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Research progress of flexible hydrogel sensor

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Abstract: With the advent of the intelligent era, the development of wearable devices has gradually attracted people's attention, and the demand for flexible sensors with the advantages of lightweight and portability has also increased significantly. The flexible sensors prepared by traditional methods have some disadvantages, such as limited ductility, poor durability, insufficient biocompatibility, weak mechanical properties, and complex manufacturing process. Compared with traditional materials, hydrogels have excellent flexibility, extensibility, fracture toughness, conductivity and biocompatibility, making them an ideal choice for flexible wearable sensors. The development of flexible hydrogel sensor is reviewed in this paper.

1. Introduction

In recent years, flexible wearable sensors have developed rapidly, and will play a critical role in the future intelligent era. [1-3] The realization of various functions of flexible sensors depends heavily on the rapid development of high-performance, multi-functional, flexible and stretchable materials.[4, 5] Among many flexible substrates, hydrogel materials have attracted the attention of researchers due to their good flexibility, elasticity and biocompatibility. Compared with traditional wearable sensors, hydrogel based sensors have significant biocompatibility, conductivity and unique mechanical properties, which are suitable candidates for monitoring human movement.

2. Properties of flexible hydrogel sensor

A major advantage of flexible hydrogel sensors is that they can closely fit with soft and irregular surfaces such as human skin. [6] The adhesive hydrogel has excellent interface compatibility, which can greatly reduce the human discomfort and monitor various movements of the human body. To adapt to the harsh environment, self-healing flexible hydrogel has been introduced into flexible sensor. [7-10] In order to improve the portability of wearable sensors, researchers have developed self powered sensors without external power supply. In this review, we generally summarize some recent developments of adhesive, self-healing and self powered hydrogel sensors.

2.1. Adhesive hydrogel sensor

The adhesion of hydrogel plays a key role in improving the accuracy of monitoring results. Zeng et al. [11] fabricated a multifunctional dual-network hydrogel consisted of chitosan, polyacrylic acid

(PAA), aluminum trichloride ($AlCl_3$) and glycerol. A part of polar groups of chitosan form a large number of hydrogen bond interactions with acrylic acid (AA). [12-13] The remaining polar groups provided outstanding adhesion performance for hydrogels to bond human skin. Al^{3+} linked chitosan and AA through coordination, which endow conductivity and improve the mechanical properties of hydrogel. The glycerol in the system ensured freezing resistance and low temperature conductivity(-20 ℃), so that the strain sensor could monitor both large human motions and subtle motions in a low-temperature environment. This hydrogel sensor had a good application prospect in monitoring human motion in harsh environments.

Wei et al. [14] reported a double network multi-functional hydrogel prepared by photoinitiated free radical copolymerization of dopamine methacrylamide (DMA), methacryloyl ethyl trimethylammonium chloride (DMC) and acrylic acid (AA). The chemical crosslinking of monomer with N, N-methylenebisacrylamide (MBA) forms the main hydrogel network and endows the hydrogel with rigidity. The hydrogen bond, cation-π interaction, π-π interaction and electrostatic interaction between molecules together constitute the physical crosslinking of hydrogel and provide toughness. The introduction of natural cellulose nanofiber (CNF) has greatly improved the tensile strength and elongation of the hydrogel. The presence of DMA endows the hydrogel with extensive adhesion to various surfaces. The wearable skin sensor based on hydrogel has high sensitivity and good reliability which could recognize human motions precisely in real time. The double network multi-functional hydrogel with the above advantages has potential application prospects in the field of wearable devices.

Shen et al. [15] reported an advanced hydrogel-based I-skin by free radical polymerization of N-acryloyl phenylalanine (APA) and acrylic acid (AA) in the presence of ferric chloride ($FeCl_3$). APA promotes formation of multiple hydrogen-bonding interactions. The coordination interaction between Fe^{3+} and carboxylic groups endowed the hydrogel with excellent mechanical properties (elongation 1100%, tensile strength 400 kPa). The P (AA-APA)-Fe^{3+} hydrogel also maintained excellent adhesion with a wide range of materials such as metal, glass, rubber, wood and human skin. Moreover, the hydrogels present impressive sensing sensitivity (GF up to 7.95 within 500% strain), wide sensing range (2.5–300%) and ultra-durability, which could be used to detect human movements of different intensities (e.g., joints flexion, walking on the ground, swallowing, speaking and even eye rotation) . This research has broad application prospects in the field of wearable electronic devices and implanted devices.

2.2. Self-healing hydrogel sensor

Flexible sensors are easily damaged when applied in harsh environments, so it is necessary to develop a self-healing hydrogel sensor. Tao et al. [16] designed a conductive polyvinyl alcohol (PVA)/Starch//tea polyphenol (TP)/Borax/MWCNTs (multi-walled carbon nanotubes)/ethylene glycol (EG) organohydrogel as a strain sensor with exhibit unique characteristic. The organohydrogel was physically crosslinked by borate ester bonds and multiple dynamic non-covalent hydrogen bonds among various hydroxyl groups from PVA, starch, TP and EG. Due to borate ester bonds and hydrogen bonds, organohydrogel exhibited excellent self-healing property,and self-healing efficiency reached 96.07% in 90 s at -20 ℃. The organohydrogel was assembled into a wearable strain sensor can stably monitor large-scale human motion such as joint bending and walking, but also accurately capture subtle motion changes such as chewing and swallowing. Moreover, the wearable strain sensor also exhibited stable sensing behaviors.

Hou et al. [17] successfully prepared ohPEI (polyethyleneimine)/PVA-based hydrogels with ultrafast self-healing ability, adhesion and conductivity. 3, 5-Dicarboxyphenylboronic sodium (DCBS) was introduced into the covalent network of PEI and PVA as a supramolecular cross-linker.

The formation of fluorescent polymer clusters promotes the hydrogelation to constitute a dual network. Hydrogen bonding, electrostatic interaction and borate ester bonds endow the DN hydrogel with instant self-healing ability (98% healing efficiency within 60 s) and reversible adhesive ability. The wearable sensor assembled with the hydrogel could monitor both large human movements such as joint bending and even tiny motions such as heartbeat and pulse. In addition, the hydrogel also has the ability to selectively adsorb acetone gas, the adsorption capacity is 4.75 g/g and exhibited outstanding stability.

2.3. Self-powered hydrogel sensor

The design of self-powered sensing system can effectively improve the portability of wearable sensors. Liu et al. [18] innovatively constructed an alkaline hydrogel electrolyte (PVA/Sulf-CMC/KOH) based on polyvinyl alcohol (PVA) and sulfonated cellulose (Sulf-CMC). Sulf-CMC provides abundant channels for rapid ion migration, with ion conductivity up to 15.03 S m^{-1}. As cathode material, poly (3, 4-propylenedioxythiophene) (PProDOT)/NiS2@hollow carbon spheres (NiS2@HCS) composite presents a very high specific capacity (728C g^{-1}, 1 A/g). The quasi-solid supercapacitor assembled by activated carbon (AC), PProDOT/NiS2@HCS and PVA/Sulf-CMC/KOH hydrogel electrolyte displays excellent energy density (54.57 Wh kg^{-1}), power density (5142 W kg^{-1}) and cycle stability (93.29% of the capacitance retained after 12000 cycles, 2A/g). The self-powered sensor assembled by combining quasi-solid capacitor and hydrogel electrolyte can monitor the motions of fingers, wrist and back of hands. Therefore, the PVA/Sulf-CMC/KOH self-powered sensor have application prospect in flexible electronics.

Li et al. [19] synthesized CMC (carboxymethyl cellulose)-PANI (polyaniline)/PEI (polyethyleneimine)/PAAM (polyacrylamide) hydrogel by two-step method. First, PANI was prepared by lotion polymerization in the presence of CMC. Then, the CMC-PANI dispersion, monomer, initiator and crosslinker were mixed homogeneously, and the precursor solution was thermally initiated to form the interpenetrating dual network. CMC promotes PANI nano filler dispersion in the hydrogel. With the optimum mass loading of PANI, the specific capacity, energy density and power density of the CMC-PANI/PEI/PAAM supercapacitor are up to 679 mF/cm^2, 58.82 μWh/cm^2 and 14.69 mW/cm^2 respectively. PEI with good flexibility improves the tensile and recovery properties of the dual network hydrogel. Significantly, a self-powered sensing system with high sensitivity was obtained by connecting the super capacitor and strain/pressure sensor made of hydrogels, which can monitor bending of fingers and wrists in real time without external power supply.

In addition to supercapacitor, primary battery can also be used as the energy storage part of self-powered sensing system. Ma et al. [20] successfully prepared a natural high-amylose starch based biodegradable hydrogel in the presence of $CaCl_2$ and glycerol. The introduction of glycerol could coordinate the hydrogen bond interaction between starch molecules and endow the hydrogel with self-healability, and antifreezing ability. The pressure sensitive Zn–Cu battery based on this hydrogel has a voltage of 0.81V. The Zn–Cu battery could be used as a compression sensor with excellent sensitivity (1.5371 kPa^{-1}), which can even record weak compressive stress such as wrist pulse. The above-mentioned results indicate that the hydrogel has great potential for application in human health monitoring.

3. Conclusions

This paper summarizes the research progress of adhesive hydrogel sensors, self-healing hydrogel sensors and self-powered hydrogel sensors in recent year. Hydrogels with various functions greatly expand the application range of flexible sensors. Although some research achievements have been

made in the preparation of high-performance flexible sensors, there are still many problems to be solved. For example, dehydration of hydrogel in dry air leads to unstable sensing performance, the large measuring range and small deformation sensitivity of strain sensor cannot be guaranteed at the same time. More attention should be paid to the development of new packaging materials and new structures to remedy the defects.

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