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Research Progress on Silver Nanoparticle-Based Multi-Responsive Composite Hydrogels

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Abstract: Hydrogels are gels that form a network structure in water-based solvents. Under environmental stimuli, hydrogels can exhibit responsive behaviors. Due to their unique properties, hydrogels have significant potential in drug delivery and chemical separation. By combining different methods for the integration of smart polymers and metal nanoparticles, it is possible to reduce metal ions, thereby enhancing the potential of the material. This review analyzes the silver nanoparticle-loaded multi-responsive composite hydrogels, discussing the properties and classifications of these composite hydrogels. The findings suggest that such materials show promise for applications in catalysis and biomedicine.

1. Introduction

Traditional hydrogels have certain limitations, such as poor mechanical properties and slow response speeds, which directly hinder their prospects as new materials[1]. By incorporating silver nanoparticles into the hydrogel matrix, it is possible to impart new and unique properties to the gel, which has become a current research hotspot. For this composite system, changes in medium ionic strength and biological substance concentrations enable rapid responses. This review summarizes the applications of various hydrogels and provides corresponding perspectives for future development[2].

2. Nanocomposite Hydrogels Research

Hydrogels, as highly water-absorbent materials and soft tissue fillers for surgical applications, are currently used in various fields such as hygiene, biomedicine, and construction[3]. Typically, hydrogels are composed of chemically crosslinked polyelectrolyte networks, with overall fracture toughness values ranging from 10 to 100 J/m^2, which limits their practical application[4].

Nanomaterials, due to their unique properties, hold significant potential in fields like electronics and optics. Nanocomposite hydrogels, which disperse nanoparticles at the nanoscale, not only retain the intrinsic characteristics of nanomaterials but also combine their rigidity and stability. These hydrogels represent a promising material with stable future prospects.

2.1. Classification of Composite Hydrogels

2.1.1 Based on Micro/Nano Structures

Currently, composite hydrogels can be categorized based on micro/nano structures, with core-shell composite hydrogels being a prominent type. These hydrogels typically involve encapsulating polymers within different types of polymers. The research group led by Xie introduced a novel hydrogel system, where a non-crosslinked polymer (P) is used to synthesize a hydrogel with a crosslinked shell. Another approach involves using composite hydrogels for precipitation, where silver nanoparticles (AgNPs) aggregate on the surface of the core, forming a polymer network. The AgNPs adhere to the surface of the hydrogel, and the overall surface coverage depends on the charge density of the hydrogel[5].

2.1.2 Based on Responsive Behaviors

Based on their responsive behaviors, AgNPs hydrogels can be categorized into temperature-responsive, ion-responsive, and multi-responsive composite hydrogels. Temperature-responsive composite hydrogels change their volume rate with variations in the surrounding temperature. At a certain temperature, the volume of the composite hydrogel continuously alters. As the glucose concentration in the medium changes, the hydrodynamic radius of the composite system also increases gradually. pH-responsive composite hydrogels are influenced by changes in the pH of the medium, causing significant changes in their hydrodynamic radius. The hydrogel’s liquid volume increases as the hydrodynamic radius expands. For ionic strength in the medium, composite hydrogels can produce responses to the objects within the medium[6].

2.2Properties of Composite Hydrogels

2.2.1 Properties Based on Hydrogel Network

Hydrogels exhibit specific properties due to the monomers present in the network structure, which are influenced by particular functional groups. The properties of composite hydrogels can be described as follows: within the hydrogel network, there are temperature-sensitive units that change in response to temperature variations. This change is primarily driven by the pH of the medium and the medium's properties. Synthesis of various acrylic acids has shown that changes in ion monomer content affect the pH sensitivity of the mixed system, which in turn depends on the ion monomers of the hydrogel. Due to the variation in ion monomer content, the mixed system's sensitivity to pH changes differs. Hydrogels with phenylboronic acid-functionalized polymers, in particular, are now being applied for glucose-responsive behavior, where they maintain a balanced charge state[7]. At temperatures of 20 ℃ and 40 ℃, the pH of the medium has a noticeable effect on the mixed system. At lower pH values, folded hydrogels generate electrostatic repulsion. Changes in ionic strength in the medium can lead to stimuli-induced responses in composite hydrogels, making them highly sensitive to various environmental factors and stimuli[8].

2.2.2 Properties of AgNPs

Silver nanoparticles (AgNPs), as plasmonic nanomaterials, undergo surface plasmon oscillations and interact with the surrounding electric field and electrons at specific energies. Under external stimuli, composite hydrogels swell when the pH of the medium decreases. As the pH increases, the swelling behavior is primarily influenced by factors such as refractive index and the distance between particles. The application of composite hydrogels has gradually expanded across various fields, with a growing focus on the stability of hydrogels. As a stable material, hydrogels utilize the electronic acceptor properties between AgNPs, and currently, the interaction of these two factors is crucial for maintaining the stability of the hydrogel[9].

3. Functional Properties of Nanocomposite Hydrogels

3.1. Mechanical Properties

Nanoparticles incorporated into the gel structure form a network that differs from the traditional hydrogel network. Observations using techniques like light scattering and small-angle neutron scattering reveal the presence of structural correlation lengths within the gel. The small-scale correlation length is related to the chemical crosslinking structure, while the large-scale correlation length typically ranges from 200 to 250 nm, contributing to the mechanical properties of the gel formation.

3.2. Electrical Response Performance

Hydrogel systems based on electrolyte monomers exhibit a certain level of responsiveness. Studies have shown that while nanoparticles have minimal impact on the overall electrical performance of the gel, they do influence the electrical conductivity. Under the influence of an electric field, ions in the solution move in a directional manner, leading to a concentration imbalance of ions across the gel. As the electric field strength increases, the response time of the hydrogel becomes faster[10].

3.3. Magnetic Sensitivity

Magnetic-field-responsive smart molecules are primarily composed of three-dimensional networks and magnetic fluids. Through the interaction between magnetic fluids and polymer chains, sensitive molecular gels can be achieved by adjusting fluid content and crosslinking density. Studies on the changes in gel behavior within magnetic fields show that the gel can undergo various motions when the magnetic field gradient is appropriately adjusted[11].

3.4. Other Properties

Gels can be synthesized via redox reactions at room temperature. When the temperature exceeds the phase transition temperature, the crystal packing degree increases, resulting in a continual transformation of the gel’s transparency. Nanogels also exhibit bioactivity in cartilage interfaces, allowing them to penetrate into the deeper layers of cartilage[12].

4. Application Effects of Silver Nanoparticle-Loaded Composite Hydrogels

4.1. Antibacterial Effect

Compared to bulk silver, silver nanoparticles (AgNPs) embedded in a porous hydrogel network exhibit superior antibacterial effects. The ability of AgNPs to penetrate bacterial membranes and interact with DNA receptors plays a key role in their antibacterial activity. AgNPs are effective against Escherichia coli and Staphylococcus epidermidis, killing bacteria by disrupting their cellular integrity. Preparation involves treating the hydrogel with triethylamine to introduce amino groups, followed by reduction with a reducing agent to synthesize the hydrogel[13]. When compared to Staphylococcus aureus, Pseudomonas aeruginosa has a thinner cell wall, allowing AgNPs to diffuse more effectively and kill the bacterial cells. Additionally, AgNPs coated on plastic surfaces prevent bacterial attack, particularly inhibiting the growth of E. coli. The antimicrobial activity is further enhanced by increasing the coating thickness, which helps to prevent degradation.

4.2. Environmental Applications

Composite hydrogels are effective for wastewater treatment. In the composite of poly-silver and nanoparticles, a porous network is formed within the hydrogel, which helps remove pollutants from wastewater. Furthermore, this composite material can act as a catalyst, promoting the degradation of contaminants and facilitating environmental cleanup[14].

4.3. Catalytic Activity

Due to their large surface area, AgNPs catalyze both organic and inorganic reactions. However, aggregation of the nanoparticles can reduce their surface area, leading to decreased catalytic activity. To optimize catalysis, it is essential to stabilize AgNPs with surface-active agents; however, these stabilizing agents are generally unsuitable for use as catalysts. In catalytic processes, the presence of stabilizing agents can lead to poisoning and contamination[15]. Compared to other catalytic systems, hydrogels provide certain advantages for AgNPs stabilization. AgNPs in hydrogels can be regulated by external stimuli, and their catalytic activity can be monitored using simple physical methods for separation. In the case of AgNPs-loaded hydrogels, they are commonly used as catalysts for various reactions, with monitoring via spectrophotometry under ultraviolet light. In aqueous media, reduction reactions are modeled to observe swelling behaviors of the hydrogel with temperature changes. When the temperature exceeds 25℃, the reduction activity increases with rising temperature. However, as the network contracts, the reactants face difficulty reaching the active sites, slowing the diffusion rate and decreasing the catalytic efficiency[16].

5. Conclusion

Nanogels are typically composed of hydrogel particles formed through physical or chemical crosslinking. As nanoscale water dispersions, nanogels can be categorized into chemical and physical gels based on the types of chemical bonds involved. Nanogels offer high overall stability as drug delivery carriers. Due to their high water content and swelling state, nanogels can enhance bioavailability in systemic drug delivery applications[17]. This review analyzed the silver nanoparticle-loaded composite hydrogels, demonstrating their applications in response to stimuli such as temperature and pH. Further research is needed to refine the application of these composite systems. The preparation of AgNPs with specific optical properties is particularly important. The porous networks formed by AgNPs and hydrogels show great potential in various fields, including environmental and pharmaceutical applications.

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