

Preparation Methods of Polypyrrole Nanocomposites and Analysis of Their Advantages and Disadvantages

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Abstract: In recent years, nanocomposites have attracted more and more attention due to their excellent properties. This material has good physical properties such as mechanics and optics, as well as good chemical properties such as catalytic activity. Its biocompatibility and photothermal conversion performance have also attracted much attention. The nanocomposite polypyrrole has a large specific capacitance, high conductivity, and good biocompatibility, which makes it widely used in electrochemistry and biomedicine. This article summarizes the development process of polypyrrole, introduces five polypyrrole nanocomposites and their common preparation methods, and combines the literature on the use of polypyrrole in biomedicine in recent years to analyze the huge uses of polypyrrole nanocomposites in biomedicine and other fields. Finally, the opportunities and challenges for the future development of polypyrrole nanocomposites are prospected, which has guiding significance for the future growth and application of polypyrrole composites.

Keywords: Polypyrrole, Nanocomposite, Biomedicine, Preparation method

1. Introduction

Since the first discovery of conductive polyacetylene in the 1970s, conductive polymers (CPs) have attracted the attention of scientists due to their excellent properties. As research has shown, polypyrrole (PPy) has the advantages of large specific capacitance and high conductivity, easy synthesis, and high chemical stability. However, because conventional polypyrrole usually has deficiencies in electricity, optics, and biology, it needs to be restricted in size, and polypyrrole nanomaterials have emerged. Compared with conventional polypyrrole, the nanostructure gives it a larger specific surface area, better conductivity, and improved optical properties. In order to meet the needs of production and life, people try to compound it with more functional materials (such as carbon materials, metals, inorganic materials, other organic matter, etc.), which greatly broadens the application range of polypyrrole.

Polypyrrole nanocomposites with improved performance are widely used in electronic devices, energy storage, biomedicine, etc. According to the study of the effect of polypyrrole on the performance of silicon/graphite composite negative electrode materials for lithium-ion batteries by Wei Binglu, he found that polypyrrole film has the dual role of binder and conductive additive. After coating the polypyrrole film, the reversible specific capacity decreased slightly, and the cycle performance and conductivity were significantly improved [1]. In his study of polypyrrole nanocomposites, Ye Tian found that it has morphology-dependent photothermal effect and immune

response, and the photothermal sensitivity of PCN depends on its morphology [2]. Xuejiao Song used bovine serum albumin (BSA) as a stabilizer to prepare polypyrrole (PPy) nanoparticles in his study and proposed a fairly simple one-step method to manufacture multifunctional nanoparticles based on conjugated polymers, which is promising in cancer imaging and combined therapy [3].

This paper uses a literature review method to study the classification and preparation methods of nanocomposite polypyrrole and analyzes its application in biomedicine. The paper summarizes and compares the preparation methods of polypyrrole nanocomposites with different uses, and proposes methods to improve and enhance their photothermal effects. This paper contributes to the research on the application of polypyrrole nanocomposites in biomedicine to a certain extent, and provides ideas for the treatment of major diseases such as cancer.

2. Types of polypyrrole nanomaterials

According to the types of materials, one or more carbon materials, metal materials, inorganic non-metallic materials, and other organic materials can be combined with polypyrrole to form nanocomposites.

2.1. PPy/carbon nanocomposite materials

Since carbon-based materials have a large specific surface area and good mechanical and optical properties, the composite of carbon-based materials and polypyrrole can greatly improve the optical and electrical properties of PPy, and has achieved remarkable research results in the fields of supercapacitors, sensors, gas sensors, etc.

Carbon nanotubes (CNTs) have good chemical and thermal stability, good electrical properties and efficient adsorption performance. Zhimin Wang et al. successfully prepared a composite material (PPy/F-MWCNTs) of polypyrrole (PPy) wrapped with acid-treated multi-walled carbon nanotubes (F-MWCNTs) by in-situ chemical oxidation polymerization. The specific surface area of PPy/F-MWCNTs is nearly 3 times higher than that of a single polypyrrole. The gas sensor based on PPy/F-MWCNTs has higher sensitivity to NH_3 at room temperature than single polypyrrole and carbon nanotubes, shorter response time and better stability [4].

2.2. PPy/organic nanocomposites

Haixia Su et al. used ferric chloride (FeCl_3) as an oxidant and sodium p-toluenesulfonate (TSANa) as a dopant to cause pyrrole (Py) to undergo an oxidative polymerization reaction between the interlayers of organic montmorillonite (OMMT) modified with an organic intercalating agent, and prepared a polypyrrole/organic montmorillonite (PPy/OMMT) nanocomposite with good conductivity. The results showed that the organic montmorillonite OMMT-O modified with octadecyltrimethylammonium chloride (OTAC) as an intercalating agent, the molar ratio of FeCl_3 to Py was 2.14, the mass ratio of Py to OMMT-O was 0.24, the concentration of TSANa was $0.023 \text{ g}\cdot\text{ml}^{-1}$, and the conductivity of the obtained PPy/OMMT-O nanocomposite reached $3.07 \text{ S}\cdot\text{cm}^{-1}$ at 20°C for 6 hours. XRD tests showed that PPy had been intercalated into the montmorillonite layer during the formation of the composite material [5]. It can be seen that the composite of organic materials and PPy helps to improve the defects of unstable conductivity and poor processing performance of polypyrrole, and can replace traditional carbon-based or metal conductive materials to prepare coatings, adhesives, sealants, etc. with antistatic functions.

2.3. PPy multi-component nanocomposites

PPy ternary composite nanomaterials combine the advantages of many materials and become the most common type of PPy nanocomposites. Shi Li et al. used silver nitrate as an oxidant to initiate the chemical in-situ polymerization of pyrrole monomers on a graphite carrier. At the same time, silver nitrate was reduced to silver particles and doped in polypyrrole to prepare a graphite composite material with graphite as the core and silver-doped polypyrrole coated with graphite [6]. Studies have shown that there are certain interactions between polypyrrole and graphite in the composite material, which helps to improve the thermal stability of the composite material; the conductivity of the composite material can reach $18.037\text{S}\cdot\text{cm}^{-1}$. It can be seen that the method of preparing composite materials by combining polypyrrole with metal particles and carbon materials not only solves the processing problem of the material, but also improves the conductive properties of the material to a certain extent.

3. Preparation method of polypyrrole nanocomposite materials

3.1. Electrochemical synthesis method

The reaction product of electrochemical polymerization is a highly conductive active film attached to the electrode surface, with a high yield and an effective yield close to 100%. The polymer film of the target product can be directly obtained, and the film thickness is uniform and controllable. Polymer films with different functions can also be prepared by changing the conditions during synthesis. The preparation process of this method is relatively simple and easy to operate. Because different properties of polymer films can be directly obtained with high reproducibility, this method is widely used in the field of electrochemistry.

Shewei Yang et al. fixed graphene oxide (GO), transition metal Co and polypyrrole (PPy) on the surface of a carbon felt electrode in one step by the constant potential method, prepared a composite membrane electrode, and used cyclic voltammetry and electrochemical impedance spectroscopy to electrochemically test the composite electrode, and used it as the anode and cathode of a microbial fuel cell (MFC). The results show that after the surface of carbon felt electrode is modified, the electrode of the carbon felt electrode is significantly enlarged under the synergistic effect of the three. This modification effectively increases the specific surface area and conductivity of the electrode, reduces the charge transfer impedance, and improves the electron transfer efficiency of the electrode. At the same time, this electrode has good biocompatibility and stability [7].

3.2. Chemical oxidation method

The chemical oxidation method is to add an oxidant to the corresponding reaction solution. While completing the doping process, the monomer to be polymerized directly undergoes a polymerization reaction to form a polymer. The oxidant added in this process will have a certain effect on the polymerization reaction. This method can synthesize almost all composite materials, has a wide range of applications, and has a low preparation cost and is easy to industrialize. The conductivity and stability of PPy powder prepared by chemical oxidation are significantly improved. However, there are still problems in forming a PPy film or coating on another material.

Chang'e Zhu et al. prepared conductive polypyrrole powder by carbon black adsorption and pyrrole chemical oxidation polymerization process. Its physical properties are significantly improved, which is suitable for the preparation of polypyrrole composite positive electrode film, so that lithium/polypyrrole secondary batteries have good performance. The addition of conductive carbon black not only improves the conductivity of the material from the original $6.52\text{S}/\text{cm}$ to $13.42\text{S}/\text{cm}$,

but also increases the packing density of the material and improves the particle morphology and film processing performance of polypyrrole [8].

3.3. Template method

The template method can be divided into two categories according to the different parts of the material growth - internal template and external template. The internal template method uses the internal spatial structure of the main material as a template, and the formed guest material is contained in the interior of the main material; the external template method uses the specific external spatial structure of the main material as a template, and the formed guest material is wrapped around the outside of the main material. Finally, the template is removed to obtain a nanostructure with a similar shape and size to the template.

Wenguang Li used various soft and hard templates as morphology inducers and dopants, and adopted a chemical oxidation method to prepare ordered polypyrrole nanowires (tubes), particles and materials with special morphology. He studied the influence of preparation conditions on the morphology, conductivity, thermal stability and other related properties of polypyrrole. The experimental results show that surfactants play a dual role of soft template and dopant in the process of oxidative polymerization to prepare polypyrrole. In addition to the oxidative polymerization of conductive polypyrrole, oxidants also play the role of dopants. The two together determine the morphology and properties of conductive polypyrrole and its composite materials [9].

4. Application of polypyrrole nanocomposites in biomedicine

In recent years, polypyrrole nanomaterials have been widely used in biomedicine due to their inherent biocompatibility, easy synthesis, low cost, excellent redox properties and special photothermal conversion performance. For example, PPy conductive hydrogel combines the good biocompatibility, porous three-dimensional structure, high water content and extracellular matrix-like properties of hydrogel with the excellent electrical properties of PPy conductive polymer, and is used in skin damage repair, nerve repair, myocardial repair and flexible sensing [10]. This paper will analyze polypyrrole nanocomposites from three aspects: photothermal therapy, antibacterial application and drug release.

4.1. Photothermal therapy

Xuejiao Song et al. prepared polypyrrole (PPy) nanoparticles using bovine serum albumin (BSA) as a stabilizer [11]. If pre-conjugated with the photosensitizer dihydrochlorin e6 (Ce6), it can provide additional functions in imaging and treatment. The resulting PPy@BSA-Ce6 nanoparticles have low dark toxicity to cells and can trigger photodynamic therapy (PDT) and photothermal therapy (PTT). As a fluorescent molecule that can form a chelate with Gd^{3+} , Ce6 in PPy@BSA-Ce6 nanoparticles can achieve dual-mode fluorescence and magnetic resonance (MR) imaging after being labeled with Gd^{3+} , indicating that these nanoparticles have strong tumor uptake ability after intravenous injection into tumor-bearing mice. Then, after systemic administration of PPy@BSA-Ce6, combined PDT and PTT treatment in vivo was performed, and the synergistic treatment effect was better than that of PDT or PTT treatment alone. They proposed a fairly simple one-step method to fabricate multifunctional nanoparticles based on conjugated polymers, which is promising in cancer imaging and combined therapy.

4.2. Antibacterial Applications

In recent years, the application of PPy nanocomposites in antibacterial applications has attracted much attention. Xiaoxi Liang et al. prepared copper-doped zinc oxide/polypyrrole (CZ/PPy) nanocomposites by in situ polymerization in a CTAB/n-hexane/n-butanol/water (W/O) quaternary reverse microemulsion system, namely a series of $\text{Cu}_{0.5}\text{Zn}_{0.95}\text{O}$ /polypyrrole nanocomposites (CZ/PPy) with core-shell structures [12]. The results showed that PPy had weak antibacterial properties, and the antibacterial properties of CZ/PPy composites were significantly enhanced compared with those of CZ, and the antibacterial properties of the composites gradually increased with the increase of CZ content. The results showed that the antibacterial activity of the samples against *Candida albicans* and *Staphylococcus aureus* was much better than that against *Escherichia coli*. This is due to the different cell walls and cell membrane structures. The cell wall of *Staphylococcus aureus* has a mesh-like peptidoglycan structure (containing 90% peptidoglycan and 10% teichoic acid), which has a smaller blocking effect on antibacterial drugs, while *Escherichia coli* has a special lipid bilayer structure, which has a stronger blocking and resistance effect on antibacterial drugs. This shows that the CZ/PPy complex is one of the excellent antibacterial agents with great potential application prospects. Similarly, Long Mao et al. used Fe^{3+} to initiate the oxidation reaction of pyrrole (Py) on the surface of layered dihydroxy metal oxides (LDHs) to form polypyrrole (PPy)-coated LDHs (LDHs@PPy); using LDHs@PPy and polycaprolactone (PCL) as raw materials, the solution casting method was used to prepare LDHs@PPy/PCL nanocomposite films [13]. The results showed that the antibacterial rate of LDHs@PPy against *Escherichia coli* and *Staphylococcus aureus* reached 99.7%, and it had good interfacial compatibility with the substrate PCL, and also had a heterogeneous nucleation effect in the substrate. The study used surface organic coating PPy to increase the interfacial compatibility and bonding between LDHs and the substrate PCL, ultimately improving the barrier and mechanical properties of the nanocomposite while giving the composite film antibacterial properties, expanding the application of layered clay/biobased polymer composites in the field of active packaging.

4.3. Drug release

The use of PPy nanocomposites for drug release has many advantages, such as convenient drug loading, little effect of the drug loading system on the activity of the drug itself, and controllable drug release rate. Xinhao Zhang et al. used a chitosan and sodium alginate (CS-Alg) gel network as carriers and introduced polypyrrole (PPy) into it by in situ oxidation to prepare PPy/CS-Alg composite sustained-release materials [14]. The microstructure, structural composition, and photothermal conversion properties of the composite were studied by SEM, FTIR, XPS, and UV-vis-NIR, and its sustained-release properties were studied using indoleacetic acid (IBA) as a model drug molecule. The experimental results show that the porous microstructure of PPy/CS-Alg microspheres is conducive to the loading and release of IBA. The oxidized PPy formed by in-situ oxidation can be slowly reduced in the CS-Alg gel network and change from a positively charged state to an uncharged state. The change in the charged state can promote the slow release of IBA from the gel network of PPy/CS-Alg microspheres, and the long-term release rate can reach 56.12%. In addition, based on the photothermal effect of PPy, the temperature of PPy/CS-Alg microspheres can rise from 26°C to 39°C under simulated sunlight, which is conducive to the formation of a temperature gradient from the inside to the outside of the microspheres, further enhancing the sustained release ability of IBA.

5. Conclusion

This paper focuses on the types and preparation methods of polypyrrole nanocomposites, as well as their applications in medical treatment, emphasizing their great significance for medical treatment,

and providing help and ideas for the treatment of diseases such as cancer. However, since this paper did not conduct an investigation, the research is not comprehensive enough. In the future, we will continue to study convenient and economical preparation methods to prepare polypyrrole nanocomposites with more optimized and comprehensive functions, continue to optimize the performance of PPy nanocomposites, and improve their feasibility for disease treatment.

Although polypyrrole nanocomposites have shown excellent prospects in biocompatibility and photothermal conversion performance, there is still a long way to go before polypyrrole can be used in clinical practice. For example, the preparation method of polypyrrole nanomaterials is costly, the conditions are harsh, and mass production is impossible; the metabolic pathway and metabolic cycle of polypyrrole in the body are not yet fully understood, and its biocompatibility needs to be further confirmed. Therefore, it is necessary to have a deep understanding of it, optimize and improve its performance, and reduce harm.

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