**Review Article**

**Poly(vinyl alcohol) Hydrogels: The Old and New Functional Materials**

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Hydrogels have three-dimensional network structures, high water content, good flexibility, biocompatibility, and stimulation response, which have provided a unique role in many fields such as industry, agriculture, and medical treatment. Poly(vinyl alcohol) PVA hydrogel is one of the oldest composite hydrogels. It has been extensively explored due to its chemical stability, nontoxic, good biocompatibility, biological aging resistance, high water-absorbing capacity, and easy processing. PVA-based hydrogels have been widely investigated in drug carriers, articular cartilage, wound dressings, tissue engineering, and other intelligent materials, such as self-healing and shape-memory materials, supercapacitors, sensors, and other fields. In this paper, the discovery, development, preparation, modification methods, and applications of PVA functionalized hydrogels are reviewed, and their potential applications and future research trends are also prospected.

1. Introduction

Polymer hydrogel networks are low crosslinking materials, which can be formed by chemical or physical crosslinking methods and form covalent or noncovalent crosslinking points. Such networks can expand or contract, absorbing and retaining large amounts of water while insoluble in water [1, 2]. Hydrogels can usually be molded into certain shapes under natural conditions and exhibit good flexibility under certain pressure. Such kind of functional polymer materials with water absorption, water retention, controlled release, and other functionalized properties have received huge research interests that developed rapidly in recent years.

Design strategies of functional hydrogels have been extensively studied. Hydrogels prepared via various chemical and physical interactions often showed excellent characteristics, such as stimulus responsive, biocompatible, reversible physicochemical, and other properties [3]. Hydrogels have similarities with human soft tissues in composition, structure,
and properties. Therefore, they are widely used in drug delivery, cell culture, tissue engineering, and other biomedical and biomimetic applications [4]. Besides, functionalized hydrogels have broad application prospects in many aspects, such as intelligent sensing and environmental treatment [5].

As one of the old polymer hydrogel materials, poly(vinyl alcohol) (PVA) has shown new vitality in recent years. Many studies have shown that it has the value of the further study. PVA (Figure 1) is a water-soluble long-chain polymer obtained by alcoholysis, hydrolysis, or ammonolysis of poly(vinyl acetate) (PVAc). PVA-based hydrogels are colloidal dispersion with three-dimensional network structures through crosslinking and swelling. They have attracted much attention due to their low toxicity, high water absorption, good mechanical properties (i.e., high elastic modulus and high mechanical strength), and good biocompatibility [6, 7]. Much attention also focused on their applications in the food industry, forestry, and super absorbent, especially in biomedicine, such as drug delivery carriers, tissue engineering scaffolds, implanted artificial muscles and organs, biosensors, wound dressings, and soft robotics.

In this review, we summarized the preparation, modification, and applications of PVA hydrogels, especially focused on the frontier works, and a prospect of future development was given at last.

2. Development, Preparation, and Modification Methods of PVA Hydrogels

2.1. Discovery and Development of PVA Hydrogels. In the early 1970s, frozen gelled PVA was proposed for biomedical applications [8]. In the same period, Peppas pioneered a series of studies on preparation techniques of PVA hydrogels. By measuring the turbidity of PVA samples crystallizing in the gelation process, the crosslinking reaction of PVA in the crystallization process was deeply understood, and the relationship between crystallization, PVA concentration, and gelation time was studied, thus, expanding the application of PVA hydrogels in sensing, biomedical, and other aspects [9–12]. Since then, more and more efforts have been devoted to researching formation, modification, characterization, and applications of PVA hydrogels. After decades of exploration, thanks to the progress of research technology (e.g., 3D printing), the applications of PVA hydrogels as advanced functional materials have been extensively expanded, such as 3D-printing tissue engineering material [13, 14], self-healing gels [15], shape-memory materials [16], wearable electronic skin, and colorimetric sensors, showing that this material has more potentials and possibilities.

2.2. Preparation and Modification of PVA. At room temperature, a solution of highly alcoholysis PVA (>98%) can autonomously and slightly gelated between molecular chains into hydrogels. However, such hydrogel has poor mechanical properties and applications due to the low gelation density [17, 18]. In order to prepare PVA hydrogels with high mechanical strength, high water content, and good transparency, the ideal polymer network structure should be obtained through different crosslinking methods and preparation conditions. According to the crosslinking mechanism of polymers, the preparation of PVA hydrogels can be divided into physical crosslinking, chemical crosslinking, and radiation crosslinking.

2.2.1. Physically Crosslinked PVA Gels. At present, the repeated “freezing-thawing method” is the most commonly used physical crosslinking process [19, 20]. The physical and mechanical properties of the hydrogels, so-called cryogels, obtained by physical crosslinking could be greatly improved, and the crosslinking process is thermally reversible. Gelation properties can be improved by changing the type of solvent or by using a mixture of dimethyl sulfoxide (DMSO) and water [21].

The gelation mechanism (c.f. Figure 2(a)) of this physical method includes (1) the polymer chain aggregation region and nonaggregation region are formed at the initial stage of gelation, resulting in an network structure due to the function of intramolecular hydrogen bond; (2) when PVA solution was frozen, the movement of molecular chains was weakened, and the contact time between chains became longer while the distance between chains was shortened,
which promoted the formation of hydrogen bond association between hydroxyl groups both inter/intramolecular [22, 23]. The PVA hydrogels prepared by the freezing-thawing method do not use toxic organic crosslinker that maintains good biocompatibility. With the change of environmental parameters (such as temperature, pH value, and osmotic pressure), the properties of the physical crosslinking points can be changed, and the sol-gel states are reversible. Thus, the physical PVA gels still have great potential in many fields.

2.2.2. Chemically Crosslinked PVA Gels. Chemical crosslinking is the most commonly used preparation method of hydrogels, and the hydrogel properties are affected by the concentration of monomer, crosslinker, and reaction conditions. For PVA, chemical crosslinkers could form chemical crosslinking points between PVA molecules to form gels (Figure 2(b)). Commonly used crosslinkers include epichlorohydrin, boric acid, aldehydes, and heavy metal compounds that form complexes with PVA molecules [24–27]. The chemically crosslinking reaction is rapid, but nonuniform crosslinking structures often occur due to the inhomogeneous dispersion of the crosslinkers. Although there are some biocompatible crosslinkers, for example, multicarboxylic acids, as an environmentally friendly solvent, are used as a crosslinking agent for chitosan/PVA nanofibers, which can increase the cellular compatibility of the fibers [28]. However, at present, most of the chemical crosslinkers are usually biotoxic and hard to remove, which have huge damage to tissue cells and cause inflammation after implantation, and hardly reduces the biocompatibility of the hydrogel materials [29].

2.2.3. PVA Gels Crosslinked by Radiation. Radiation crosslinking utilizes high-energy rays, such as gamma-ray, electron beams, and X-ray, that directly radiate PVA solutions. As shown in Figure 2(c), when PVA is irradiated at high energy, it can generate macromolecular free radicals (P·), mainly from the direct action of irradiation and the action of water radiolysis active particles (S·). The free radicals generated by the irradiated PVA can be located on secondary and tertiary carbons, respectively. Two macromolecular free radicals are crosslinked together through the double-group coupling reaction to produce crosslinking bonds. With the increase of crosslinking bonds, they begin to gel and gradually form a three-dimensional network structure throughout the whole system [31–33]. The PVA hydrogels produced by radiation are free of crosslinkers and therefore have high purity and good optical transparency. At the same time, high-energy reaction conditions often cause the loss of mechanical properties and other aspects. Another advantage of PVA hydrogels prepared by radiation crosslinking is that the reaction is rapid and can be achieved at room temperature and atmospheric pressure [30, 34]. However, due to radiation intensity, many materials cannot be added to the hydrogel systems.

2.3. Modification of PVA Hydrogels

2.3.1. Chemical Modification. Neat PVA hydrogels are not sensitive to environmental stimuli. Thus, functional monomers/polymer are used to prepare hybrid hydrogels with modified properties [35]. The molecular structure of PVA could commonly be modified by grafting functional groups onto PVA backbones. For instance, the PVA containing...
carboxyl side group can be obtained by esterifying PVA with phthalic anhydride or succinic anhydride [36]. A charged group-modified PVA hydrogel was reported on the basis of copolymerization crosslinking of acylated PVA with [2-((methacryloyloxy) ethyl) trimethyl ammonium chloride (DMC) monomers, such hydrogel possessed a macroporous structure, high porosity, appropriate swelling ability, and mechanical property. It exhibited excellent stability over a broad pH range [37]. PVA can also react with bifunctional compounds such as aromatic diglycidyl ether to obtain crosslinked PVA with a stereoscopic network structure, which improves the chemical stability and selectivity of PVA hydrogels [30]. As shown in Figure 3(a), PVA-based hydrogels such as 4-carboxybenzaldehyde (CBA)-PVA [38] and 2,3-dialdehyde cellulose (DAC)-PVA [39] have also been reported.

2.3.2. Physical Modification. By utilizing the intermolecular force between polymer chains to form molecular aggregates, the composite system with excellent properties could be achieved. Physical crosslinking chitosan (CS)/PVA blend hydrogels with only PVA gelated networks have been widely used in many fields [40, 41]. A 3D-printing hydrogel was developed by cooperating the physically gelated PVA as the stretchable polymer network together with alkaline polysaccharide CS, as shown in Figure 3(b), which improved the mechanical strength of such blend system [42]. Solvents including DMSO, ethylene glycol, and glycerol could serve as plasticizers that promote structural stability and help produce firmer PVA hydrogels due to the penetration of the PVA gel matrix [43–45]. A high-concentration solution of alkaline metal hydroxide can also promote the physical crosslinking of PVA, increase the crystallinity, and form elastic hydrogels with low water content and the swelling ratio [46, 47]. Besides, dual physical gels such as poly(ethylene glycol) (PEG)/PVA by one-pot method [48, 49] and poly(acrylamide-co-acrylic acid) (PAM-co-PAA)/PVA [4] by two-step method were also reported.

2.3.3. Filler Reinforcement. Composite with inorganic fillers or organic small molecules can also enhance the PVA hydrogels [34, 50]. Such kind of blending not only keeps the biological activity but also improves the mechanical properties (e.g., friction properties) of the PVA hydrogels [51–53]. At the same time, fillers have the advantage of increasing the content of borax to improve the mechanical strength of hydrogels, but also have the disadvantage of destroying the structure of hydrogels. Filling can promote the crosslinking degree of the gel, thus, reducing the water content and swelling rate of the gel, resulting in the shrinkage of the pores in the hydrogel [54]. Defects in the filler may affect the application of the gel. It has been reported that the addition of tri-calcium phosphate nanoparticles increases the mechanical strength while decreases the swelling and degradation rate, pore size, permeability, and quercetin release rate of the hydrogel [55]. For instance, as shown in Figure 3(c), a series of hybrid graphene oxide (GO)/PVA composite hydrogels have been reported with different potential applications in artificial cartilage and tissue engineering [56, 57]. Besides, Figure 3(d) shows a CS/PVA/CeO2 hydrogel system that combined polymer modification and filler functionalization, which can be utilized as a wound-healing material [58].

3. Applications of Functionalized PVA Hydrogels

Biomedical polymer materials should have a series of characteristics such as nontoxic, good biocompatibility, degradability, and processability. The excellent properties of PVA hydrogel meet the requirements of biomedical polymers. Therefore, PVA has been widely used in drug delivery carriers [59, 60] and microcapsules [61], wound dressings [62], artificial organs and tissues [63], intelligent materials, and other fields.

3.1. Drug Delivery Carriers and Microcapsules. PVA hydrogels are used as drug carriers while small drug molecules are embedded, and the stability of the drug can be increased [59]. With the swelling of the hydrogels due to the Donnan potential, the releasing time of drugs can be greatly prolong while the dosage of the drug can be reduced [63, 64]. Since PVA is stable to environmental stimulus, the releasing mechanism of drugs from PVA gels is proved and calculated as zero-order releasing mode [39, 62, 65, 66]. As can be seen in Figure 4(a), PEG/PVA hydrogel system could perform stable releasing of aspirin under different pH buffer solutions [50]. Such materials are investigated for certain cancer treatment and localized delivery [59, 66, 67]. Diabetes is a metabolic disease characterized by glucose, protein, fat, and other metabolic disorders that occur due to hypofunction of islets and insufficient insulin secretion [68], and glycerol adjusted PVA hydrogel with a long-acting effect was reported for the released of insulin [69]. The PVA/PEG system also showed good physical and chemical properties in pH-dependent drug delivery [36, 41] and wound healing [58, 70].

3.2. Wound Dressing. Although the traditional gauze dressings have a wide range of uses, there are many disadvantages in their application due to their small amount of absorption of excess wound exudate, frequent replacement, and adhesion with the wound [71]. Developing a nontoxic, super-absorbent, and antibacterial hydrogel as a skin wound dressing is of significant importance. As a wound dressing, PVA hydrogels can protect the wound and reduce the second injuries of external environment stimulus and external mechanical force applied to the wound, which is convenient for clinical operation (Figure 4(c)) [39]. Moreover, PVA hydrogels also have good permeability to water and oxygen and high moisture content that can maintain the moist environment of a wound during wound healing, promote the growth of new tissue, and promote wound healing [59, 72]. However, the PVA hydrogels themselves do not have antibacterial properties; in order, it is necessary to enhance the antibacterial performance of PVA hydrogels as dressing materials. Antibacterial modification mainly includes inorganic, organic, and natural antibacterial molecules. Silver nanoparticles are commonly used inorganic antibacterial
Figure 3: Modification of PVA by: (a) CBA-PVA (chemically) [38], (b) CS/PVA (physically) [42], (c) GO/PVA ( filler) [57], and (d) CS/PVA/CeO$_2$ (polymer and filler) [58].
agents, which are considered efficient and broad-spectrum antibacterial, but the main barrier for industry application is the high cost [73]. As mentioned above, the main strategies of organic modification for bio-oriented PVA hydrogels include filler reinforcement and chemical modification [50]. An in situ formed PVA-based hydrogel wound dressing that triggered by glucose in wound exudate due to the existence of glucose oxidase in gel solution was reported [74]. Natural antibacterial molecules, such as CS, are green and environmentally friendly materials. In the PVA/CS system, the addition of CS can not only improve the thermal stability and mechanical properties of PVA hydrogels but also adjust the water content of PVA hydrogels [40, 58, 75–79].

The antibacterial materials of the PVA hydrogel systems are generally expensive, and the modification methods are complicated. Therefore, the preparation of antibacterial PVA hydrogels with low cost and simple preparation, large-scaled production method is the research focus [80].

3.3. Tissue Engineering. Scaffold material plays an important role in tissue engineering. An ideal scaffold material should have the following characteristics: nonimmunogenicity, nontoxicity, good biocompatibility, high porosity, degradability, appropriate degradation rate, and easy manufacturing [81]. With the development of cartilage tissue

Figure 4: The biomedical applications: (a) controlled drug releasing from PVA/PEG hydrogels [48], (b) artificial acetabulum fabricated by PVA hydrogel [90], (c) bioadhesive wound dressing PVA hydrogel [39], and (d) PVA hydrogel-based ear-shaped artificial auricular cartilage [86].
engineering, the composite of hydrogel/cells is one of the main materials for cartilage regeneration [82]. Hydrogels have many similarities with articular cartilage and therefore are ideal substitutes for articular cartilage [83]. As a spatial framework for cell proliferation and differentiation, hydrogels can be beneficial to cell transplantation, which also allow free entry of nutrients and oxygen and provide transport conditions for the secretion of cells.

Hydrogel elastomers have similar tribological properties and physical properties such as high water content as articular cartilage [57, 84], which may serve as a substitute for articular cartilage to repair articular cartilage defects, restore the integrity of the articular surface, and maintain joint function, and their potential advantages are (1) many synthetic polymer gels have shown good biocompatibility [81]; (2) similar to natural cartilage, in addition to the basic structure of solid-liquid phase, they also show expansion, viscoelasticity, and considerable compression stiffness and can withstand a certain load cycle; (3) after modification, the natural lubrication mechanism in cartilage tissue can be simulated [82–88]. Currently, hydrogels have been used to repair articular cartilage in two ways: (1) permanent implants replacement of damaged cartilage tissue and (2) being injected as cell carrier materials to stimulate tissue regeneration. Figure 4(d) showed an ear-shaped artificial auricular cartilage, which proposed that PVA hydrogel-based hydrogels might have found their applications as artificial organs [86]. As a kind of cell-free implant, hydrogels can be structurally and mechanically similar to cartilage and suffer effective load [89].

PVA hydrogels materials are potential candidates for artificial joints, artificial muscles, artificial vitreous body, artificial cornea, and iris. PVA hydrogel has porous, permeable structures that are similar to natural cartilage and contain much water. Liquid can be infiltrated and extruded under a certain load, which can be entrained as a lubricant. Hydrogels’ high water content and surface structure are very similar to natural cartilage fabrics [52]; Figure 4(b) shows an artificial acetabulum fabricated by PVA hydrogel, which could suffer harsh friction test [90]. Under the condition of hyaluronic acid (HA) lubrication, PVA and human articular cartilage have similar tribological properties [59, 81]. However, like most synthetic polymer materials, PVA is non-toxic. However, it is a biologically inert polymer, which has a weak ability to adsorb proteins and cannot adhere to cells to form binding with living tissue. As a kind of natural polymer material, gelatin, a degradation product of collagen, has a protein chain similar to collagen and maintains a large number of amino (-NH2) and carboxyl (-COOH) groups [91–93]. Therefore, through the composite modification of PVA hydrogel, the introduction of charged groups into the hydrogel composition can enhance its cell affinity and facilitate cell adhesion [94].

3.4. Intelligent Materials. Intelligent hydrogels can respond promptly to subtle changes or stimuli in the environment, such as temperature, pH value, electric field, and pressure. For instance, the thermosensitive hydrogel can shift its swelling degree according to the temperature of the environment to control drug release at desirable conditions. In recent years, more attention has been paid to self-healable, shape memory, and stimulus responsive materials, which can be made from PVA hydrogels and be implemented in intelligent devices. However, the structures and functionality of hydrogels can be damaged by external mechanical or chemical erosion, especially under complex internal environment conditions. Therefore, designing and synthesizing hydrogels with self-healing/shape memory ability is widely concerned by researchers.

3.4.1. Self-Healing and Shape Memory Materials. Unlike traditional hydrogels, self-healing hydrogel forms a spatial network through dynamic connectivity. Recently, self-healing hydrogels have attracted extensive research interest and have been applied to constructing various new intelligent materials [96]. Injection of self-healing hydrogels can deliver drugs in vivo without significant damage to the body since the hydrogels are embedded without surgical incision [97]. Therefore, compared with traditional hydrogels, self-healing hydrogels show great potential in various fields, such as self-healing, in vivo drug delivery, and sensors. The self-healing process and its results are mainly manifested in two aspects: (1) the recovery of micro/macromorphology (micro/macromorphology) and (2) the recovery of mechanical and rheological properties [38]. The strategies for synthesizing self-healing hydrogels are also including noncovalent (physical crosslinking) such as hydrophilic and hydrophobic bonds, hydrogen bonds, host-guest interactions, ionic bonds [98–102], and dynamic covalent bonds (chemical crosslinking) such as Schiff base linkages and disulfide linkages [103, 104].

PVA contains large amounts of hydroxyl groups that can form intermolecular hydrogen bonds via freezing-thawing methods and form a self-healing hydrogel network [15, 38, 95]. Figure 5(a) showed that PVA hydrogels with high polymer content could exhibit self-healing properties [17]. With the functionalization of other materials such as quantum dots, crystal array, and polymers, the healable PVA gels could reveal interesting applications. The dual physically crosslinked hydrogel was reported that formed by firstly entanglement between PAM-co-PAA and then cooperated with PVA by freezing/thawing process [4]. Such hydrogel showed not only good mechanical properties (1230 ± 90 kPa in strength, 364 ± 38 kPa in modulus, and 1250 ± 50 kJ/m3 in toughness) but also rapid self-healing ability due to the hydrogen bond between PVA molecules and the PAA segment. In addition, the self-healing ability can be chemically enhanced due to the weak hydrogen bond effect. A series of PVA-based double/triple network hydrogels containing hydrogen bonding and metal ion coordination were reported [105–107]. Based on the synergistic effect of hydrogen bond and metal ion coordination, the hydrogel showed excellent self-healing efficiency. The self-healing properties of typical materials mentioned can be compared in Table 1.

In addition, the physically crosslinked PVA was introduced into the chemically crosslinked PEG network to form a double crosslinking network, such PEG/PVA hydrogel not only showed self-healing property but also available of shape
Shape memory hydrogels are reactive hydrogels that respond to shape change stimuli, which can deform and fix a deformed shape and can return to the original shape when stimulated by external forces [5]. The stimulus involves thermal, ion, pH, solvent, etc. Fully hydrated gels can be penetrated by small molecules that can trigger shape memory behavior. In general, chemically excited shape memory hydrogels have the dual properties of reversible and dynamic, which is helpful for the shape fixation and recovery of hydrogels. Reversible interactions like ammonia bond, host-guest interaction, and metal coordination interaction are used to realize the shape memory performance of hydrogels [16, 47]. Figures 5(b) and 5(c) show shape memory properties of different PVA hydrogels induced by solvent and temperature, respectively [16, 95].

3.4.2. Supercapacitor. An early electrochemical supercapacitor was assembled with glutaraldehyde crosslinked PVA hydrogel as electrolyte and activated carbon fiber cloth as electrode [108]. Compared with electrochemical capacitors using 1 mol/L \( \text{H}_2\text{SO}_4 \) aqueous solution as an electrolyte, the results showed that the ionic conductivity of the PVA hydrogel electrolyte was similar to that of the 1 mol/L \( \text{H}_2\text{SO}_4 \) aqueous solution, and the PVA hydrogel assembled electrochemical capacitors showed a lower self-discharge effect. With the modification of PVA hydrogel, such as PAM/PVA, the specific capacitance can reach 230 F/g while the capacitance retention rate can be maintained at 98% after 5000 cycles [109]. Recently, acrylamide (AA) monomer was introduced into PVA/H\( _2\text{SO}_4 \) solution to form a dual-crosslinked hydrogel electrolyte as all-in-one flexible supercapacitors whose energy density and power density reach up to 14.2 \( \mu \text{Wh/cm}^2 \) and 0.94 mW/cm\(^2\), respectively [110]. This supercapacitor also exhibited good mechanical strength that can suffer compressive stress of 0.53 MPa and be stretched up to 500%. Other recently reported PVA-based hydrogels also show excellent properties including high stability, capacitance, current density, and repeatability [46, 111–113].

![Self-healable PVA Hydrogel](image)

**Figure 5:** Schemes of PVA showing: (a) self-healing [15], (b) solvent-induced shape memory [16], and (c) temperature-induced shape memory behaviors [95].

**Table 1:** Self-healing properties of some reported PVA materials.

| Synthetic strategy                      | Mechanical property                             | Healing time | Healing efficiency | Ref. |
|----------------------------------------|------------------------------------------------|--------------|--------------------|------|
| Hydrogen bond                          | Fracture stress ~105 kPa                        | 10 s to 48 h | Up to 70%          | 15   |
| Synergistic crosslinking of bimetallic ions | Tensile strain ≈ 1.011 mm/mm, tensile stress ≈ 0.34 MPa, elongation at break ≈ 74% | <60 s        | Up to 95%          | 98   |
| Hydrogen bond                          | Compression modulus is 39.6 kPa–74.0 kPa, maximum stress ≈ 29.0 kPa | ≥4.68 min    | 63.21%             | 101  |
| Reversible hydrogen bond               | Storage modulus ≈ 11.38 kPa, loss modulus ≈ 4.036 kPa | ~10 min      | /                  | 102  |
| Hydrogen bond                          | Tensile stress =60 kPa                          | <24 h        | ~74%               | 134  |
3.4.3. Conductive and Antifreeze Materials. As functional materials, thermostolerance is also a very important characteristic. Similar to self-healing, acid/alkali resistance, antifreeze, and compression resistance can bring more possibilities for intelligent materials. As functional devices, frozen resistance property is also very important [110]. An antifreezing conductive hydrogel was reported, which was prepared by combing PVA with poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate (PEDOT: PSS) with the assistance of ethylene glycol [114]. The hybrid hydrogel showed excellent strain-sensitive and conductive performance even at a low temperature of ~40°C. Recently, PVA/cellulose nanofibril (CNF) composite hydrogels were reported with freezing tolerant and conductive properties [115]. The hydrogels are obtained through freezing-thawing treatment with DMSO/water as an antifreeze solvent system. The introduction of CNF increased the mechanical properties and ionic conductivity of the composite hydrogels, resulting in tough products with 2.1 MPa in tensile strength and can be stretched up to 660%. The ionic conductivity maintained 1.1 S/m even at ~70°C. Similarly, antifreeze solvents such as diols and triols can be used to improve the properties of PVA hydrogels [43, 44]. However, the conductivity and mechanical properties of hydrogels and their application in ultrasensitive hydrogel electronic devices might be affected due to the introduction of solvents. In addition, biotoxic organic solvent-assisted hydrogels limit the practical applications in contact hydrogel devices, such as bionic electronic skin and bio-oriented sensors.

### 3.4.4. Sensors.

Based on excellent physical and chemical properties, other functions such as antifreeze, self-healing, and stimuli response of PVA-based hydrogels can also be applied to act as specific sensing applications. The hydrogels respond to changes in the external environment, causing a swelling/shrinkage behavior. The change of the environment can be speculated by measuring the volume change of the hydrogels.

A PVA hydrogel-based temperature sensor with frost resistance, water retention, and moldability was prepared by introducing glycerol and silver nanofibers (AgNWs) into PVA hydrogel [44]. The hydrogel can be remolded due to the reversible physical crosslinking through freezing-thawing treatment. As a sensor, the hydrogel showed the good moisturizing properties. It can linearly change its conductivity according to the temperature change in the range from 5°C to 55°C with a short response time and good repeatability. Interestingly, a similar PVA/AgNWs hydrogel sensor with biocompatibility and high stretchability was reported that can be applied as strain sensors. The hydrogel material can be stretched up to 500% while maintaining its sensing linearity, which can be applied to human skin and monitor the body motion [116]. Previous studies also showed that the introduction of PVA hydrogels in ion-conducting cellulose hydrogels increases the tensile properties of the sensors [117, 118]. In addition, this type of PVA-based hydrogel pressure sensor also has the characteristics of good sensitivity, high transparency, fast response time, and high reliability, demonstrating the great potential of wearable devices [119, 120].

Another sensing mechanism utilizes the so-called photonic crystals as colorimetric elements [121]. The long-term ordered colloidal crystal was embedded inside hydrogel; the crystal can diffract a certain frequency of visible light while the diffraction wavelength can be tuned by the lattice distance of the crystal [122]. Thus, as the hydrogel exhibit volume changes due to the environmental stimuli, the embedded crystal changes its lattice constant and shifts the diffraction color of the hydrogel system. Based on this mechanism, modified PVA hydrogels can be applied as a series of colorimetric sensors, including heavy metal [123], glucose [124], pH [41], and strain [43]. For instance, a glucose-sensitive photonic crystal material was reported, coated by a 4-boronobenzaldehyde-functionalized PVA hydrogel. During the glucose detection, glucose binds to borate and shrinks the hydrogel, and thus causing diffraction color of the hydrogel blue shift. As a result, 0.1-0.6 mM of glucose was distinguished by the color change of the sensor gel. The performances of typical PVA-based hydrogel sensors were listed in Table 2.

The long-term stability and sensitivity of flexible sensors designed with injectable, antifreeze, and intelligent sensing hydrogels as electrolytes at low temperatures remain urgent challenges. In addition, compared with traditional electronic materials, the disadvantages of hydrogels include low modulus and high water percentage, which may lead to poor integration of hydrogels and devices. Therefore, optimizing and improving the integration process of hydrogel-based sensors are urgent challenges.

**Table 2: The properties of typical PVA-based hydrogel sensors.**

| Sensing target         | Response time | Mechanical property                                      | Characteristic                                                                 | Ref.   |
|------------------------|---------------|---------------------------------------------------------|-------------------------------------------------------------------------------|--------|
| Temperature            | ~1 s          | Good elastic and mechanical properties                  | Moisture retention under normal temperature and moderate conditions (water retention 37% – 95%) | [44]   |
| Strain                 | 0.32 s        | High tensile strain up to 500%, mechanical strength ≈ 900 kPa | Conductivity ≈ 1.85 S m⁻¹                                                   | [116]  |
| Strain                 | 170 ms        | Tensile strength = 1360 kPa, elastic modulus = 110 kPa   | Low detection strain (0.25%), wide sensing range (0.8 kPa~ 50 kPa), durable operation | [120]  |
| pH and Pb²⁻            | /             | /                                                       | Capable of dehydration and rehydration                                       | [123]  |
| Glucose concentration  | 180 s         | /                                                       | Low detection limit (glucose concentration: 0 – 20 mM)                        | [124]  |
3.4.5. Other Applications. In addition to the intensive studies and reports described above, there are more interesting studies showing specific properties of PVA materials that deserve attention. Such as an ultrastrong nacre-inspired double network PVA hydrogel with the impact-resistance property was reported [125]. There are also important applications in water treatment, such as high-efficiency removal of pollutants in wastewater and simple two-step preparation of PVA-based double network hydrogels as gel adsorbents to adsorb heavy metal ions in wastewater [126]. The crucial mechanism is that heavy metal ions form chelating bonds with hydrogen and excess hydroxyl groups in the PVA-based hydrogel, thus, are finally removed from the water by being adsorbed. Such PVA-based double network hydrogel has good reusability as a chemical adsorbent. Moreover, it can also remove anions and cations and organic pollutants in dye wastewater. Very meaningful research results including remote liquefaction (Figure 6(a)) [127], molecular ink [128], contact lens sensor [129], and so on [130–133] are also reported. As a biocompatible polymer, PVA-based hydrogels prepared with bimetallic ions as crosslinking agents have high water retention properties, excellent mechanical strength, and self-healing properties and have also been studied for artificial skin and wearable sensor
devices (Figure 6(b)) [120, 134]. Moreover, in the aspect of anticounterfeiting, it is also reported that the self-healable PVA hydrogel can display embedded fluorescent color under ultraviolet, as shown in Figure 6(c) [135]. In addition to some of the applications mentioned above, it is also reported that PVA-based diffusion membranes can be used in many separation processes. For instance, a composite membrane prepared with PVA as a skeleton and glutaraldehyde as a cross-linking agent is used as an anion channel for the recovery of acid or alkali solutions [136], besides, interesting works such as solar water purification [137, 138], seawater desalination (Figure 6(d)) [139], and oil/water separation [140] are also reported. Most recently, biomimetic tendon materials based on PVA have also been reported, showing more application prospects of PVA [141].

4. Conclusions and Perspectives

The future design of hydrogels should have the following advantages: (1) functionalized hydrogel materials should utilize nontoxic, biodegradable macromolecules, that is, good biocompatibility and biodegradability, and hydrogels can be self-healed to extend their lifecycles; (2) for tissue engineering, the mechanical properties (such as hardness and elasticity) and structure (such as porosity and density) of the hydrogels should be highly matched with the embedded tissues; (3) the injected or implanted hydrogels could be tracked in vivo that further expanding their biomedical applications; (4) development of the multifunctional hydrogels to meet the complex biological conditions in vivo and achieving synergy. PVA hydrogels have great potential for development and intensive application prospects due to their excellent physical and chemical properties. Meanwhile, further study of PVA hydrogels should focus on structural design and modification, especially the strengthening of the long-term biocompatibility and mechanical strength of the hydrogel materials.

The improvement of the preparation and processing technology of hydrogels also played a very positive role in improving their performance. During the past decade, 3D printing technology has developed rapidly, and 3D printing devices with different principles and materials have been developed one after another. Among them, smart materials are a kind of material that has attracted much attention recently. In 2013, the importance of developing 3D printing for multifunctional intelligent, responsive materials was emphasized, and the concept of 4D printing was proposed [142]. The printed materials can change with time under certain external stimuli (temperature, light, external force, or pH), which was considered as the fourth dimension [143], and PVA hydrogels showed the potentials in 3D/4D printings for future intelligent applications [144].

With the continuous development of hydrogel design and continuous improvement, as well as the optimization of processing and molding methods, the traditional PVA hydrogel materials keep revealing more possibilities, and the future potential of PVA is enormous as illustrated in Figure 7.

Conflicts of Interest

The authors declare no conflict of interest.

Authors’ Contributions

M.W., J.B., and W. T. wrote the paper under the supervision of C.C.; and Z.D., K.S., D.L., J.Y., and S.H. revised the review paper. Menghan Wang and Jianzhong Bai contributed equally to this work.

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