.2. Other than hydrogels, different gels are also available, such as aerogels, xerogels, organogels, etc. An aerogel is a gel whose dispersed phase is air, organogels contain organic liquid as a dispersed phase, and xerogels are obtained by removing all the swelling agents from the gel [26,27]. Among all, hydrogel has great advantages as it is hydrophilic, biocompatible, soft, flexible, and possesses tunable properties. In addition, hydrogel has more widespread application in areas that retain moisture, such as in drug delivery, wound healing, etc.

The term "hydrogel" first appeared in the year 1894 and it was described as a colloidal gel of inorganic salts. However, the first cross-linked hydrogel as we know it today was highlighted after the synthesis of poly(2-hydroxy ethyl methacrylate) (pHEMA) by Wichterle and Lim in 1960 for its utilization as a contact lens. It was considered the first biomaterial to be used in direct contact with the patient [28,29]. After the successful application of pHEMA on contact lenses, the use of pHEMA-based hydrogel was further explored for drug delivery application, afterward there was a boom

in the exploitation of hydrogel. Based on specific areas, the history of hydrogels can be categorized into three main categories as shown in Figure 1.1 [30-35].

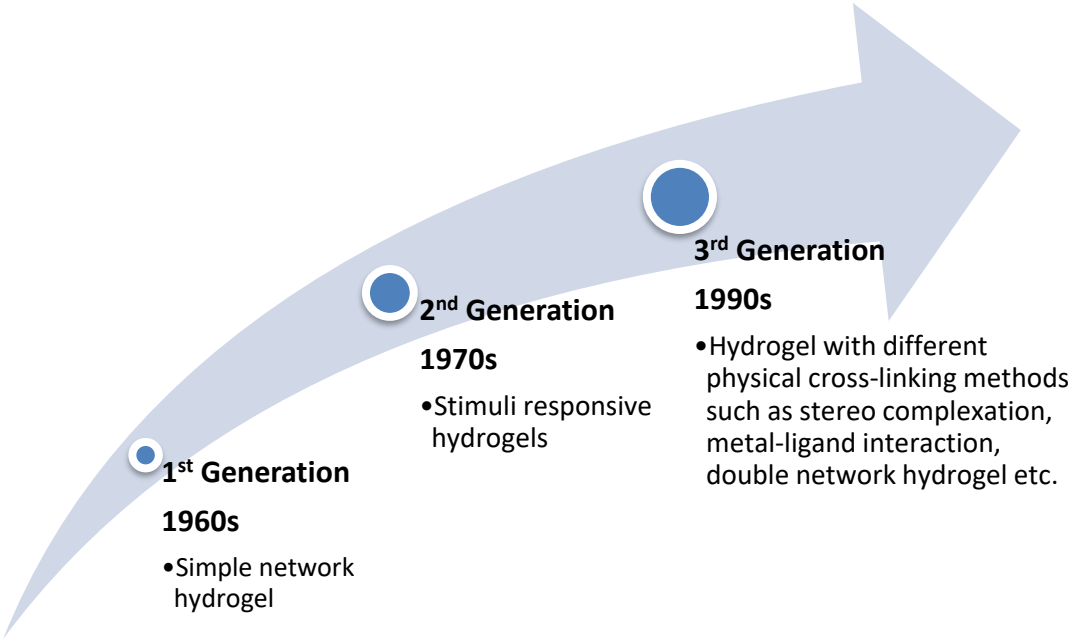


Figure 1.1 Different generations of hydrogels over the years.

1.2 Classification of hydrogel

Hydrogel can be classified into several groups based on different aspects including its origin, preparation methods, response to various stimuli, cross-linking mechanism, and ionic charge [36-38]. The classification of hydrogel is shown in Figure 1.2. A few of the classifications are described below.

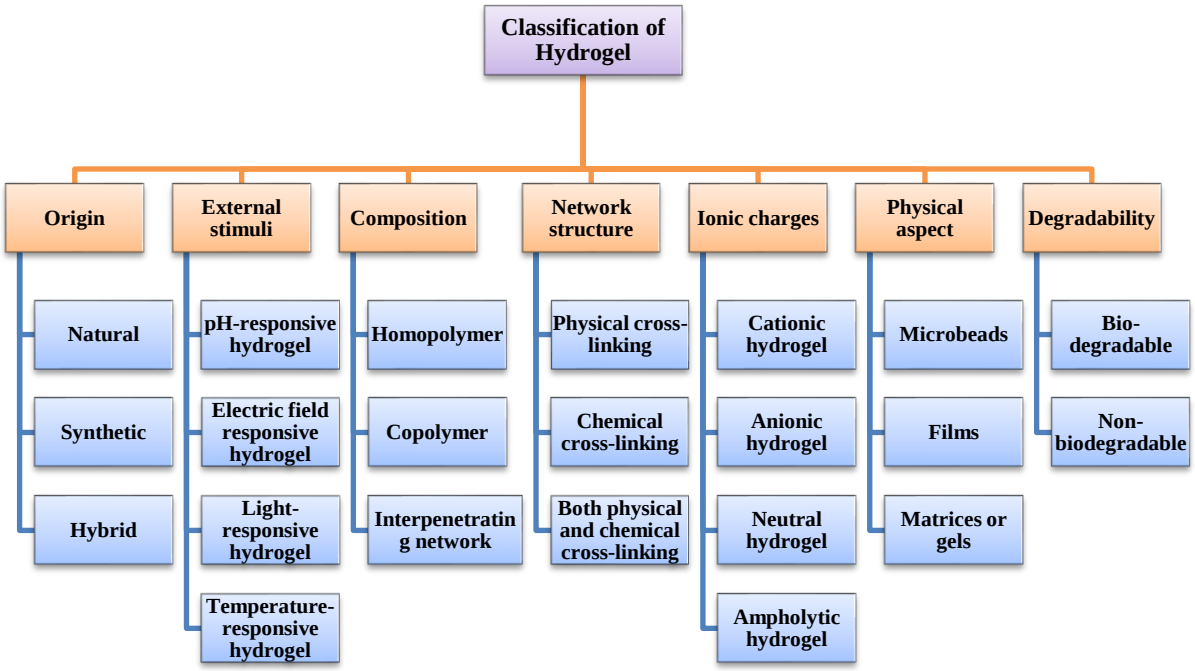


Figure 1.2 Classification of hydrogels based on different aspects

1.2.1 Classification based on origin

Based on the origin of polymeric molecules, hydrogels can be further categorized as natural, synthetic, and hybrid hydrogels. Hydrogels originating from natural sources are called natural polymer hydrogels, those originating from synthetic sources are called synthetic polymer hydrogels, and those derived from a combination of both natural and synthetic sources are called hybrid polymer hydrogels.

Among the three, the combination of natural and synthetic hydrogel surpasses the properties of the hydrogel when used individually. Hybrid polymer hydrogel is advantageous in various aspects. The biocompatibility and functionality of natural polymers when blended with stable and mechanically strong synthetic polymers lead to an improved hydrogel with properties from both sources. Therefore, in our thesis work, we have developed hybrid polymer hydrogels by using precursors (i) gelatin and (ii) starch, which are of natural origin, and (iii) acrylic acid, (iv) acrylamide, and (v) 2-acrylamido-2-methylpropane sulphonic acid (AMPS) of synthetic origin.

1.2.2 Classification based on response to external stimuli

Stimuli-responsive hydrogels undergo alteration in their physical or chemical properties in response to minute changes in their external environment. The changes include physical stimuli such as temperature, light, pressure, magnetic fields, and electric fields. Chemical stimuli include pH, ionic strength, and chemical agents. These hydrogels are more effective in their application than conventional hydrogels and are also known as smart hydrogels [39,40]. Based on the type of stimulus, they are further classified into various categories as shown in Figure 1.3.

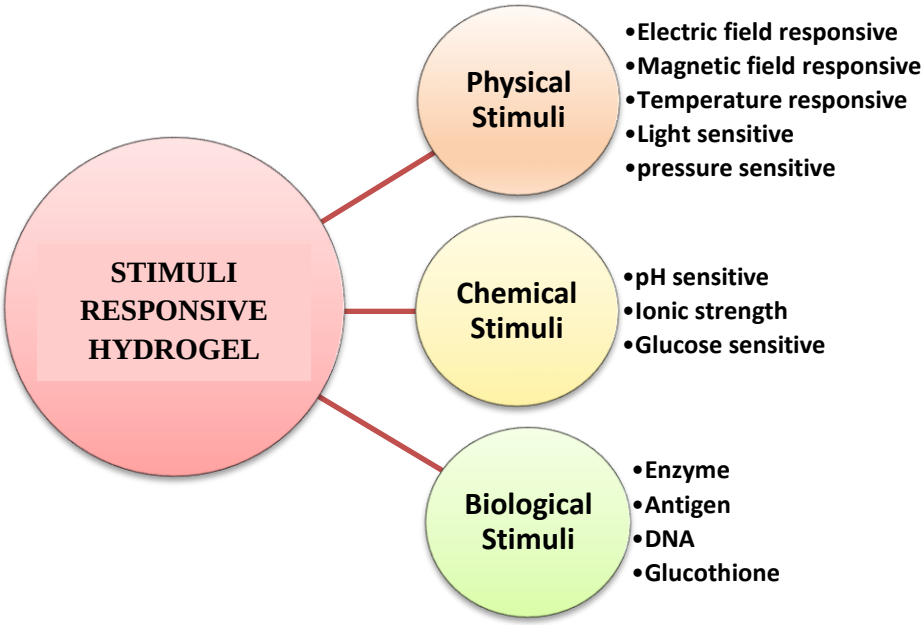


Figure 1.3 Different types of stimuli-responsive hydrogel

1.2.2.1 pH-responsive hydrogels

A hydrogel must contain ionizable groups in the polymeric network to respond to changes in pH. Polymers with weak acidic or basic groups form a pH-responsive hydrogel that accepts protons or releases them under changing environmental pH. As shown in Figure 1.4 the hydrogel with acidic (carboxylic acid or sulphonic acid) group undergoes deprotonation at a pH higher than the pK_a value of the acidic pendant group and swell. On the other hand, a hydrogel with basic (ammonium) groups in its structures undergoes protonation at a pH lower than pK_b of the pendant basic groups and starts swelling. These ionizations develop charges on the polymeric chain resulting in electrostatic interaction and thereby causing swelling or deswelling of the hydrogel [41,42]. These bring change in the structure of the hydrogel, change in color, or show

actuation with changing pH conditions. There are three types of pH-responsive hydrogel such as acidic, basic, or neutral pH-responsive hydrogel depending on the type of ionizable groups present. Hydrogels containing weak polyacids like poly(acrylic acid) PAAc, poly(2-acrylamido-2-methyl-1-propane sulphonic acid) PAMPS, and poly(methacrylic acid), etc. form pH-responsive acidic hydrogel. Those containing weakly polybasic groups like chitosan, poly(ethylene imine), poly[(2-dimethylamino)ethyl methacrylate] (PDMA), etc. forms pH responsive basic hydrogel [43]. However, hydrogel containing both acidic and basic group show amphoteric behavior and swells in a wider pH range.

The unique properties of pH-sensitive hydrogel have led to their numerous applications in biomedical fields particularly in drug delivery systems [44,45]. The human body has different pH at different parts of the body, which enables the pH-sensitive hydrogel to deliver drugs or other therapeutic agents in a controlled manner. It also found applications in wound healing and monitoring, biosensors like BioMEMS (Biomedical microelectrochemical systems) [46], pH monitoring [47]. For example, Scarpa *et al.* developed a wearable sensor for sweat pH monitoring by fabricating a piezoelectric aluminum nitride (AlN) membrane supported by a pH-responsive hydrogel, which is prepared by co-polymerizing poly(ethylene glycol)-diacrylate (PEG-DA) macromer with 2-carboxyethyl acrylate (CEA) [48]. Apart from that, pH-sensitive hydrogels have also been exploited in the field of engineering in preparing microdevices like microfluidic valves [49].

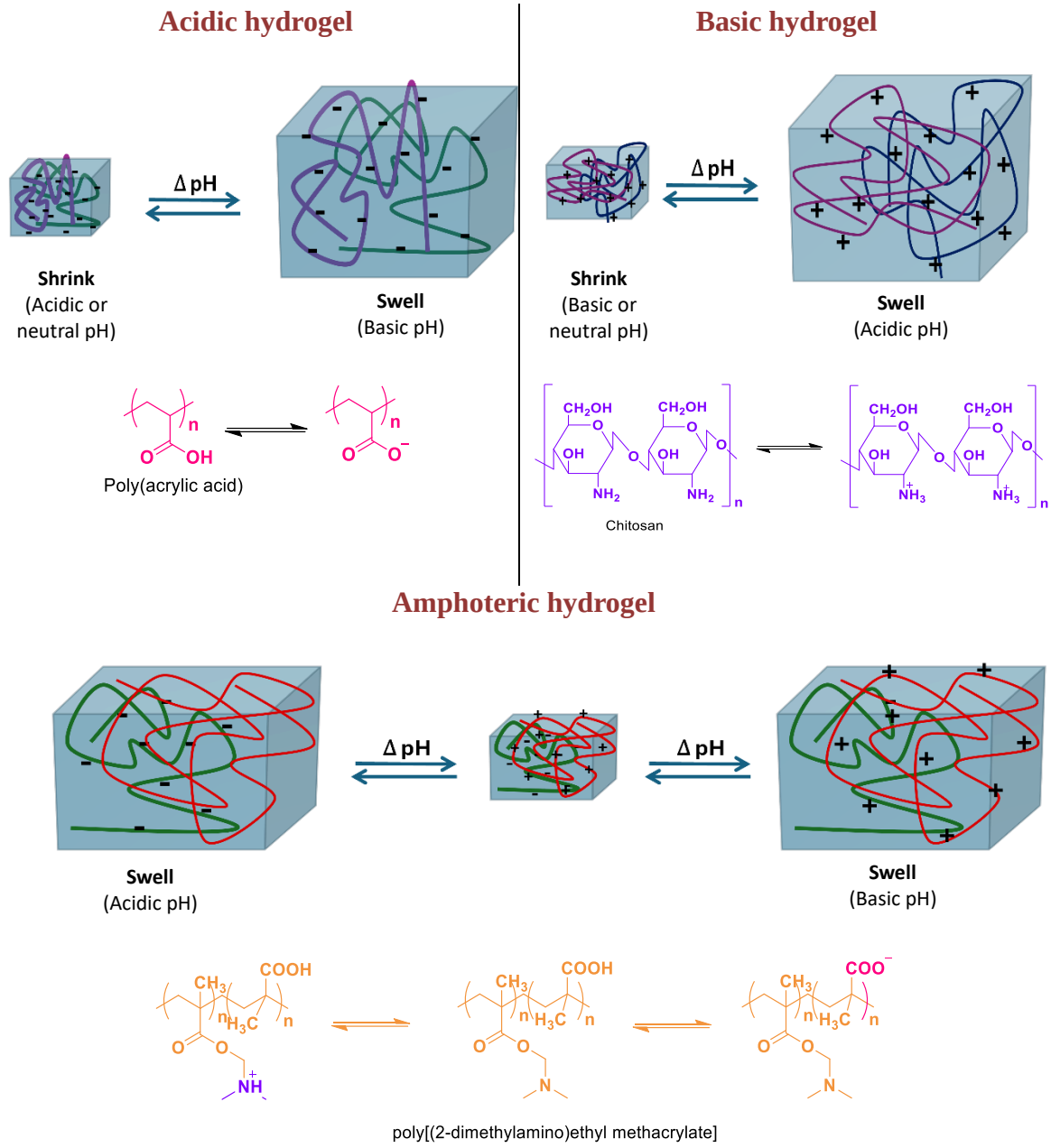


Figure 1.4 Graphical representation of swelling behavior of pH-responsive hydrogel at different pH conditions

1.2.2.2 Electric field responsive hydrogels

Electric field responsive hydrogels are a class of smart hydrogels that show a visible change when an electric stimulus is applied. These hydrogels contain a polyelectrolyte network, and when put under an electric field, they can convert electrical energy to mechanical energy through various deformations such as swelling/deswelling, bending actuation, and elongation/shortening [50]. This deformation arises from the combined coulombic, electroosmosis, and electrophoretic effects. The mechanism behind this response can be explained by Donnan equilibrium theory [51]. This behavior of

electric field-responsive hydrogel occurs mainly in an electrolyte solution. When an electric field is applied, the charged ions on the hydrogel network and counterion are attracted in opposite directions. However, the movement of the charged ions is restricted by the cross-linking within the hydrogel matrix. Therefore, an osmotic potential is generated, leading to an electroosmotic movement of the water molecule. Finally, the hydrogel swells on increasing the osmotic pressure and deswells on decreasing the same, which causes bending and other deformation within the hydrogel (Figure 1.5). Some of the common polyelectrolytes used for the synthesis of electric field-responsive hydrogel are chitosan, PAAc, PAMPS, and 4-hydroxybutylacrylate (4-HBA) [52,53]. Further addition of conducting polymers such as polyaniline (PANI), polypyrrole (PPy), and conductive materials such as graphene oxide, carbon nanotubes, etc., improve the electro-active properties of the hydrogel. The attractive features of the electric-field responsive hydrogels, such as their precise frequency, bending, and controllable signal, allow their smooth application as implantable devices for drug delivery [54], sensing, actuators [55], soft-robotics [56], and tissue engineering [57]. A work by Li and coworkers demonstrated the enhancement of electro-response and mechanical properties of polyacrylamide/sodium alginate hydrogel by the incorporation of graphene oxide into the hydrogel. They found that by adjusting the composition of GO and *N,N′*-methylenebisacrylamide (BIS), the hydrogel could be highly stretchable [58]. In another work, Chao and coworkers developed an electro-driven hydrogel walker for cargo transport by using polyanionic poly(2-acrylamido-2-methylpropanesulfonic) acid and acrylamide. The hydrogel walker demonstrates reversible bending and stretching and can achieve one-directional movement in an electrolyte solution [59].

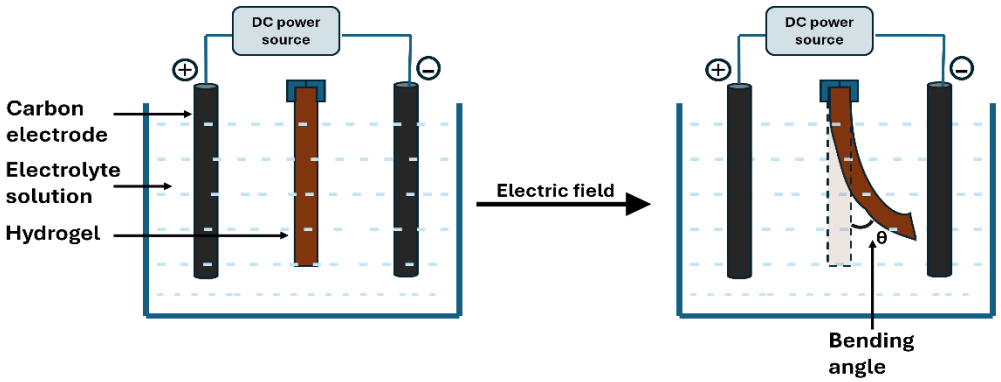


Figure 1.5 Graphical representation of bending behavior of an electroactive hydrogel

1.2.2.3 Light-responsive hydrogels

Light-responsive or photo-responsive hydrogels are another type of smart hydrogel that changes their structure and conformation when exposed to light. Photoreactive groups such as chromophores are incorporated into a hydrogel matrix to obtain a photo-responsive hydrogel. Some of their applications include drug delivery and microfluidics [60,61].

1.2.2.4 Temperature-responsive hydrogels

Temperature-responsive hydrogels are those that show volume phase transition. They can be further classified into two categories; one is a positive response, and another is a negative response system where the hydrogel undergoes swelling and deswelling respectively on increasing the temperature. This swelling and shrinking behavior with varying temperatures has been utilized in drug delivery, and membrane separation applications [62].

1.3 Synthesis of hydrogel

Hydrogels are composed of polymeric materials that undergo cross-linking to form a non-soluble hydrophilic material. Therefore, they follow the same synthetic route that has been used for the synthesis of any cross-linked polymer. The properties and functionalities of a hydrogel are highly dependent on the polymerization process.

1.3.1 Cross-linked through chemical reactions

Chemical cross-linking involves the formation of covalent bonds between different polymeric chains. The hydrogels formed by chemical cross-linking are highly stable in a physiological environment. In addition, they are durable and have good mechanical strength. Chemical cross-linking falls under two categories: (i) Chain growth and (ii) Step growth polymerization techniques. These are the most used polymerization techniques for hydrogel synthesis [63,64].

1.3.2 Cross-linked *via* various physical cross-linking

Hydrogels formed through physical cross-linking do not involve any cross-linking agent and are also known as self-assembled hydrogel. They usually proceed through a simple and convenient synthesis method. Physical cross-linking involves the formation of hydrogels by self-assembling macromolecules through non-covalent and secondary molecular interactions such as H-bonding, electrostatic interactions, etc. These physical

interactions make the hydrogel reversible and show changes in the hydrogel properties with minute alterations in the reaction conditions. Many processes are involved in hydrogel synthesis through physical interactions [65-67].

1.4 Properties of hydrogel

Figure 1.6 Pictorial representation showing different properties of hydrogel

Hydrogels with their hydrophilic multifunctional groups possess tunable properties. The type of monomers used, and the degree of cross-linking play an important role in determining their properties. Some of the properties of hydrogels are discussed below (Figure 1.6).

1.4.1 Swelling properties

The hydrophilic groups in the polymeric network allow hydrogels to uptake a huge amount of water by swelling and retaining an aqueous solution a hundredth of times their dry weight for a longer period. This unique ability of the hydrogel to display a significant change in volume makes it a versatile material for numerous applications. Hydrogels undergo swelling through three major steps (i) water molecules diffuse into the hydrogel matrix, (ii) hydration of the network chain, and (iii) expansion of the three-

dimensional network structure [68]. The cross-linking within the network structure restricts its dissolution in water. The swelling of the hydrogel is attributed to various factors such as hydrophilicity, chemical potential, elasticity, and osmotic pressure. The osmotic pressure created by the mobile ion's concentration gradient causes the hydrogel's expansion [69,70]. The water molecule first absorbed by the dry hydrogel matrix interacts with the polar group within the hydrogel and is termed primary bound water. Afterward, the water molecules interact with the hydrophobic site leading to secondary bound water. After the saturation of polar and hydrophobic sites, the additional swelling is opposed by the cross-linked network thereby an equilibrium swelling level is reached. The swelling behavior of the hydrogel can also determine the quality of the hydrogel as it can affect other properties such as mechanical strength, degradation, etc.

1.4.2 Mechanical properties

The mechanical properties of the hydrogel are crucial for determining the stability of the hydrogel in its desired application. The mechanical properties of hydrogel involve its strength, toughness, self-healing ability, and fracture energy. These properties of the hydrogel can be varied and tuned by varying the cross-linking density to obtain the desired mechanical properties. The mechanical properties of the hydrogel can be determined by various techniques such as tensile and compression testing, indentation testing, cyclical testing, bulge testing, and strip extensometer [71]. From the tensile test, along with stress-strain, Young’s modulus, yield strength, and toughness can also be evaluated.

1.4.3 Biocompatibility

Biocompatibility of a material can be broadly categorized into two categories i.e. bulk biocompatibility and interfacial biocompatibility. Bulk biocompatibility refers to the overall compatibility of the hydrogel to the biological environment such as mechanical biocompatibility, design compatibility, and biodegradability. However interfacial biocompatibility refers to the compatibility of the interface of the hydrogel material to that of the biological surface. It includes cell adhesion, inflammation, and biofouling. Various factors that affect biocompatibility, include chemical composition, surface properties, porosity, and cross-linking density. Hydrogels derived from natural sources are generally biocompatible [72,73].

1.4.4 Porosity

The porosity of hydrogel is defined as the empty void within the material and is usually expressed as a percentage. It is a key property of hydrogel that significantly determines other properties and applications of hydrogel. Porosity can be affected by various factors including polymer compositions, cross-linking density, synthesis method, and environmental conditions. The porosity of the hydrogel can be tuned during its synthesis or can form during swelling. In hydrogel, porosity plays an important role in swelling, mass transport, and mechanical properties by influencing the stiffness and strength of the hydrogel [74].

1.4.5 Self-healing property

Self-healing is the most fascinating property of hydrogel. It is defined as the ability of a hydrogel to repair itself without any external intervention after a cut or any other damage, like tissues. Although this property is not a fundamental property of hydrogel, endowing it to hydrogel makes it the most versatile material for a wide range of applications ranging from biomedical areas to soft robotics. The mechanism of self-healing relies mostly on the reversibility of the cross-linking structures. The reversibility of the chemical bonds often involves dynamic covalent bonds such as Schiff bond, borate ester bond, Diels Alder reaction, and dynamic non-covalent interactions such as hydrogen bonding, hydrophobic interaction, ion interactions, etc. [75-77] The dynamic covalent bonds generally show slow equilibrium between the dissociation and association of chemical bonds. However, non-covalent interactions show rapid dynamic equilibrium [78]. Some applications of self-healing hydrogels are wound healing [79], drug delivery [80], adhesives [81], flexible strain sensors [82], 3D printing [83], actuators [84], supercapacitors [85], soft robotics [86], etc.

Besides these properties of hydrogels, many other properties such as adhesive property, photocatalytic property, etc. have gained significant attention. A thorough study of hydrogel application highlights its importance as an adhesive, photocatalyst, and electroactive material. Therefore, in our thesis work, we have explored these properties of hydrogels and their potential application in different areas.

1.5 Hydrogel as an adhesive material

Hydrogel with adhesive properties is highly fascinating in the field of biomaterial chemistry. The unique flexibility and biocompatibility of hydrogel with adhesion

capability make it a promising material for biomedical engineering, flexible electronics, construction, etc. In biomedicine, adhesive hydrogel plays a major role, it can be used as a replacement for sutures or staples during surgery, useful for wound closure, burn treatment, and many others. In addition, an adhesive hydrogel can be utilized to repair cracks and as a sealant to prevent water leakage. The basic mechanisms of hydrogel adhesion are shown in Figure 1.7.

(i) Mechanical interlocking: It refers to the permeation of the adhesive hydrogel to the roughness or irregularities in the adhering surface thus creating a mechanical interlock like the lock and key mechanism.

(ii) Intermolecular interaction: This is considered the primary mechanism of adhesion and includes primary forces such as ionic, covalent, and metallic bonds. The secondary forces of intermolecular interaction include dipole-dipole interactions, hydrogen bonding, and electrostatic interaction [87-89].

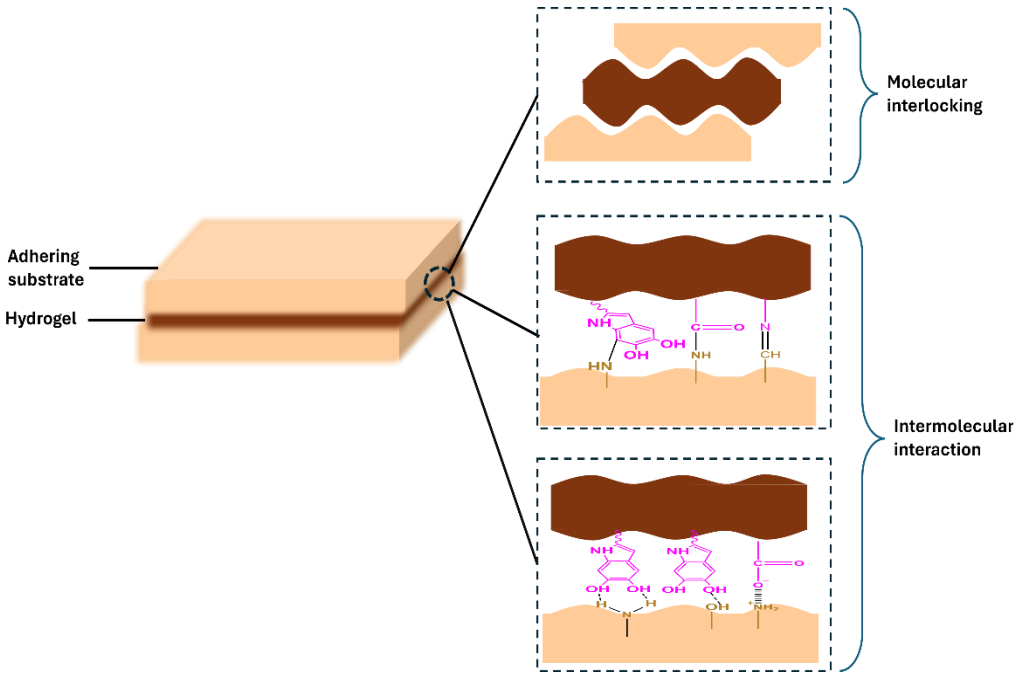


Figure 1.7 Schematic diagram of the mechanism involved in hydrogel adhesion

Adhesive hydrogels are advantageous over other adhesives in various terms such as self-adhesion, tunability, flexibility, elasticity, multifunctionality, biocompatibility, and their ability to adhere to wet surfaces. Furthermore, the ease of application and painless removal from the skin surface reduces discomfort and minimizes the risk of damage to the skin. Again, the water content in the hydrogel keeps the surface moist, promoting wound healing. Therefore, the development of adhesive hydrogel has reached a great height. For example, Gao *et al*. synthesized a bioglass (BG)/oxidized sodium alginate (OSA) composite hydrogel with dual adhesiveness to tissue and implant biomaterial. Here, BG plays a major role in imparting dual adhesiveness and bioactive properties. The hydrogel also stimulates angiogenesis and promotes wound healing *in vivo* [90]. In another work, Ren and coworkers developed a tough and stretchable adhesive hydrogel for motion monitoring by copolymerizing acrylated adenine/chitosan/polyacrylamide/Fe(III) (Aa/CS/PAM/Fe(III)). The hydrogel shows good mechanical strength and adhesion reaching a fracture stress of 11.17 kPa and strain of 1400% for wood surfaces [91].

1.5.1 Application of adhesive hydrogel

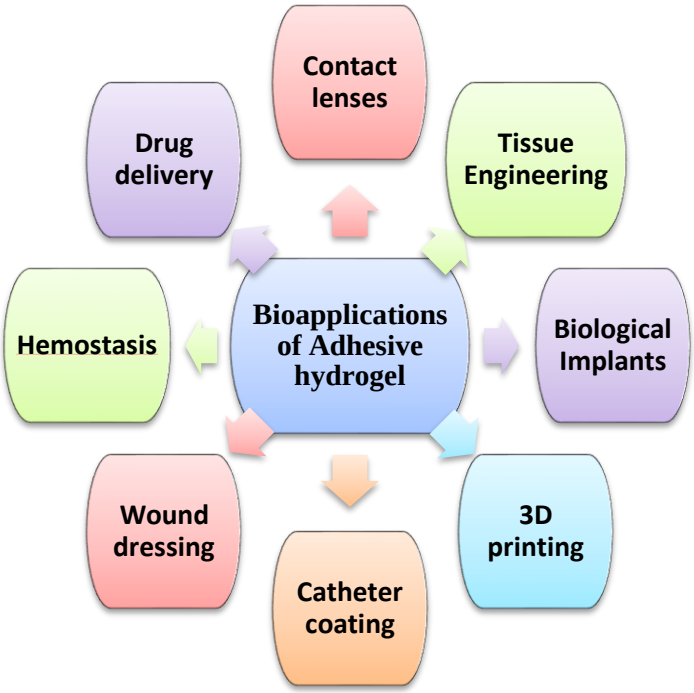


Figure 1.8 Different bio-applications of adhesive hydrogel

The development of adhesive hydrogel brings a revolutionary change in the biomedical field. The resemblance of hydrogels to natural tissue has led to their applications in numerous areas. Some of the applications are shown in Figure 1.8. They

have been applied as tissue sealants or in wound healing, to deliver therapeutic molecules or drugs through the skin, hemostasis, tissue engineering, adhesion to wet tissue, protecting tissues on radiotherapy, medical implants, biosensors, and different bioelectronic devices. In addition, the tunable physicochemical properties, non-toxicity, and ease of preparation made adhesive hydrogel an attractive biomaterial for their biomedical application.

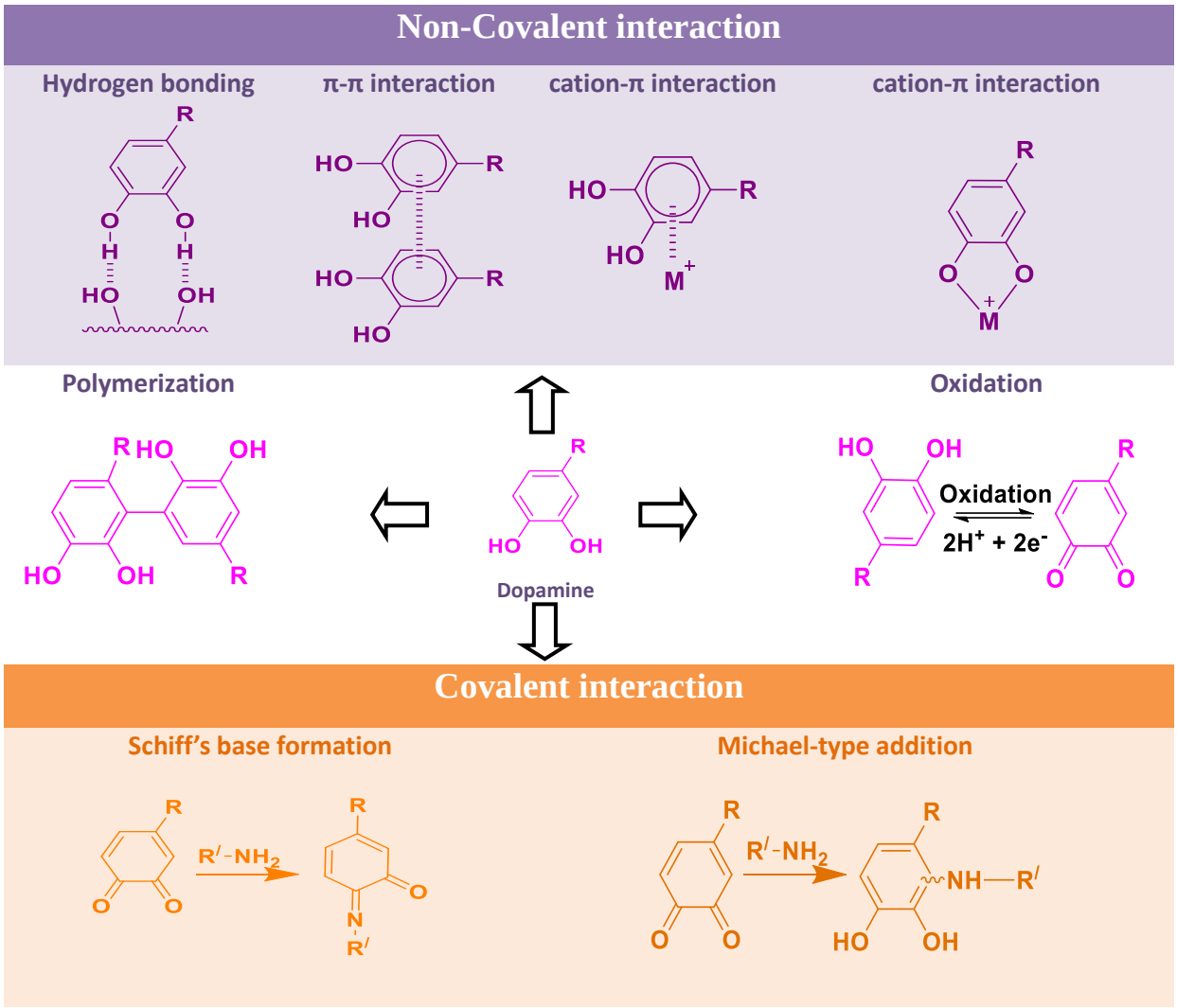
Moreover, the porous structure and hydration effect of the adhesive hydrogel allow easy permeation of the loaded substance through the skin surfaces. Tuning the hydrogel matrix with various stimuli-sensitive properties allows the controlled release of the drug to the targeted sites, thereby reducing the side effects. Some examples of the combination of monomers in synthesizing hydrogel for transdermal drug delivery system include gelatin/Acrylic acid/Acrylamide [92], gelatin/dopamine [93], cellulose/lignin [94], etc.

Hydrogel-based bioelectronic devices are in high demand because of their flexible human-friendly behavior. They have been fabricated for various physical, electrical, and biochemical information and have shown promising applications in wearable devices, implantable bioelectronics, and electronic skin. However, these devices require long-term adhesion to the skin's surface for proper functioning. Therefore, hydrogel bioelectronics with adhesive properties have been developed to eradicate the need for bandages or stitches.

Owing to their applications in various biomedical areas, which mostly involve moist tissue surfaces and in many marine devices, adhesive hydrogel often shows failures when applied to moist or underwater surfaces. Therefore, it is necessary to design hydrogel that withstands wet environments to overcome such limitations. In general, it is challenging for hydrogel to form a strong adhesion to a surface when submerged in aqueous solution as the water molecule on the surface forms a hydration layer which weakens the interfacial adhesion [95]. Moreover, the water molecules might form covalent or non-covalent interactions with the hydrogel matrix's functional group, thereby restricting the adhesion. Although many hydrogels have been synthesized for wet adhesion, attaining reversible and durable underwater adhesion is still difficult. Therefore, inspired by marine organisms such as mussels, sandcastle worms, and barnacles [96], adhesive hydrogels for wet surfaces have been designed with reversible and durable properties. All these marine organisms contain proteinaceous material as an

adhesive component. However, the protein found in mussels is rich in modified amino acids 3,4-dihydroxyphenylalanine (DOPA) and is responsible for the adhesion to wet surfaces in mussels. They interact with various surfaces including bidentate hydrogen bonding, electrostatic interaction, π-π and cation-π interactions, oxidative cross-linking, and metal-catechol coordination bonds [97] (Table 1.1).

Table 1.1: Table showing various interactions and reactions of dopamine



Hence, the focus on developing adhesive hydrogel for wet or underwater surfaces using dopamine has increased in the last decade. For example, Feng and coworkers developed a transparent under-adhesive hydrogel by modifying poly(vinyl alcohol)/glycerol–tannic acid/Cu^{2+} hydrogel with poly(dopamine methacrylamide-co-methoxyethyl acrylate). They found that the hydrogel can reach a tensile strength of 4.4

MPa and an adhesive strength of 14 kPa under seawater [98]. In another work, Zhou and coworkers demonstrate a mussel-inspired hyaluronic acid adhesive hydrogel using a facile synthetic route. The hydrogel is cytocompatible and can gel rapidly within 60 sec. It exhibits tissue adhesive strength of 90 kPa [99]. Although numerous catechol-based hydrogels have been developed so far, many suffer from poor adhesion due to overoxidation of the catechol group leading to limited reusability and short-term adhesiveness [100]. Therefore, the development of adhesive hydrogel that can tackle those limitations is in high demand. Hence, in our thesis work, we developed adhesive hydrogels based on catechol chemistry and performed various applications.

1.6 Hydrogel as a photocatalyst

The combination of the properties of hydrogels and photocatalysts has opened new opportunities in material chemistry. Photocatalytic hydrogel comprises a nanometer-sized photocatalyst embedded within a 3D hydrogel network. Photocatalysts play a major role in many applications including the photodegradation of pollutants [101], hydrogen production [102], CO_2 reduction [103], and photodynamic therapy [104]. However, many photocatalysts possess drawbacks such as fast charge recombination, poor adsorption capacity, poor stability, and low surface area. Therefore, over the years, many effective strategies such as elemental doping, using co-catalysts, etc. have been devoted to improving the properties of photocatalysts [105,106]. Hydrogel, a versatile material possessing high photocatalyst loading capability and high transmittance is considered the most suitable for efficient energy conversion and environmental remediation [107,108].

The porous structure of the hydrogel allows large loading of photocatalysts, thus increasing the active sites, resulting in efficient absorption of light and contact with reactants. It also lowers charge recombination of the photocatalytic material. In addition, the cross-linked structure of the hydrogel provides an appropriate platform for photocatalysts by limiting the leakage of catalyst into the reaction media, thereby promoting easy recyclability. Moreover, hydrogels are often transparent, allowing efficient light penetration through the photocatalytic material, leading to efficient use [109].

1.6.1 Application of Photocatalytic Hydrogel

1.6.1.1 Application in environmental remediation

The application of photocatalytic hydrogels for environmental protection is remarkable. The unique properties of hydrogel make it an effective material in various ecological challenges. The photocatalytic hydrogel can effectively adsorb and remove heavy metals, organic pollutants, and dyes through photocatalytic degradation. With the increasing global population, pollution in water by heavy metals and dyes from industries is alarming. Hence, wastewater treatment has become an integral part of sustainable water management. Recently, there has been a rapid increase in the development of hydrogel for treating polluted water. The porous structure of the hydrogel allows easy diffusion of the polluted molecule into the hydrogel matrix. Again, the ability of the hydrogel to be functionalized with different functional groups allows it to tailor with specific functionalities hence improving the efficiency and providing selective binding sites for pollutants.

Numerous heterogenous hydrogel-based photocatalysts have been synthesized to tackle waste in water. Kuckhoff *et al*. developed a high-transmission photocatalytic hydrogel by copolymerizing photoactive benzothiadiazole acrylamide with *N*,*N*-dimethylacrylamide. The synthesized hydrogel showed photoreduction of Cr^{VI} and photodegradation of glycophosphate under visible light irradiation [110]. Again, Chen and coworkers synthesized a cellulose/GO/TiO_2 based hydrogel that removes methylene blue dye under UV light from wastewater by photocatalytic degradation and adsorption by the hydrogel material. The hydrogel showed superior degradability and recyclability up to 10 consecutive cycles without significant change [111].

The photocatalytic hydrogel can be of two types depending on the photocatalysts incorporated.

(i) Inorganic semiconductor-based hydrogel photocatalysts such as metal oxide-based (TiO_2, ZnO, etc.), metal sulfide-based (CdS, ZnS, etc.)

(ii) Organic semiconductor-based hydrogel photocatalysts such as graphitic carbon nitride (g-C_3N_4)

Among various photocatalysts, g-C_3N_4 exhibits numerous benefits, such as low costs, visible light absorption, high chemical and thermal stability, non-toxicity, and tunable band gap. These properties of g-C_3N_4 make it a superior photocatalyst over other inorganic photocatalysts. In addition, g-C_3N_4 also acts as a photoinitiator for hydrogel

polymerization. However, bulk g-C_3N_4 exhibits disadvantages, such as low specific surface area and fast charge recombination [112]. These drawbacks can be minimized by incorporating g-C_3N_4 into the hydrogel matrix. Recently, Ruan and coworkers synthesized a g-C_3N_4-based hydrogel using hydroxyethyl cellulose (HEC) and graphitic carbon nitride (g-C_3N_4). The hydrogel shows the removal of bisphenol A under visible light irradiation due to the synergistic effect of adsorption and photocatalytic degradation. They found the removal rate by the hydrogel is 3.4 times higher than that of g-C_3N_4 powders [113,114]. The schematic diagram for the removal of pollutants from water bodies by the hydrogel is shown in Figure 1.9.

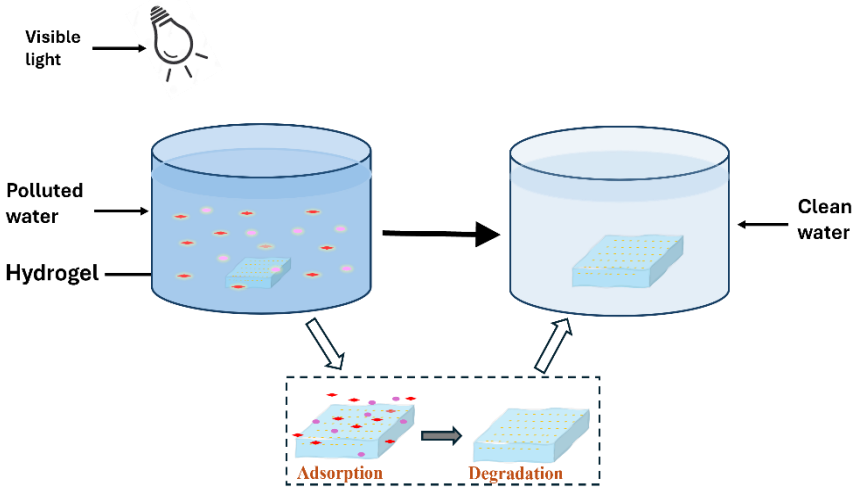


Figure 1.9 Schematic diagram showing removal of pollutants in water

1.6.1.2 Application in energy conversion

Photocatalytic hydrogels also find applications in many energy conversion reactions. One such reaction is hydrogen evolution, which is the process of splitting water into hydrogen in the presence of sunlight. The abundant water in the hydrogel makes it an efficient photocatalyst by maintaining water for hydrogen production in an anhydrous setting. Furthermore, photocatalytic hydrogels are also utilized in H_2O_2 generation and CO_2 conversion [115,116].

1.7 Hydrogel as an electroactive material

Electroactive hydrogel (EAH) is a polymeric smart hydrogel that responds to an electric field. The conversion of electrical energy to mechanical energy within the hydrogel changes its volume, shape, and other physical or chemical properties. These unique properties have drawn widespread attention for their numerous applications such

as soft robotics [117], drug delivery [118], biomimetic applications [119], actuation [120], batteries [121], etc. The electroactive property of the hydrogel can be affected by various factors such as polymer concentration, cross-linking density, electrolyte concentration, and electroactive components.

There are different types of electroactive hydrogel depending on the type of polymer used.

(i) Hydrogels synthesized from ionic conductive polymers such as strong acidic monomers. Examples include 2-acrylamido-2-methylpropane sulphonic acid (AMPS), poly(sodium 4-vinyl benzenesulfonate), etc.

(ii) Hydrogels incorporated with electronic conductive polymers such as polyaniline, polypyrrole, polythiophene, poly(phenylene vinylene), etc., carbon-based nanomaterial (e.g. carbon nanotube, carbon nanowires, graphene, graphene oxide, reduced graphene, etc.), and metallic nanoparticles (e.g. Ag, Au, Cu, etc.) [122-124].

Electroactive hydrogels have several distinct advantages over other stimuli-responsive hydrogels. Advantages include precise control, rapid response, versatility, and remote actuation [125,126]. By modulating the intensity, frequency, and duration of the electric field, the responses of the hydrogel can be accurately controlled. Again, electroactive hydrogel responds almost immediately to electrical stimuli, thus offering rapid and dynamic behavior. In addition, using wireless technology, electroactive hydrogel can be remotely actuated and hence applicable in areas where physical access is limited.

1.7.1 Application of electroactive hydrogels

1.7.1.1 Application in soft robotics and actuators

The soft nature, flexibility, biomimetic property, and high deformation of electroactive hydrogel have garnered significant attention for its application in soft robotics and actuators. When an electric stimulus is applied, electroactive hydrogel changes shape and size and shows fast actuation. This conversion of electrical energy into mechanical energy allows the hydrogel to swell or shrink, resulting in the bending and unbending of hydrogel when put in an electrolyte solution under an applied electric field. It enables the hydrogel to perform different motions and actuations, often

applicable as an artificial muscle. Hence, it is essential to develop electroactive hydrogel with good mechanical strength, while keeping it as close to natural tissue to mimic in a better way [127-129].

1.7.1.2 Applications in drug delivery

The innovation of stimuli-responsive drug delivery systems has allowed one to deliver drugs and other therapeutic agents in a precise and controlled manner. In particular, the exploration of electroactive hydrogel for drug delivery has gained wide attention in recent years due to its fast, accurate, and repeatable response. They can be devised as miniature wireless implants. For many years, a variety of natural and synthetic polymers, such as gelatin, chitosan, poly(acrylic acid), poly(lactic acid) (PLA), etc., have been widely used in a variety of drug delivery applications, and when combined with conducting polymer materials such as polyaniline gives electroactive hydrogel for drug delivery applications. The entrapped drug in the hydrogel matrix can be released by electro-induced swelling of the hydrogel. The swelling and shrinking of the hydrogel act as an on-off switch in the controlled release of the drug. Ovando-medina *et al.* developed a polyacrylamide/chitosan/polypyrrole hydrogel for control release of captopril drug under an applied electric field. They found that the drug release rate increases with voltage, revealing the potential application of the synthesized hydrogel in biomedical applications [130-132].

1.7.1.3 Application in wearable technologies

Wearable technologies such as soft sensors have been developed using electroactive hydrogels. The stretchable and flexible properties of hydrogel allow a smooth application of hydrogel-based soft sensors. They have been utilized in various ways such as in health monitoring, human-machine interfaces, electronic skin, strain sensors, etc.

In addition, using hydrogel in energy devices has opened tremendous opportunities for developing energy sources. The unique functionalities of hydrogels such as tunable ionic or electronic conductivity and electrolyte permeability promote their application for long-term performance in energy devices such as supercapacitors, fuel cells, and batteries. Hydrogel can be applied as electrolytes, electrodes, and separators in energy devices [133-135].

1.8 Characterization of hydrogel

The performance of a hydrogel is dependent on various parameters such as chemical structure, swelling behavior, morphology, thermal and mechanical properties, biocompatibility, and biodegradability. Therefore, during the synthesis of a hydrogel, the structure and each parameter of the hydrogel must be determined. Over time, the advancement in material science resulted in the development of various characterization techniques. Some of the important characterization techniques are discussed below.

1.8.1 Structural characterization

Various spectroscopic methods such as Fourier transform infrared (FTIR) spectroscopy, Ultraviolet-Visible (UV-Vis) spectroscopy, X-ray diffraction (XRD) Spectroscopy, Raman Spectroscopy are some of the common characterization techniques used for determining the structure of the hydrogel.

FTIR is mostly used to determine chemical bonds and atoms in the structure of the hydrogel by measuring the vibrational energy transition. UV-vis spectroscopy is a technique that helps to determine specific chemical bonds in a polymeric material by measuring the absorption of light by the hydrogel sample. In addition, UV-vis spectra tell a lot about the hydrogel such as chemical cross-linking density, UV barrier properties, humidity detection, etc. [136,137]. Hydrogels often show amorphous properties, however, sometimes they display some semi-crystalline properties also. This can be characterized by using XRD spectroscopy. Similarly, like FTIR, Raman spectroscopy is also used to confirm the chemical composition of the hydrogel.

1.8.2 Morphology

Various morphological characterization techniques are used to determine the microporous structure of the hydrogel. Some of the commonly used techniques are Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and Scanning Tunneling Microscopy (STM).

1.8.3 Thermal properties

The thermal characterization of a hydrogel is useful in many aspects such as in determining thermal stability, thermal conductivity, and thermos responsiveness. Different techniques have been employed to determine the thermal properties including

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA determines the rate of thermal degradation and the percentage of mass loss. Similarly, DSC is used to measure the transition of the hydrogel as a function of temperature. It also determines the glass transition temperature, crystal structure, and crystal transition temperature.

1.8.4 Swelling Behavior

Determination of the swelling properties of hydrogel is important as it determines other factors such as cross-linking density, rate of degradation, and mechanical properties of the hydrogel. The general method for measuring the swelling ratio of the hydrogel is to immerse the hydrogel in water for a certain period and measure the ratio of the weight of the hydrogel before and after swelling as shown below

$$\text{Swelling \%} = \frac{W_S - W_d}{W_d} \times 100\%$$

where W_s and W_d are the weights of the swollen and dried hydrogel samples respectively.

Another method of measuring the swelling of the hydrogel is to directly measure the dimension of the hydrogel before and after swelling and the volume swelling ratio is then calculated [138].

1.8.5 Mechanical properties

The performance and stability of the hydrogel is highly influenced by the mechanical properties of the hydrogels. Therefore, it is essential to evaluate the mechanical properties of the hydrogel for their desired applications. The various techniques used for measuring mechanical strength include tensile testing, compression testing, cyclical testing, bulge testing, etc. The tensile test of the hydrogel is done by placing the hydrogel sample between two clamps and extending by giving different loads and rates [139]. It gives stress-strain data from which Young's modulus, yield strength, and ultimate strength can be determined. For compression tests, the hydrogel sample is placed between two plates, and pressure is applied on the top plate up to a certain strain or until it fails. Again, cyclical tests on the hydrogel determine its longevity and durability [140].

1.8.6 Biocompatibility and biodegradability

Biocompatibility is an essential feature of a hydrogel for its application in biomedical areas. Therefore, it is crucial to determine the compatibility of a hydrogel with various biological surfaces. The commonly used methods for characterizing biocompatibility include cytotoxicity tests, hemocompatibility tests, and implant studies. Cytotoxicity can be carried out both *in vitro* and *in vivo*. The cell culture assays used for this test are agar diffusion, direct contact, and elution. The abnormalities in cell morphology and cellular degeneration determine the cytotoxicity of the hydrogel material. Again, the hemolysis assay measures the hemolytic activity of the hydrogel material. Hemolysis assays below 5% are considered safe. It is performed by incubating the hydrogel in diluted whole blood.

Moreover, a hydrogel must be biodegradable. The degradability of the hydrogel is carried out in various ways, some of them are incubation in PBS and soil burial test. During incubation in PBS, the hydrogel sample undergoes hydrolysis. It is performed by incubating the sample at 37°C for a certain period and the percentage of residual mass is calculated by using the following formula

$$\text{Residual mass (\%)} = \frac{W_0 - W_t}{W_0} \times 100\%$$

Here W_o and W_t are the masses of the hydrogel before and after degradation. Soil burial tests evaluate the degradation of hydrogel in soil by measuring the weight loss of the hydrogel over time [141].

1.9 Objectives

The potential applications of hydrogel as an adhesive, photocatalytic, and electroactive material have led to the development of various functional hydrogels with improved physical and chemical properties. Most synthesized hydrogel-based adhesive which show adhesion to wet surfaces contain catechol as an adhesive moiety. However, during the synthesis process, overoxidation of catechol often takes place, leading to poor adhesion behavior and weak mechanical strength. Thus, in this thesis work, improvements have been made to overcome these limitations of the adhesive hydrogel.

Again, wastewater remediation using hydrogels mostly occurs through adsorption, resulting in the further removal of dye or other organic pollutants from the adsorbed hydrogel, which again causes further pollution. Hence, developing hydrogel

with the synergistic effect of adsorption and degradation will be much more advantageous as it degrades the pollutant within the hydrogel without requiring further removal.

Similarly, the application of electroactive hydrogel has gained widespread attention in various fields. However, the poor electroactive properties under low electric voltages and weak mechanical strength often deteriorate its actuation behavior. Thus, in this thesis work, we develop an electroactive hydrogel that exhibits fast and better actuation properties under low electric voltages with excellent mechanical strength.

Therefore, the following objectives have been proposed, to explore functional hydrogels as adhesives, photocatalysts, and electroactive materials with enhanced properties.

- To develop hydrogel-based adhesive by polymerization of hydrophilic precursors such as gelatin, acrylic acid, acrylamide, and dopamine, and to explore the application of synthesized adhesive hydrogel on various wet surfaces and its pH-responsive application in drug delivery.
- To develop photocatalytic hydrogel using acrylic acid and 2-acrylamido-2-methyl propane sulphonic acid by photopolymerization using g-C_3N_4 as a photoinitiator, and to utilize the synthesized photocatalytic hydrogel for photodegradation of various organic dyes.
- To develop electric field responsive hydrogel by incorporating conductive polyaniline into the copolymer of starch, acrylic acid, and 2-acrylamido-2-methyl propane sulphonic acid. To explore the bending behavior of hydrogel to determine its potential application as an actuator.
- To characterize all the synthesized hydrogels using different analytical methods and spectroscopic tools. For the chemical and morphological structure, the hydrogel will be analyzed by using Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), thermo-gravimetric analysis (TGA), Scanning electron microscopy (SEM), etc.

1.10 Plan of research work

To accomplish the objectives, the thesis work has been planned in the following manner.

I. Development of adhesive hydrogels

- ☑ Synthesis of adhesive hydrogels by incorporating catechol moiety into the polymeric chains of gelatin/poly(acrylic acid) and gelatin/poly(acrylic acid)/poly(acrylamide).
- ☑ Optimization of the prepared hydrogel by varying the concentration of all the precursors, initiators, and crosslinkers and the best composition would be applied for further studies.
- ☑ Various properties of the hydrogel such as swelling behavior, self-healing, mechanical strength, pH-responsiveness, etc. must be determined by various analytical methods
- ☑ The utilization of the optimized hydrogel as a wet adhesive and its potential application in controlled drug delivery will be determined.

II. Development of photocatalytic hydrogels

- ☑ Synthesis of g-C_3N_4 from nitrogen-containing precursor melamine and further analyzing its structural and morphological characteristics using different spectroscopic methods.
- ☑ Synthesis of photocatalytic hydrogel *via* photopolymerization of acrylamide and 2-acrylamido-2-methylpropane sulphonic acid using g-C_3N_4 as a photoinitiator.
- ☑ To optimize the synthesized hydrogel by varying the reaction conditions and at different concentrations of monomers and initiators would be performed.
- ☑ Evaluation of swelling behavior of the hydrogel at different pH solutions and determination of mechanical strength using a Universal Testing Machine (UTM).
- ☑ The synthesized photocatalytic hydrogel will be applied for the adsorption and degradation of various organic dyes.

III. Development of electroactive hydrogels

- ☑ Synthesis of hydrogel by copolymerizing starch, 2-acrylamido-2-methylpropane sulphonic acid, and acrylamide by a facile one-pot synthesis method.
- ☑ Impregnation of conductive polymer into the synthesized hydrogel by in situ polymerization of polyaniline within the hydrogel matrix.

- ☑ The potential application of the hydrogel will be explored by observing the bending actuation of the hydrogel at different conditions under the influence of an electric field.

References

[1] Li, J., Jia, X., and Yin, L. Hydrogel: Diversity of structures and applications in food science. *Food Reviews International*, 37(3):313-372, 2021.

[2] Chamkouri, H. and Chamkouri, M. A review of hydrogels, their properties and applications in medicine. *Am. J. Biomed. Sci. Res*, 11(6):485-493, 2021.

[3] Gyles, D.A., Castro, L.D., Silva Jr, J.O.C. and Ribeiro-Costa, R.M. A review of the designs and prominent biomedical advances of natural and synthetic hydrogel formulations. *European Polymer Journal*, 88:373-392, 2017.

[4] Badsha, M.A., Khan, M., Wu, B., Kumar, A. and Lo, I.M. Role of surface functional groups of hydrogels in metal adsorption: From performance to mechanism. *Journal of Hazardous Materials*, 408:124463, 2021.

[5] Salehi, A.A., Ghannadi-Maragheh, M., Torab-Mostaedi, M., Torkaman, R. and Asadollahzadeh, M. Hydrogel materials as an emerging platform for desalination and the production of purified water. *Separation & Purification Reviews*, *50*(4):380-399, 2021.

[6] Mathew, A.P., Uthaman, S., Cho, K.H., Cho, C.S. and Park, I.K. Injectable hydrogels for delivering biotherapeutic molecules. *International Journal of Biological Macromolecules*, 110:17-29, 2018.

[7] Bashir, S., Hina, M., Iqbal, J., Rajpar, A.H., Mujtaba, M.A., Alghamdi, N.A., Wageh, S., Ramesh, K. and Ramesh, S. Fundamental concepts of hydrogels: Synthesis, properties, and their applications. *Polymers*, 12(11):2702, 2020.

[8] Panteli, P.A. and Patrickios, C.S. Multiply interpenetrating polymer networks: Preparation, mechanical properties, and applications. *Gels*, 5(3):36, 2019.

[9] Spicer, C.D. Hydrogel scaffolds for tissue engineering: the importance of polymer choice. *Polymer Chemistry*, 11(2):184-219, 2020.

[10] Wang, K., Amin, K., An, Z., Cai, Z., Chen, H., Chen, H., Dong, Y., Feng, X., Fu, W., Gu, J. and Han, Y. Advanced functional polymer materials. *Materials Chemistry Frontiers*, 4(7):1803-1915, 2020.

[11] Palanivelu, S.D., Armir, N.A.Z., Zulkifli, A., Hair, A.H.A., Salleh, K.M., Lindsey, K., Che-Othman, M.H. and Zakaria, S. Hydrogel application in urban farming: Potentials and limitations—A review. *Polymers*, 14(13):2590, 2022.

[12] Mitura S, Sionkowska A, Jaiswal A. Biopolymers for hydrogels in cosmetics: review. *Journal of Materials Science: Materials in Medicine*, 31(6):50, 2020.

[13] Batista, R.A., Espitia, P.J.P., Quintans, J.D.S.S., Freitas, M.M., Cerqueira, M.Â., Teixeira, J.A. and Cardoso, J.C. Hydrogel as an alternative structure for food packaging systems. *Carbohydrate polymers*, 205:106-116, 2019.

[14] Zhao, H., Liu, M., Zhang, Y., Yin, J., & Pei, R. Nanocomposite hydrogels for tissue engineering applications. *Nanoscale*, 12(28):14976-14995, 2020.

[15] Schacht, E.H. Polymer chemistry and hydrogel systems. In *Journal of Physics: Conference Series*, Vol. 3, page 22, 2004. IOP Publishing.

[16] Dodda, J.M., Deshmukh, K., Bezuidenhout, D. and Yeh, Y.C. *Hydrogels: definition, history, classifications, formation, constitutive characteristics, and applications*. Biomaterial Science Series, pages 1-25, 2023.

[17] Garg, S., Garg, A. and Vishwavidyalaya, R.D. Hydrogel: Classification, properties, preparation and technical features. *Asian J. Biomater. Res*, 2(6):163-170, 2016.

[18] Huang, H., Chauhan, S., Geng, J., Qin, Y., Watson, D.F. and Lovell, J.F. Implantable tin porphyrin-PEG hydrogels with pH-responsive fluorescence. *Biomacromolecules*, 18(2):562-567, 2017.

[19] Li, Z., Bai, H., Zhang, S., Wang, W., Ma, P. and Dong, W. DN strategy constructed photo-cross-linked PVA/CNC/P (NIPPAm-co-AA) hydrogels with temperature-sensitive and pH-sensitive properties. *New Journal of Chemistry*, 42(16):13453-13460, 2018.

[20] Wang, E., Desai, M.S. and Lee, S.W. Light-controlled graphene-elastin composite hydrogel actuators. *Nano letters*, 13(6):2826-2830, 2013.

[21] O'Grady, M.L., Kuo, P.L. and Parker, K.K., 2010. Optimization of electroactive hydrogel actuators. ACS applied materials & interfaces, 2(2), pp.343-346.

[22] Li, H., Go, G., Ko, S.Y., Park, J.O. and Park, S. Magnetic actuated pH-responsive hydrogel-based soft micro-robot for targeted drug delivery. *Smart Materials and Structures*, 25(2):027001, 2016.

[23] Zhao, Y., Su, H., Fang, L. and Tan, T., 2005. Superabsorbent hydrogels from poly (aspartic acid) with salt-, temperature-and pH-responsiveness properties. *Polymer*, 46(14), pp.5368-5376.

[24] Ahmad, Z., Salman, S., Khan, S.A., Amin, A., Rahman, Z.U., Al-Ghamdi, Y.O., Akhtar, K., Bakhsh, E.M. and Khan, S.B. Versatility of hydrogels: from synthetic strategies, classification, and properties to biomedical applications. *Gels*, 8(3):167, 2022.

[25] Nath, J. and Dolui, S.K. Synthesis of carboxymethyl cellulose-g-poly (acrylic acid)/LDH hydrogel for *in vitro* controlled release of vitamin B12. *Applied Clay Science*, 155:65-73, 2018.

[26] Kuzina, M.A., Kartsev, D.D., Stratonovich, A.V. and Levkin, P.A. Organogels versus hydrogels: advantages, challenges, and applications. *Advanced Functional Materials*, 33(27):2301421, 2023.

[27] Tofanica, B.M., Belosinschi, D. and Volf, I. Gels, Aerogels and Hydrogels: A Challenge for the Cellulose-Based Product Industries. *Gels*, 8(8):497, 2022.

[28] Kopeček, J. Hydrogel biomaterials: a smart future?. *Biomaterials*, 28(34):5185-5192, 2007.

[29] Lee, S.C., Kwon, I.K. and Park, K. Hydrogels for delivery of bioactive agents: A historical perspective. *Advanced Drug Delivery Reviews*, 65(1):17-20, 2013.

[30] Kuhn, W., Hargitay, B., Katchalsky, A. and Eisenberg, H. Reversible dilation and contraction by changing the state of ionization of high-polymer acid networks. *Nature*, 165(4196):514-516, 1950.

[31] Chirani, N., Yahia, L.H., Gritsch, L., Motta, F.L., Chirani, S. and Farè, S. History and applications of hydrogels. *Journal of biomedical sciences*, 4(02):1-23, 2015.

[32] El-Sherbiny, I.M., Khalil, I.A. and Ali, I.H. Updates on stimuli-responsive polymers: Synthesis approaches and features. In *Polymer Gels: Science and Fundamentals*, pages 129-146, ISBN 978-981-10-6086-1. Springer, Singapore, 2018.

[33] Buwalda, S.J., Boere, K.W., Dijkstra, P.J., Feijen, J., Vermonden, T. and Hennink, W.E. Hydrogels in a historical perspective: From simple networks to smart materials. *Journal of Controlled Release*, 190:254-273, 2014.

[34] Taaca, K.L.M., Prieto, E.I. and Vasquez Jr, M.R. Current trends in biomedical hydrogels: From traditional cross-linking to plasma-assisted synthesis. *Polymers*, 14(13):2560, 2022.

[35] Cascone, S. and Lamberti, G. Hydrogel-based commercial products for biomedical applications: A review. *International journal of pharmaceutics*, 573:118803, 2020.

[36] Varaprasad, K., Raghavendra, G.M., Jayaramudu, T., Yallapu, M.M. and Sadiku, R. A mini review on hydrogels classification and recent developments in miscellaneous applications. *Materials Science and Engineering: C*, 79:958-971, 2017.

[37] Dhara, M. Polymer hydrogels: Classification and recent advances. *Journal of Macromolecular Science, Part A*, 61(5):265-288, 2024.

[38] Ahmed, E.M. Hydrogel: Preparation, characterization, and applications: A review. *Journal of Advanced Research*, 6(2):105-121, 2015.

[39] Bustamante-Torres, M., Romero-Fierro, D., Arcentales-Vera, B., Palomino, K., Magaña, H. and Bucio, E. Hydrogels classification according to the physical or chemical interactions and as stimuli-sensitive materials. *Gels*, 7(4):182, 2021.

[40] Ullah, F., Othman, M.B.H., Javed, F., Ahmad, Z. and Akil, H.M. Classification, processing and application of hydrogels: A review. *Materials Science and Engineering: C*, 57:414-433, 2015.

[41] Bustamante-Torres, M., Romero-Fierro, D., Arcentales-Vera, B., Palomino, K., Magaña, H. and Bucio, E. Hydrogels classification according to the physical or chemical interactions and as stimuli-sensitive materials. *Gels*, 7(4):182, 2021.

[42] Kocak, G., Tuncer, C.A.N.S.E.L. and Bütün, V.J.P.C. pH-Responsive polymers. *Polymer Chemistry*, 8(1):144-176, 2017.

[43] Rizwan, M., Yahya, R., Hassan, A., Yar, M., Azzahari, A.D., Selvanathan, V., Sonsudin, F. and Abouloula, C.N. pH sensitive hydrogels in drug delivery: Brief history, properties, swelling, and release mechanism, material selection and applications. *Polymer*s, 9(4):137, 2017.

[44] Rizwan, M., Yahya, R., Hassan, A., Yar, M., Azzahari, A.D., Selvanathan, V., Sonsudin, F. and Abouloula, C.N. pH sensitive hydrogels in drug delivery: Brief history, properties, swelling, and release mechanism, material selection and applications. *Polymers*, 9(4):137, 2017.

[45] Hendi, A., Umair Hassan, M., Elsherif, M., Alqattan, B., Park, S., Yetisen, A.K. and Butt, H. Healthcare applications of pH-sensitive hydrogel-based devices: a review. *International Journal of Nanomedicine*, 15:3887-3901, 2020.

[46] Hilt, J.Z., Gupta, A.K., Bashir, R. and Peppas, N.A. Ultrasensitive biomems sensors based on microcantilevers patterned with environmentally responsive hydrogels. *Biomedical Microdevices*, 5:177-184, 2003.

[47] Rungsima, C., Boonyan, N., Klorvan, M. and Kusuktham, B. Hydrogel sensors with pH sensitivity. *Polymer Bulletin*, 78:5769-5787, 2021.

[48] Scarpa, E., Mastronardi, V.M., Guido, F., Algieri, L., Qualtieri, A., Fiammengo, R., Rizzi, F. and De Vittorio, M. Wearable piezoelectric mass sensor based on pH sensitive hydrogels for sweat pH monitoring. *Scientific reports*, 10(1):10854, 2020.

[49] Zhang, Y., Liu, Z., Swaddiwudhipong, S., Miao, H., Ding, Z. and Yang, Z., 2012. pH-sensitive hydrogel for micro-fluidic valve. *Journal of Functional Biomaterials*, 3(3):464-479.

[50] Ying, Z., Wang, Q., Xie, J., Li, B., Lin, X. and Hui, S.. Novel electrically-conductive electro-responsive hydrogels for smart actuators with a carbon-nanotube-enriched three-dimensional conductive network and a physical-phase-type three-dimensional interpenetrating network. *Journal of Materials Chemistry C*, 8(12):.4192-4205, 2020.

[51] Kim, D.I., Song, S., Jang, S., Kim, G., Lee, J., Lee, Y. and Park, S. Untethered gripper-type hydrogel millirobot actuated by electric field and magnetic field. *Smart Materials and Structures*, 29(8):085024, 2020.

[52] Shi, Q., Liu, H., Tang, D., Li, Y., Li, X. and Xu, F. Bioactuators based on stimulus-responsive hydrogels and their emerging biomedical applications. *NPG Asia Materials*, 11(1):64, 2019.

[53] Kulkarni, R.V. and Biswanath, S.A. Electrically responsive smart hydrogels in drug delivery: a review. *Journal of Applied Biomaterials and Biomechanics*, 5(3):125-139, 2007.

[54] Bagheri, B., Zarrintaj, P., Surwase, S.S., Baheiraei, N., Saeb, M.R., Mozafari, M., Kim, Y.C. and Park, O.O. Self-gelling electroactive hydrogels based on chitosan–aniline oligomers/agarose for neural tissue engineering with on-demand drug release. *Colloids and Surfaces B: Biointerfaces*, 184:110549, 2019.

[55] Jiang, H., Fan, L., Yan, S., Li, F., Li, H. and Tang, J. Tough and electro-responsive hydrogel actuators with bidirectional bending behavior. Nanoscale, 11(5):2231-2237, 2019.

[56] Yang, C., Wang, W., Yao, C., Xie, R., Ju, X.J., Liu, Z. and Chu, L.Y. Hydrogel walkers with electro-driven motility for cargo transport. *Scientific reports*, 5(1):13622, 2015.

[57] Ghasemi-Mobarakeh, L., Prabhakaran, M.P., Morshed, M., Nasr-Esfahani, M.H., Baharvand, H., Kiani, S., Al-Deyab, S.S. and Ramakrishna, S. Application of conductive polymers, scaffolds and electrical stimulation for nerve tissue engineering. *Journal of Tissue Engineering and Regenerative medicine*, *5*(4):e17-e35, 2011.

[58] Peng, L., Liu, Y., Huang, J., Li, J., Gong, J. and Ma, J. Microfluidic fabrication of highly stretchable and fast electro-responsive graphene oxide/polyacrylamide/alginate hydrogel fibers. *European Polymer Journal*, 103:335-341, 2018.

[59] Yang, C., Wang, W., Yao, C., Xie, R., Ju, X.J., Liu, Z. and Chu, L.Y. Hydrogel walkers with electro-driven motility for cargo transport. *Scientific reports*, 5(1):13622, 2015.

[60] Tomatsu, I., Peng, K. and Kros, A. Photoresponsive hydrogels for biomedical applications. *Advanced drug delivery reviews*, 63(14-15):1257-1266, 2011.

[61] Bustamante-Torres, M., Romero-Fierro, D., Arcentales-Vera, B., Palomino, K., Magaña, H. and Bucio, E. Hydrogels classification according to the physical or chemical interactions and as stimuli-sensitive materials. *Gels*, 7(4):182, 2021.

[62] Huang, H., Qi, X., Chen, Y. and Wu, Z. Thermo-sensitive hydrogels for delivering biotherapeutic molecules: A review. *Saudi Pharmaceutical Journal*, 27(7):990-999, 2019.

[63] Ranganathan, N., Bensingh, R.J., Kader, M.A. and Nayak, S.K. Synthesis and properties of hydrogels prepared by various polymerization reaction systems. *Polymers and Polymeric Composites: A Reference Series*, pages 1-25, ISBN 978-3-319-76573-0. Springer, Cham. 2018.

[64] Rizwan, M., Gilani, S.R., Durani, A.I. and Naseem, S. Materials diversity of hydrogel: Synthesis, polymerization process and soil conditioning properties in agricultural field. *Journal of Advanced Research*, 33:15-40, 2021.

[65] Parhi, R. Cross-linked hydrogel for pharmaceutical applications: a review. *Advanced Pharmaceutical Bulletin*, 7(4):515-530, 2017.

[66] Hennink, W.E. and van Nostrum, C.F. Novel cross-linking methods to design hydrogels. *Advanced drug delivery reviews*, 64:223-236, 2012.

[67] Hu, W., Wang, Z., Xiao, Y., Zhang, S. and Wang, J. Advances in cross-linking strategies of biomedical hydrogels. Biomaterials science, 7(3):843-855, 2019.

[68] Vasile, C., Pamfil, D., Stoleru, E. and Baican, M. New developments in medical applications of hybrid hydrogels containing natural polymers. *Molecules*, 25(7):1539, 2020.

[69] Saunders, J.R., Abu-Salih, S., Khaleque, T., Hanula, S. and Moussa, W. Modeling theories of intelligent hydrogel polymers. *Journal of Computational and Theoretical Nanoscience*, 5(10):1942-1960, 2008.

[70] Shao, Z. and Liu, Q. Independent characterization of the elastic and the mixing parts of hydrogel osmotic pressure. *Extreme Mechanics Letters*, 64:102085, 2023.

[71] Ahearne, M., Yang, Y. and Liu, K.K. Mechanical characterisation of hydrogels for tissue engineering applications. *Topics in tissue Engineering*, 4(12):1-16, 2008.

[72] Hong, Y., Lin, Z., Yang, Y., Jiang, T., Shang, J. and Luo, Z. Biocompatible conductive hydrogels: applications in the field of biomedicine. *International Journal of Molecular Sciences*, 23(9):4578, 2022.

[73] Ikada, Y. Biocompatibility of hydrogels. In *Gels Handbook*, Volume 2, pages 388-407. Academic Press, 2001.

[74] Jayawardena, I., Turunen, P., Garms, B. C., Rowan, A., Corrie, S., and Grøndahl, L. Evaluation of techniques used for visualization of hydrogel morphology and determination of pore size distributions. *Materials Advances*, 4(2):669-682, 2023.

[75] Quan, L., Xin, Y., Wu, X. and Ao, Q. Mechanism of self-healing hydrogels and application in tissue engineering. *Polymers*, 14(11):2184, 2022.

[76] Liu, Y. and Hsu, S.H. Synthesis and biomedical applications of self-healing hydrogels. *Frontiers in chemistry*, 6:449, 2018.

[77] Quan, L., Xin, Y., Wu, X. and Ao, Q. Mechanism of self-healing hydrogels and application in tissue engineering. *Polymers*, 14(11):2184, 2022.

[78] Liu, Y. and Hsu, S.H. Synthesis and biomedical applications of self-healing hydrogels. *Frontiers in chemistry*, 6:449, 2018.

[79] Gaharwar, A.K., Avery, R.K., Assmann, A., Paul, A., McKinley, G.H., Khademhosseini, A. and Olsen, B.D. Shear-thinning nanocomposite hydrogels for the treatment of hemorrhage. *ACS nano*, 8(10):9833-9842, 2014.

[80] Huebsch, N., Kearney, C.J., Zhao, X., Kim, J., Cezar, C.A., Suo, Z. and Mooney, D.J. Ultrasound-triggered disruption and self-healing of reversibly cross-linked hydrogels for drug delivery and enhanced chemotherapy. *Proceedings of the National Academy of Sciences*, 111(27):9762-9767, 2014.

[81] Peng, W., Han, L., Huang, H., Xuan, X., Pan, G., Wan, L., Lu, T., Xu, M. and Pan, L. A direction-aware and ultrafast self-healing dual network hydrogel for a flexible electronic skin strain sensor. *Journal of Materials Chemistry A*, 8(48):26109-26118, 2020.

[82] Li, G., Li, C., Li, G., Yu, D., Song, Z., Wang, H., Liu, X., Liu, H. and Liu, W. Development of conductive hydrogels for fabricating flexible strain sensors. Small, 18(5):2101518, 2022.

[83] Wang, L.L., Highley, C.B., Yeh, Y.C., Galarraga, J.H., Uman, S. and Burdick, J.A. Three-dimensional extrusion bioprinting of single-and double-network hydrogels containing dynamic covalent crosslinks. *Journal of Biomedical Materials Research Part A*, 106(4):865-875, 2018.

[84] Guo, M., Wu, Y., Xue, S., Xia, Y., Yang, X., Dzenis, Y., Li, Z., Lei, W., Smith, A.T. and Sun, L.. A highly stretchable, ultra-tough, remarkably tolerant, and robust self-healing glycerol-hydrogel for a dual-responsive soft actuator. *Journal of Materials Chemistry A*, 7(45):25969-25977, 2019.

[85] Peng, H., Lv, Y., Wei, G., Zhou, J., Gao, X., Sun, K., Ma, G. and Lei, Z. A flexible and self-healing hydrogel electrolyte for smart supercapacitor. *Journal of Power Sources*, 431:210-219, 2019.

[86] Naranjo, A., Martin, C., Lopez-Diaz, A., Martin-Pacheco, A., Rodriguez, A.M., Patiño, F.J., Herrero, M.A., Vazquez, A.S. and Vazquez, E. Autonomous self-healing hydrogel with anti-drying properties and applications in soft robotics. *Applied Materials Today*, 21:100806, 2020.

[87] Wang, C., Zhang, X., Fan, Y., Yu, S., Liu, M., Feng, L., Sun, Q. and Pan, P. Principles and Design of Bionic Hydrogel Adhesives for Skin Wound Treatment. *Polymers*, 16(13):1937, 2024.

[88] Duan, W.L., Zhang, L.N., Bohara, R., Martin-Saldaña, S., Yang, F., Zhao, Y.Y., Xie, Y., Bu, Y.Z. and Pandit, A. Adhesive hydrogels in osteoarthritis: From design to application. *Military Medical Research*, 10(1):4, 2023.

[89] Kharaziha, M., Scheibel, T. and Salehi, S. Multifunctional naturally derived bioadhesives: from strategic molecular design toward advanced biomedical applications. *Progress in Polymer Science*, 150:01792, 2024.

[90] Gao, L., Zhou, Y., Peng, J., Xu, C., Xu, Q., Xing, M. and Chang, J. A novel dual-adhesive and bioactive hydrogel activated by bioglass for wound healing. *NPG Asia Materials*, 11(1):66, 2019.

[91] Ren, J., Li, M., Wang, X., Li, Y. and Yang, W. Adhesive hydrogels with toughness, stretchability, and conductivity performances for motion monitoring. *Polymer Bulletin*, 80(2):1335-1351, 2023.

[92] Nath, J., Chowdhury, A., Ali, I. and Dolui, S.K. Development of a gelatin-g-poly (acrylic acid-co-acrylamide)–montmorillonite superabsorbent hydrogels for *in vitro* controlled release of vitamin B_{12}. *Journal of Applied Polymer Science*, 136(22):47596, 2019.

[93] Fan, C. and Wang, D.A. Novel gelatin-based nano-gels with coordination-induced drug loading for intracellular delivery. *Journal of Materials Science & Technology*, 32(9):840-844, 2016.

[94] Culebras, M., Barrett, A., Pishnamazi, M., Walker, G.M. and Collins, M.N. Wood-derived hydrogels as a platform for drug-release systems. *ACS sustainable Chemistry & Engineering*, 9(6):2515-2522, 2021.

[95] Ma, X., Zhou, X., Ding, J., Huang, B., Wang, P., Zhao, Y., Mu, Q., Zhang, S., Ren, C. and Xu, W. Hydrogels for underwater adhesion: adhesion mechanism, design strategies and applications. *Journal of Materials Chemistry A*, 10(22):11823-11853, 2022.

[96] Xu, Z., Liu, Z., Zhang, C. and Xu, D. Advance in barnacle cement with high underwater adhesion. *Journal of Applied Polymer Science*, 139(37):e52894, 2022.

[97] Liu, Y., He, W., Zhang, Z. and Lee, B.P. Recent developments in tough hydrogels for biomedical applications. *Gels*, 4(2):46, 2018.

[98] Feng, H., Zhang, J., Yang, W., Ma, Y., Wang, R., Ma, S., Cai, M., Yu, B. and Zhou, F. Transparent Janus hydrogel wet adhesive for underwater self-cleaning. *ACS Applied Materials & Interfaces*, 13(42):50505-50515, 2021.

[99] Zhou, D., Li, S., Pei, M., Yang, H., Gu, S., Tao, Y., Ye, D., Zhou, Y., Xu, W. and Xiao, P. Dopamine-modified hyaluronic acid hydrogel adhesives with fast-forming and high tissue adhesion. ACS Applied Materials & Interfaces, 12(16):18225-18234, 2020.

[100] Pan, F., Ye, S., Wang, R., She, W., Liu, J., Sun, Z. and Zhang, W. Hydrogel networks as underwater contact adhesives for different surfaces. Materials Horizons, 7(8):2063-2070, 2020.

[101] Zhao, H. and Li, Y. Removal of heavy metal ion by floatable hydrogel and reusability of its waste material in photocatalytic degradation of organic dyes. *Journal of Environmental Chemical Engineering*, 9(4):105316, 2021.

[102] Weingarten, A.S., Kazantsev, R.V., Palmer, L.C., McClendon, M., Koltonow, A.R., Samuel, A.P., Kiebala, D.J., Wasielewski, M.R. and Stupp, S.I. Self-assembling hydrogel scaffolds for photocatalytic hydrogen production. *Nature chemistry*, 6(11):964-970, 2014.

[103] Ma, C., Xie, Z., Seo, W.C., Din, S.T.U., Lee, J., Kim, Y., Jung, H. and Yang, W. Carbon dot-coupled BiVO4/reduced graphene hydrogel for significant enhancement of photocatalytic activity: Antibiotic degradation and CO2 reduction. *Applied Surface Science*, 565:150564, 2021.

[104] Ran, P., Xia, T., Zheng, H., Lei, F., Zhang, Z., Wei, J. and Li, X. Light-triggered theranostic hydrogels for real-time imaging and on-demand photodynamic therapy of skin abscesses. *Acta Biomaterialia*, 155:292-303, 2023.

[105] Lee, W.H., Lee, C.W., Cha, G.D., Lee, B.H., Jeong, J.H., Park, H., Heo, J., Bootharaju, M.S., Sunwoo, S.H., Kim, J.H. and Ahn, K.H. Floatable photocatalytic hydrogel nanocomposites for large-scale solar hydrogen production. *Nature nanotechnology*, 18(7):754-762, 2023.

[106] Lei, W., Suzuki, N., Terashima, C. and Fujishima, A. Hydrogel photocatalysts for efficient energy conversion and environmental treatment. *Frontiers in Energy*, 15:1-19, 2021.

[107] Gao, W., Zhong, M. and Su, B. Hydrogel-Based Photocatalysts: Applications in Environmental Remediation and Energy Conversion. *Journal of Polymers and the Environment*, 32:1-18, 2024.

[108] Yang, J., Liu, D., Song, X., Zhao, Y., Wang, Y., Rao, L., Fu, L., Wang, Z., Yang, X., Li, Y. and Liu, Y. Recent progress of cellulose-based hydrogel photocatalysts and their applications. *Gels*, 8(5):270, 2022.

[109] Nguyen, B.C., Truong, T.M., Nguyen, N.T., Dinh, D.N., Hollmann, D. and Nguyen, M.N. Advanced cellulose-based hydrogel TiO_2 catalyst composites for efficient photocatalytic degradation of organic dye methylene blue. *Scientific Reports*, 14(1):10935, 2024.

[110] Kuckhoff, T., Landfester, K., Zhang, K.A. and Ferguson, C.T. Photocatalytic hydrogels with a high transmission polymer network for pollutant remediation. *Chemistry of Materials*, 33(23):9131-9138, 2021.

[111] Chen, Y., Xiang, Z., Wang, D., Kang, J. and Qi, H. Effective photocatalytic degradation and physical adsorption of methylene blue using cellulose/GO/TiO_2 hydrogels. *RSC advances*, 10(40):23936-23943, 2020.

[112] Hu, C., Lin, Y.R. and Yang, H.C. Recent developments in graphitic carbon nitride based hydrogels as photocatalysts. *ChemSusChem*, 12(9):1794-1806, 2019.

[113] Li, K., Wen, Y., Song, Y., Qi, N. and Li, Y. Visible light-responsive nanocomposite g-C_3N_4/CNC/PAM aerogel constructed through in-situ photoinitiation for management of wastewater containing organic/heavy metal compound contaminants. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 663:131101, 2023.

[114] Ruan, X., Wang, L., Liang, D. and Shi, Y. Environmental Applications of 3D g-C_3N_4-Based Hydrogel with Synergistic Effect of Adsorption and Photodegradation. *Langmuir*, 39(9):3379, 2023.

[115] Balakrishnan, A., Kunnel, E.S., Sasidharan, R., Chinthala, M. and Kumar, A. 3D black g-C_3N_4 isotype heterojunction hydrogels as a sustainable photocatalyst for

tetracycline degradation and H_2O_2 production. *Chemical Engineering Journal*, 475:146163, 2023.

[116] Qin, H., Li, N., Xu, H.M., Guo, Q.Y., Cong, H.P. and Yu, S.H. Double Confinement Hydrogel Network Enables Continuously Regenerative Solar-to-Hydrogen Conversion. *Angewandte Chemie*, 134(42):e202209687, 2022.

[117] López-Díaz, A., Vázquez, A.S. and Vázquez, E. Hydrogels in soft robotics: Past, present, and future. *ACS nano*, 18(32):20817-20826, 2024.

[118] Alkahtani, M.E., Elbadawi, M., Chapman, C.A., Green, R.A., Gaisford, S., Orlu, M. and Basit, A.W. Electroactive Polymers for On-Demand Drug Release. *Advanced Healthcare Materials*, 13(3):2301759, 2024.

[119] Meyers, K., Lee, B.P. and Rajachar, R.M. Electroactive polymeric composites to mimic the electromechanical properties of myocardium in cardiac tissue repair. *Gels*, 7(2):53, 2021.

[120] Choi, M.Y., Shin, Y., Lee, H.S., Kim, S.Y. and Na, J.H. Multipolar spatial electric field modulation for freeform electroactive hydrogel actuation. *Scientific reports*, 10(1):2482, 2020.

[121] Badawi, M.N., Kuniyil, M., Bhatia, M., Kumar, S.S.A., Mrutunjaya, B., Luqman, M. and Adil, S.F., 2023. Recent advances in flexible/stretchable hydrogel electrolytes in energy storage devices. *Journal of Energy Storage*, 73, p.108810.

[122] Palza, H., Zapata, P.A. and Angulo-Pineda, C. Electroactive smart polymers for biomedical applications. *Materials*, 12(2):277, 2019.

[123] Peng, Q., Chen, J., Wang, T., Peng, X., Liu, J., Wang, X., Wang, J. and Zeng, H. Recent advances in designing conductive hydrogels for flexible electronics. *InfoMat*, 2(5):843-865, 2020.

[124] Ying, Z., Wang, Q., Xie, J., Li, B., Lin, X. and Hui, S. Novel electrically-conductive electro-responsive hydrogels for smart actuators with a carbon-nanotube-enriched three-dimensional conductive network and a physical-phase-type three-dimensional interpenetrating network. *Journal of Materials Chemistry C*, 8(12):4192-4205, 2020.

[125] Thirabowonkitphithan, P., Maksuk, K., Permpoka, K., Jiraseree-amornkun, A., Wattanapanitch, W., Nilaratanakul, V., Tasca, F. and Laiwattanapaisal, W. A

flexible non-enzymatic hydrogel-assisted electrochemical sensor: Wireless, sensitive, and selective uric acid detection for home monitoring. *Microchemical Journal*, 205:111268, 2024.

[126] Li, Y., Sun, Y., Xiao, Y., Gao, G., Liu, S., Zhang, J. and Fu, J. Electric field actuation of tough electroactive hydrogels cross-linked by functional triblock copolymer micelles. *ACS Applied Materials & Interfaces*, 8(39):26326-26331, 2016.

[127] Banerjee, H., Suhail, M. and Ren, H. Hydrogel actuators and sensors for biomedical soft robots: brief overview with impending challenges. *Biomimetics*, 3(3):15, 2018.

[128] Han, D., Farino, C., Yang, C., Scott, T., Browe, D., Choi, W., Freeman, J.W. and Lee, H. Soft robotic manipulation and locomotion with a 3D printed electroactive hydrogel. *ACS applied materials & interfaces*, 10(21):17512-17518, 2018.

[129] Migliorini, L., Santaniello, T., Yan, Y., Lenardi, C. and Milani, P. Low-voltage electrically driven homeostatic hydrogel-based actuators for underwater soft robotics. *Sensors and Actuators B: Chemical*, 228:758-766, 2016.

[130] Ovando-Medina, V.M., Reyes-Palacios, G.A., García-Montejano, L.A., Antonio-Carmona, I.D. and Martínez-Gutiérrez, H. Electroactive polyacrylamide/chitosan/polypyrrole hydrogel for captopril release controlled by electricity. *Journal of Vinyl and Additive Technology*, 27(4):679-690, 2021.

[131] Bansal, M., Dravid, A., Aqrawe, Z., Montgomery, J., Wu, Z. and Svirskis, D. Conducting polymer hydrogels for electrically responsive drug delivery. *Journal of Controlled Release*, 328:192-209, 2020.

[132] Puiggalí-Jou, A., Cazorla, E., Ruano, G., Babeli, I., Ginebra, M.P., García-Torres, J. and Alemán, C. Electroresponsive alginate-based hydrogels for controlled release of hydrophobic drugs. *ACS biomaterials Science & Engineering*, 6(11):6228-6240, 2020.

[133] López-Díaz, A., Vázquez, A.S. and Vázquez, E. Hydrogels in Soft Robotics: Past, Present, and Future. *ACS nano*, 18(32):20817-20826, 2024.

[134] Chenani, H., Saeidi, M., Rastkhiz, M.A., Bolghanabadi, N., Aghaii, A.H., Orouji, M., Hatamie, A. and Simchi, A. Challenges and advances of hydrogel-

based wearable electrochemical biosensors for real-time monitoring of biofluids: from lab to market. A Review. *Analytical Chemistry*, 96(20):8160-8183, 2024.

[135] Lee, H.K., Yang, Y.J., Koirala, G.R., Oh, S. and Kim, T.I. From Lab to Wearables: Innovations in Multifunctional Hydrogel Chemistry for Next-Generation Bioelectronic Devices. *Biomaterials*, 310:122632, 2024.

[136] Kang, X., Yu, Y., Bao, Y., Cai, W. and Cui, S. Real time quantification of the chemical cross-link density of a hydrogel by in situ UV-vis spectroscopy. *Polymer Chemistry*, 6(23):4252-4257, 2015.

[137] Sobhanimatin, M.B., Pourmahdian, S. and Tehranchi, M.M. Colorimetric monitoring of humidity by opal photonic hydrogel. *Polymer Testing*, 98:106999, 2021.

[138] Sievers, J., Sperlich, K., Stahnke, T., Kreiner, C., Eickner, T., Martin, H., Guthoff, R.F., Schünemann, M., Bohn, S. and Stachs, O. Determination of hydrogel swelling factors by two established and a novel non-contact continuous method. *Journal of Applied Polymer Science*, 138 (18):50326, 2021.

[139] Vedadghavami, A., Minooei, F., Mohammadi, M.H., Khetani, S., Kolahchi, A.R., Mashayekhan, S. and Sanati-Nezhad, A. Manufacturing of hydrogel biomaterials with controlled mechanical properties for tissue engineering applications. *Acta biomaterialia*, 62:42-63, 2017.

[140] Madduma-Bandarage, U.S. and Madihally, S.V. Synthetic hydrogels: Synthesis, novel trends, and applications. *Journal of Applied Polymer Science*, *138*(19):50376, 2021.

[141] Adjuik, T.A., Nokes, S.E. and Montross, M.D. Biodegradability of bio-based and synthetic hydrogels as sustainable soil amendments: A review. *Journal of Applied Polymer Science*, 140(12):e53655, 2023.