Application of biopolymer materials and polymer-based photoelectric materials

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Abstract. Due to the excellent physical and chemical properties of polymers, a diverse of different functional polymer materials have been widely used in our daily life. As a new type of material, functional polymer materials can be able to play a significant role in the progress of science and technology. In addition, functional polymer materials are closely related to many everyday products in our daily life. Leaving the traditional polymer materials will bring a lot of inconvenience to our life. Recently, functional polymer materials, which have become hot spots, have concentrated various research achievements in various disciplines and fields. At the same time, they have the characteristics of polymer materials and functional materials, and play an important role in specific fields. Among these functional polymer materials, biopolymer materials are widely used in the medical field, which is helpful to prolong the life of patients, improve human health and improve the quality of human life. Polymer-based photoelectric materials are mainly used in the fields of automobile power and folding mobile phones, and the mass production of photovoltaic solar materials has become a new hot spot. As a result, this research will mainly introduce the main application status and future development trend of biopolymer materials and polymer-based photoelectric materials.

Keywords: Polymer, Biopolymer materials, Photoelectric materials, Application.

1. Introduction

Polymer is a kind of material based on high molecular weight compounds-polymer compounds, which includes such traditional polymer materials as rubber, plastic and fiber, as well as polymer composite materials, polymer biomedical materials, polymer functional materials and other emerging materials. Generally, polymers are covalently bonded to each other through thousands of atoms, thus forming organic compounds with extremely high relative molecular weight and many repeating structural units. When the atoms are connected into a long chain, this polymer is called a linear polymer. When these atoms are connected into a network, these polymers are generally not planar structures but three-dimensional structures, so they are also called bulk polymers [1].

Functional material refers to the material that has a specific function through the action of light, electricity, magnetism, heat, chemistry or biochemistry. These functional materials hold a diverse of various functionalities, such as electrochemical properties and magnetic responsiveness. Compared with common structural materials, these materials generally have other functional characteristics besides mechanical properties. Typical functional materials are practical superconducting materials such as NbTi and Nb3Sn. After breaking through the temperature barrier, superconductor materials are no longer limited to ultra-low temperature materials, and some high-temperature oxide superconductors emerge. Solar cell material is a hot spot in the research and development of new energy materials, and the research of solid oxide fuel cell is very active. The focus is on battery materials, such as solid electrolyte membrane and cathode materials, development of new and efficient functional battery materials is still research hotspots. In addition, the research on functional materials such as bioactive ceramics and medical composite biomaterials is also very active. It can be seen that the development of functional materials is very promising.

Functional polymer materials synthesized from polymers generally have many advantages, such as chemical stability and light-responsive properties, but they are prone to stress relaxation and creep [2]. For example, although most functional polymer materials are chemical inert and have good
corrosion resistance, their surface still need to be treated in the bonding process. Polymer usually has the characteristics of low density, high resistivity and low melting point. Some functional polymer materials are easy to absorb infrared rays, visible rays and ultraviolet rays and degrade. The disadvantage of polymers is that they are obviously not aging-resistant, and they usually have strong limitations in high-temperature performance. Coating the polymer surface is difficult, and there are many limitations on the strength of polymer materials. Traditional polymer materials, such as rubber, fiber and plastic, are widely used in our daily life. They can be used to make clothes out of fiber, tires out of rubber and containers out of plastic. It can be said that without these polymer materials, there would be no such beautiful world as ours today.

The research of functional polymer materials began in 1960s, and the discovery of photoelectric polymer can be said to open the door of the new century. For the most common polymer polyethylene, it is known that polyethylene contains a large number of σ bonds, so polyethylene is a common organic insulator. But for polycetylene, a large π bond is formed in polycetylene, which makes polycetylene have weak conductivity. Masaaki Shirakawa and McDiarmid won the Nobel Prize in Chemistry in 2000 for this discovery. The conjugated double bonds and triple bonds of organic semiconductors have delocalized free electrons, which can also form energy band structures similar to those of inorganic semiconductors. Compared with inorganic photoelectric materials, the manufacturing cost of polymer photoelectric materials is much lower than that of materials represented by silicon. Even less than one tenth of the cost. The processing conditions of photoelectric materials are usually direct printing at room temperature. However, silicon needs to be prepared by multi-step lithography in an ultra-clean room. Photoelectric materials can be prepared into large-area uniform thin films by low-cost solution processing. In addition, polymer functional materials are also used for energy sources, such as organic solar cells that are characterized by all-solid, clear quality, solution processing, flexibility and translucency. Compared with inorganic silicon solar cells which absorb light and produce electron-hole pairs with low binding energy, organic solar cells absorb light and produce excitons with high binding energy [3].

Generally speaking, functional polymer materials almost completely inherit some common characteristics of polymer materials. The appearance and preparation of functional polymer materials are just to make up for the deficiency of some inorganic functional materials or reduce the cost of materials. Functional polymer materials are gradually integrated into all aspects of our lives. To this end, this study will mainly introduce the application of two typical functional polymer materials, including biopolymer materials and polymer-based photoelectric materials.

2. Application of biopolymer materials

2.1. The introduction of biopolymer materials

Biopolymer materials have broad application prospects in the diagnosis, treatment and prevention of diseases, as well as the replacement, repair and regeneration of human tissues and organs. It is an international frontier research field of materials science, chemistry, biomedicine, clinical medicine and other disciplines, and has high basic and applied research value [4]. The application of different biopolymer materials can create huge economic and social benefits, such as medical devices (including surgical sutures, artificial blood vessels, contact lenses, vascular stents, artificial joints, hemodialysis membranes, etc.), biological tissue engineering, in vivo and in vitro diagnosis, targeted release and drug sustained release, protein sustained and release gene release, etc. In addition, these biopolymer materials are usually used in the diagnosis and treatment of physiological system diseases. They can be used to repair or replace tissues or organs of organisms, and promote the function and functional recovery of human organs.

Because the research of biopolymer materials involves many fields such as materials, chemistry, biology and life sciences. For example, based on biomaterial hydrogel scaffold, it can be used as a delivery carrier for siRNA and transplanted cell groups [5]. Its application advantages are obvious, so it has developed rapidly in recent years. Many biopolymer materials can be implanted or coated
on the body surface, and act on human tissues in some way. Modern bioengineering technology has pushed the development and exploration of biopolymer materials to a new space. Because of the excellent physical and chemical properties, biopolymer materials are gradually gaining attention. Biopolymer materials can repair body tissues and even replace some body tissues. It can be polymerized to prepare biopolymer materials with special functions, which is an important this material. And biopolymer materials can be also used as an implant material for a long time, which is convenient for disinfection and sterilization, so it has been widely concerned by people. Up to now, more than 100 kinds of biomedical polymer materials have been widely used in the world.

2.2. Classification and application of biopolymer materials

Biopolymer materials include natural biomaterials and synthetic biomaterials. Among them, natural biomaterials refer to natural active polymers extracted from animals that already exist in nature. Because they come from living organisms, they have good biological applicability, and some of them can accelerate wound healing, and show strong advantages. Their performance is generally better than that of synthetic materials. The research of synthetic biopolymer materials began in the 1940s. The first gums were made of methyl acrylate, followed by silicone rubber. People have changed from looking for synthetic materials to actively creating new materials conducive to the regeneration of human tissues and organs. Biopolymer materials have entered a new stage of development [6]. Materials prepared by combining living tissues with artificial materials can better promote cell division and growth, and provide support for the recovery of tissues and organs. Although biopolymer materials have many excellent properties, they still have many limitations in practical applications. In order to improve its performance and meet the increasing demand, it is necessary to modify biopolymer materials.

Figure 1. Application of the polymer replica nanoparticles for template removal [7]

At present, biomaterials have been extensively modified in terms of biocompatibility, biodegradability, temperature responsiveness, pH responsiveness, magnetic responsiveness, hydrophilicity and crystallinity. For example, for the development of safety perfume, the main modification methods are copolymerization, blending, small molecule modification and branched structure modification. The specific research methods need to be continuously improved according
to the actual application, such as the improvement of hydrophilicity. Nanocellulose, as a new functional polymer material, contains a lot of hydroxyl groups in its structure. Therefore, it has excellent hydrophilicity and can be used to modify polymers with poor water solubility or water dispersibility. In addition, regarding the influence of pH, the application of biopolymer materials in drug release and molecular imaging can be more extensive and effective through pH responsive modification. Drug delivery system needs to make use of the difference between tumor microenvironment and normal tissues to intelligently release drugs to the target of tumor cells. For example, the temperature of tumor microenvironment is relatively high, the enzyme system is special and the pH value is low.

Caruso et al. used polymer replica nanoparticles to evaluate the effect of surface modification on nanomaterial bio interactions [7], as shown in Figure 1. The results show that PEG-modified nanoparticles exhibit the best stealth performance, and PMA-modified nanoparticles have the highest cell binding. This work provides a new insight into the choice of polymer nanoparticles for biological applications. To realize the practicality of biopolymer materials, Yu et al. synthesized a high-strength, high-toughness, high-stretch, energy-dissipative biopolymer material, that is, biomimetic hydrogel fiber (BHF) [8]. As shown in Figure 2, their results show that the BHF is highly resistant to stretching and its strength value can reach ~ 83 MPa., relying on self-dependent plastic deformation and local failure. In addition, if the BHF is used in surgery, the risk of cutting the skin of delicate wounds and secondary injuries is avoided.

![Figure 1. Polymer replica nanoparticles](image)

Figure 2. Application performance of the prepared BHF [8]

As shown in Figure 3, Pei et al. prepared a polyrotaxane-alginate double-network hydrogel [9]. Due to the unique dual network structure, the prepared hydrogel has excellent stretchability and toughness. The fracture energy of the used hydrogel can be up to 215±25 J/m$^2$, 219±20 J/m$^2$ and 140±28 J/m$^2$, respectively, under different experimental conditions. In addition, the prepared biopolymer material holds a good biocompatibility, allowing it to use in artificial small-diameter blood vessels.
3. Application of polymer-based photoelectric materials

Photoelectric materials are the material basis for the development of information high technology. And polymer-based photoelectric materials have the characteristics of both conductive polymer and luminescent polymer. They not only have the electronic characteristics of metal or semiconductor, but also are easier to process than metal or crystalline semiconductor, which brings hope for cheap processing of electronic devices. More importantly, polymer-based photoelectric materials that can be treated in solution can be used as electronic “ink”. Combination with traditional printing technology (inkjet printing, offset printing, etc.), this will completely change the manufacture of electronic devices, and some applications requiring special mechanical properties (such as flexible devices) can also be realized. Because of these special advantages, both domestic and foreign academic and industrial circles are increasing their investment in this field, which makes organic electronics develop rapidly [10].

Since the advent of polymer light emitting diodes in 1990s, the synthetic chemistry of conjugated polymers has attracted more and more attention of material scientists. At the same time, organic chemists have developed various efficient carbon-carbon coupling methods [11], such as cross-coupling reactions. These reactions were then applied to the synthesis of conjugated polymers, and gradually became the main synthesis methods of conjugated polymers. Although the synthetic chemistry of conjugated polymers is becoming more and more mature, there is still a big gap in structure control compared with traditional polymers, such as controllability of polymer molecular weight and distribution of important structural parameters, toxicity of metal catalysts, structural defects (including terminal groups, conformation/configuration isomerism, etc.). The free rotation of the trapezoidal photoelectric polymer around the main chain is locked. Therefore, molecules have greater
rigidity and better conjugation. However, the synthesis of trapezoidal photoelectric polymers requires a large number of intramolecular cyclization reactions, which is very easy to produce structural defects, showing the behavior that electrons and excited states are controlled by defects. The synthesis of classical trapezoidal conjugated polymers includes three main processes: the reaction of aryl lithium with ester group to obtain tertiary alcohol, the synthesis of polystyrene precursor polymer with ester group, and the intramolecular cyclization catalyzed by Lewis’s acid. Among them, the reaction between lithium reagent and ester group easily leads to the appearance of non-closed loop defect structure, and the emission peak of about 530 nm often appears in the fluorescence spectrum of trapezoidal polystyrene film, which is generally considered as the emission of aggregates. Low energy emission comes from defects (fluorenones) rather than chain aggregation. Ladder polymer is usually synthesized from amino-containing precursors and ketones by intramolecular Schiff base formation, but this synthesis method has great limitations.

The discovery of conductive polymer broke through the traditional idea that polymer is an insulator. Common conductive polymers include conductive polyvinyl acetylene, polypyrrole, polyaniline and polythiophene. As early as the early 1980s, the research of polyacetylene made great progress. Among them, conductive polyacetylene is unstable in air, and the doped oxidation states of conductive polypyrrole and polyaniline have good stability, so they become the main research objects of conductive polymers. The research of conductive polypyrrole began, and a series of important research results were obtained in the electrochemical preparation and electrochemical properties of conductive polypyrrole. Polyaniline is an important conductive polymer material. The early synthesis and application of polyaniline can be traced back to the mid-19th century. By the now, polyaniline is often used in combination with graphene [12].

In 1970s, the discovery of conductive polymer opened up a new research field of photoelectric polymer. Compared with traditional inorganic semiconductor materials, photoelectric polymer materials have a series of advantages, such as easy adjustment and control of properties, good mechanical properties, low price and convenient processing [13]. This has aroused widespread concern in academia and industry. The excellent photoelectric properties of photoelectrochemicals can be realized by adjusting the intra-chain interaction, chain arrangement, disorder degree, conjugate length and so on. Functional polymer materials are incompatible with traditional inorganic semiconductor integration methods, which is one of the challenges to promote the industrial application of polymer integrated optoelectronic devices. Therefore, the precise and controllable processing of polymer materials, especially on the micro-nano scale has become the core problem of its application from synthetic production to real large-scale production of optoelectronic devices. Here are some methods of polymer patterning.

Photolithography is a method of transferring the pattern to the substrate by etching, which has the advantages of high throughput and high precision [14]. This process usually involves coating the liquid photoresist on the silicon substrate, and then “baking” the substrate to remove the solvent in the resist and improve the adhesion of the substrate. After that, the photoresist film is selectively exposed to light irradiation, and a series of reactions induced by light change the physical and chemical properties of the exposed position.
Figure 4. Performance of the used polymer-based photoelectric responsive device [15]

Moulding is a relatively simple patterning method, which has the advantage that it can directly deform the material, and the resolution can break through the traditional light diffraction limit. The feature of mold induction method is that the pattern is reproduced by means of the mold, and the interaction between the mold and the controlled material layer plays an important role in the mold induction method. For polymer materials, because the lateral diffusion of macromolecules is restrained, it is easier to obtain high-resolution patterns when processing and preparing with molds. According to the hardness of the mold, the mold induction methods can be divided into hard mold method (molding method, nano-imprint method) and soft mold method (soft imprint method).

Shen et al. prepared a bionic artificial retina (BAR) based on folate-functionalized photoelectric responsive polymer microarray [15]. As shown in Figure 4, the prepared polymer-based photoelectric responsive microarray shows the outstanding photoelectric properties, where exists a good linear relationship between irradiation intensity and the applied voltage. In addition, the developed polymer-
based photoelectric device exhibits a fast response to light at on/off frequencies of 5 Hz and 10 Hz. Relying on the excellent photoelectric response characteristics, this polymer-based photoelectric device has great application potential in the fields of artificial intelligence and biomedicine.

4. Conclusions

The excellent performance of functional polymer materials can bring a qualitative leap in all fields, create huge economic value in all walks of life, and promote the emergence of new products. Functional polymer materials have strong mechanical properties and other advantages and characteristics, and can be widely popularized and applied in the development of modern industry. In this research, two classes of typical functional polymer materials, biopolymer materials and polymer-based photoelectric materials, are introduced. Moreover, their synthesis methods and application status are systematically analyzed, which is expected to provide a new idea for the preparation and application of new functional polymer materials.

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