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Research Progress of Nanomaterials As Food Packaging Materials

Zixuan Guo[1,a,*]

[1]*School of Light Industry Science and Engineering, Sichuan University, Sichuan, 610065, China*
a. guozixuan@stu.scu.edu.cn
**corresponding author*

Abstract: This paper reviews the research progress on nanomaterials used as food packaging materials, focusing on their structural and functional characteristics. The study initially discusses the properties of organic nanomaterials, such as nanocellulose, and inorganic nanomaterials, including nano metal oxides and nano silicon dioxide, emphasizing how their unique properties differentiate them from conventional packaging materials. Nanomaterials exhibit superior mechanical strength, barrier properties, antibacterial activity, and environmental friendliness compared to traditional petroleum-based packaging, which is challenging to degrade and environmentally polluting. Organic nanomaterials, such as nanocellulose, have demonstrated particular promise for enhancing food quality and safety, while inorganic options provide additional stability and durability. Despite these advantages, nanomaterial applications in food packaging raise potential toxicological concerns and environmental health risks that require further investigation and regulation. Technical and cost-related challenges also remain as barriers to their widespread adoption.

Keywords: Nanocellulose, inorganic nanomaterials, antibacterial effect, food packaging

1. Introduction

Environmental issues and food quality and safety have attracted widespread social attention in recent years. Traditional food packaging is dominated by petroleum-based materials [1], which are chemically stable and difficult to degrade naturally, and can cause significant pollution to the natural environment. Traditional material waste disposal is very environmentally unfriendly, not only will cause pollution to the environment, but also in the economy will cause losses. The function of traditional materials is simple, cannot meet the special needs of today's food preservation, as well as people's higher requirements for food preservation time [2]. With the research on nanomaterials, they began to be gradually applied to food packaging. Nanoparticles can be divided into two categories according to the raw materials, organic nanomaterials: nanocellulose, nanostarch, nanoprotein, etc., and inorganic nanomaterials: nano-metal oxides, nanoclay, non-metallic nano-oxides, etc. [3]. Nano packaging materials have unique properties that are different from traditional packaging materials mainly because the original packaging materials are synthesized and modified by nanotechnology, and have properties that are different from the original materials such as nanoparticle interfacial effect and quantum effect [4]. Nanomaterials are bio-based biodegradable packaging materials, which can be a good solution to the environmental pollution problems of traditional packaging materials [5]. At the same time, the mechanical strength, antibacterial activity, high barrier property, high gloss and

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transparency, and intelligent indication of nanomaterials are better than traditional packaging materials [6], which make up for the shortcomings of traditional packaging materials such as poor antibacterial performance, poor UV resistance, and poor mechanical properties. Although nanomaterials have advantages different from those of traditional packaging materials, some countries and organizations have put forward restrictions or warnings on the use of nanomaterials due to the fact that a large number of studies and experiments have shown that it will migrate after being applied to food packaging materials [7], and there are potential health and safety hazards [8].

Although there have been research reports on the application of nanomaterials in packaging, there are fewer summaries of the different types of nanomaterials, their own structures and their applications in food packaging. Therefore, this paper focuses on the types and basic structures of organic and inorganic nano-nano-materials and their applications in packaging, research progress, and safety issues of nanomaterials applications, with an emphasis on the structure of nanocellulose and its applications in food packaging. Through the review of related literature, the research progress of nanomaterials as food packaging is clearly explained, with the aim that this paper contributes to the subsequent research in related fields.

2. Types and basic nature of organic nanomaterials

2.1. Nanocellulose

Cellulose, as one of the most abundant renewable natural polymers in nature, is mainly derived from renewable resources such as wood, bagasse, straw, cotton stalks, corn stover, and grain hulls, and also includes cellulose acetate, bacterial cellulose, and carboxymethyl cellulose [9]. These cellulosic materials are able to be processed down to the nanometer level to form nanocellulose divided into cellulose nanocrystals (CNCs), cellulose nanofibers (CNFs),bacterial nanocellulose (BNCs). CNCs are short, nanoscale rod-like microfibers derived from plant fibers, which are typically no longer than 500 nm in length and between 3 and 50 nm in width, and have a high elastic modulus of 130 to 150 GPa [10]. CNFs, on the other hand, are fine filamentary nanocellulose extracted from plant fibers with lengths exceeding 500 nm and diameters less than 100 nm, exhibiting high aspect ratios [10]. These two types of nanocellulose materials offer a wide range of potential applications in materials science and engineering due to their unique size and morphology.

Nanocellulose is a natural polymer material with a nanoscale structure, which is transformed into a single linear fiber with a diameter of less than 100 nm by a special treatment. Despite the change in its microscopic size, its basic properties are similar to those of ordinary cellulose. This material is insoluble in ordinary water or organic solvents at room temperature, and its thermal stability is affected by factors such as size, crystallinity, degree of polymerization, and type of moiety, and it will be rapidly thermally degraded when the temperature exceeds 220 °C [10]. Nanocellulose, due to its nanoscale size and abundant hydroxyl functional groups, exhibits unique physical and chemical properties. These hydroxyl groups not only give nanocellulose a large specific surface area but also enable nanocellulose to build a three-dimensional network of cross-linked structures due to their ability to form hydrogen bonds. This structure gives nanocellulose excellent barrier properties, as its hydrogen bonding interactions can form a fine membrane that effectively prevents the penetration of substances [9].

Nanocellulose comes from a variety of sources, including cellulose in plant cell walls and metabolites produced by certain bacteria such as Acetobacter saccharolyticus, Rhodobacter erythropolis, and Acetobacter xylosus in the growth process. Due to its excellent mechanical properties, barrier ability, biocompatibility and degradability, nanocellulose has received a great deal of attention from researchers around the world.

2.2. Other organic nanomaterials

2.2.1. Nanostarch

Starch, as a very common type of carbohydrate in our daily diet, provides important energy to the human body. It is abundant in many foods, such as potatoes, corn, rice, and chestnuts. Nanostarch, on the other hand, specifically refers to those starch granules with particle sizes between 1 and 1,000 nanometers, usually not exceeding 300 nanometers. These tiny starch granules have some remarkable characteristics: they are insoluble in water, can shape food products well, are light in color, have a large specific surface area, contain a large number of hydroxyl groups on the surface, and exhibit typical rheological behavior [11]. These properties make nanostarch have great potential for application in food processing and improvement.

Nanostarch is mainly categorized into two main groups: starch nanocrystals (SNCs) and starch nanoparticles (SNPs). Their preparation methods and properties are different:

SNCs are obtained by hydrolyzing the amorphous regions of starch granules, preserving the crystalline regions of the starch and therefore having a high degree of crystallinity. The preparation of SNC usually involves acidic hydrolysis, a process that selectively erodes the amorphous regions leaving behind particles of the crystalline regions, resulting in nanocrystals with high degree of crystallinity [12].

SNPs are prepared from gelatinized starch and may contain both crystalline and amorphous regions, thus their crystallinity is generally lower than that of SNC. Methods for the preparation of SNP include physical methods (e.g., ultrasonic treatment, high pressure homogenization), chemical methods (e.g., acid hydrolysis), enzymatic methods, and combinations of these methods [12].

The crystal structure of starch nanoparticles is related to the crystal type of the original starch. For example, A-, B-, and C-type crystal structures are common in starch, whereas V-type crystal structures may occur in complexes formed by starch with lipids. The properties of starch nanoparticles, such as morphology, size distribution, crystallinity and thermal properties, can be affected by the preparation method and the source of raw materials.

2.2.2. Chitosan nanoparticles (CSNPs)

CSNPs are nanofillers with excellent antimicrobial and antioxidant properties, and they can be prepared by a variety of synthetic methods including sodium tripolyphosphate cross-linking, microemulsions, precipitation, co-precipitation, anticolloid micelles, self-assembly, nano-spray drying, supercritical fluids, electrospraying, and emulsification [13]. The application of these nanoparticles in food packaging materials can effectively enhance the antimicrobial properties of the materials, especially against both Gram-positive and Gram-negative bacteria showing significant inhibitory effects [13].

3. Types and basic properties of inorganic nanomaterials

3.1. Metal oxide nanomaterials

Zinc oxide (ZnO), often referred to as zinc white in its white powder form, is not readily soluble in water but is soluble in acidic or alkaline solutions. When the particle size of zinc oxides is reduced to the nanometer level, i.e., zinc oxide nanoparticles (ZnONPs) are formed, they are transformed into a material with a wide range of excellent properties [14]. ZnO nanoparticles showed susceptibility to both Gram-positive (e.g., Staphylococcus aureus S. aureus) and Gram-negative bacteria (e.g., Escherichia coli E. coli) [2]. Although scientists have not yet fully revealed the principle of ZnO's antimicrobial action, it is known that in the presence of ultraviolet light, ZnO releases an abundance

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of hydrogen peroxide, which causes oxidative damage to bacterial cells. Some studies have shown that ZnO ions play a key inhibitory role in controlling bacterial reproduction, rather than acting by directly killing the bacteria [2].

On the other hand, magnetic nanoparticles (MNPs) are a class of advanced nanomaterials capable of responding to magnetic fields and exhibiting superparamagnetic properties. These particles are capable of concentrating and localizing in the presence of a magnetic field or generating heat by absorbing electromagnetic waves in an alternating magnetic field (AMF) [14]. These nanomaterials possess a unique set of physicochemical properties, such as excellent chemical stability, good photostability, high electrochemical coupling coefficient, and the ability to absorb and disperse ultraviolet light.

As an emerging antimicrobial material, the nanomorphology of metal oxides exhibits a wide range of antimicrobial activities and possesses efficient and long-lasting antimicrobial efficacy. In particular, nanomorphs of titanium dioxide (TiO2 NPs) have attracted attention for their excellent photocatalytic properties and chemical resistance [15]. Researchers such as Díaz-Visurraga found that a complex combining titanium dioxide nanoparticles with chitosan effectively inhibited the growth of Escherichia coli and gram-negative bacteria and that the composite prevented the breakdown of chitosan [15]. Meanwhile, the nanoforms of ZnONPs also showed remarkable antimicrobial effects, in addition to their ability to withstand extreme temperatures and pressures and maintain good stability. These nanosized metal oxides not only excel in the antimicrobial field but also show great potential in several industrial applications due to their resistance to high heat and pressure.

3.2. Nano-silica

Due to its large specific surface area and porous structure, nano-silica exhibits excellent adsorption properties, which makes it often used as an anti-caking agent for powdered foodstuffs to minimize the caking phenomenon of foodstuffs. However, the application of nanosilica as an anti-caking agent for food salt is somewhat limited due to its water-insoluble property [2].

Thanks to its high specific surface area, stability, low toxicity, excellent insulating properties and good thermal conductivity, nano-silica has become a preferred material in food packaging materials. Research by Mallakpour and Nazari, developed an easy and fast method to synthesize polymer-based nanocomposite membranes based on polyvinyl alcohol (PVA) and silica using ultrasound-assisted casting technique. It was shown that the solubility of silica can be significantly reduced by surface modification, which may help to improve its biocompatibility in food packaging [2]. In addition, nanosilica can be compounded with other materials, such as polylactic acid, to form nanocomposite packaging materials with better performance [16].

3.3. Other inorganic nanomaterials

Thanks to their outstanding physicochemical properties, such as large specific surface area, excellent mechanical strength and good thermal stability, carbon nanotubes play an important role in enhancing the mechanical and thermal properties of conventional plastics. The ability of these nanotubes to be uniformly dispersed in the polymer matrix of thermoplastics significantly enhances the thermal and mechanical properties of the materials by tuning the fluidity of the plastic molecules and the relaxation properties of the polymers. Moreover, the high specific surface area and activity of carbon nanotubes provide additional advantages in material modification [2].

4. Current status of nanomaterials in the field of packaging

4.1. Applications

4.1.1. Applications of nanocellulose in packaging

Nanocellulose has become increasingly useful in the food packaging industry, not only thanks to its rich source and safety, but also because of its unique structural properties. Thanks to its large specific surface area and numerous hydroxyl groups, nanocellulose is able to build three-dimensional network structures that form dense films through hydrogen bonding, demonstrating excellent oxygen and water vapor barrier capabilities [9]. In one study, Trifol et al. fabricated films by combining cellulose nanofibers (CNFs) and lignocellulose nanofibers (LCNFs), with lignin as the linking material, and showed that the composite films outperformed those using CNFs or LCNFs alone in reducing water vapor and oxygen permeation [17]. Another study was conducted by Naidu et al. who added cellulose nanofibers (CNF) to a mixture of xylan and sodium alginate to prepare a novel film that showed lower permeability than conventional films in blocking water vapor transmission [18].

In addition, nanocellulose, as a reinforcing component in composites, can effectively enhance the mechanical properties of packaging materials and provide excellent barrier effects. It can also be used to make packaging materials that are directly edible, and some of the products have antimicrobial properties [9]. In Dai et al.'s study, they used sodium alginate and cellulose nanofibers as the substrate, incorporated thymol and catechol-rich peanut red skin extract, and through the cross-linking of calcium ions (Ca2+), they successfully developed a new antimicrobial composite film named SCCP-4, which showed significant inhibition effects on several major foodborne pathogens: Salmonella typhimurium The inhibition efficiency reached 94.48% against Salmonella typhimurium, 93.38% against Staphylococcus aureus, 79.88% against Escherichia coli, and 71.50% against Listeria monocytogenes. In the experiment, when the SCCP-4 film was applied to the surface of fruits, the formation of bacterial communities was not detected on the surface of the fruits even after seven days, which confirms that the SCCP-4 film has an excellent antimicrobial performance, which can effectively prolong the freshness period of the fruits and delay the spoilage process [19].

When nanocellulose is used as a component of the food surface coating, it also significantly enhances the wettability of the coating. Due to its excellent compatibility and environmental protection properties, nanocellulose has a promising application in food packaging with significant market potential.

4.1.2. Application of nano-TiO2 in packaging

Nano TiO2 has a great potential for application in food packaging, including the enhancement of UV shielding performance, antimicrobial performance, ethylene scavenging ability, barrier performance, and smart response properties of packaging materials, thus enhancing the freshness and safety of food products [1].

UV shielding performance: Dash et al. aimed to investigate the UV shielding efficacy of titanium dioxide (TiO2)-enhanced nanostructured starch-pectin matrix films, which is important for the prevention of UV-induced oxidization and deterioration of food products. In the experiments, the transmittance of TiO2-doped starch-pectin films doped with nanoTiO2 was measured in the wavelength range of 200 to 800 nm using a UV-visible spectrophotometer. The film samples used for the experiments were all of uniform thickness, were cut and fixed in the measurement cell for testing, and the experiments were performed using a blank test cell as a control. The results showed that the transmittance of pure starch-pectin films without added TiO2 was only 2% in the ultraviolet region (200-400 nm) and gradually increased to 5-25% in the visible region (400-800 nm). Whereas, with the addition of TiO2 nanoparticles, the transmittance of the films decreased significantly, from

8% to 4% in the visible region, as the TiO2 concentration increased from 0.5% to 2%. The transmittance of the films at all TiO2 concentrations was below 2% in the UV region, showing the excellent absorption and scattering ability of these films for both visible and UV light. In summary, the introduction of nano TiO2 significantly enhanced the UV shielding properties of the films, making them a potential food-grade UV shielding packaging material that effectively protects food from UV damage [20].

Antimicrobial properties: In the study of Yan Xingmei et al. an edible composite film liquid was successfully prepared by combining gellan gum, black rice anthocyanin and titanium dioxide (TiO2) nanoparticles. The study delved into the inhibitory effect of the composite membrane on common food-borne microorganisms, including Staphylococcus aureus (S. aureus), Escherichia coli (E. coli) and baker's yeast (Saccharomyces cerevisiae). The experimental results showed that the gellan gum-black rice anthocyanin-TiO2 composite membrane exhibited significant antimicrobial activity, with inhibition zones of 4.14 mm, 2.77 mm, and 3.55 mm against the above microorganisms, respectively. These data indicate that the composite membrane was particularly effective in inhibiting Gram-positive bacteria, and exhibited greater antimicrobial capacity compared to Gram-negative bacteria and fungi. Therefore, this study concluded that the gellan gum-black rice anthocyanin-TiO2 composite film has practical applications as a potential antimicrobial packaging material [1].

4.2. Research progress

In the food industry, nanoscale materials have been widely adopted for their ability to impart a wide range of properties to food products, which include improving the sensory experience, flavor, color, and texture, as well as prolonging the shelf life and enhancing the nutritional value. Organic nanomaterials, with their natural properties, safety and non-toxicity, are commonly used in food composition modification to optimize the structural and nutritional composition of food products or as substitutes for certain ingredients. Inorganic nanomaterials, on the other hand, are mainly used as micronutrient supplements and food preservation additives to extend the shelf life of food products due to their excellent antimicrobial and anticorrosive properties as well as their unique elemental composition. In addition, certain inorganic nanomaterials are capable of improving the appearance and enhancing the attractiveness of food products [11].

4.3. Problems

Although the application of nanomaterials in food packaging brings significant effects such as freshness preservation, antibacterial and barrier, their safety issues cannot be ignored. First of all, nanoparticles are prone to migrate from packaging materials to food due to their special properties, and this migration may pose a threat to food safety. The extent of migration is affected by a variety of factors, including the properties of the food, temperature, contact time and plastic material. Secondly, nanoparticles may also be toxic to the reproductive system and are able to pass the placenta-blood barrier to affect the normal growth and development of the fetus, e.g., nanoTiO2 and nanoSiO2 can reduce the sperm count and survival rate of rats at certain doses. In addition, nanoparticles may cause oxidative damage and inflammatory reactions in tissues and organs, leading to cellular dysfunction. Nanoparticles, when ingested through the oral cavity, may accumulate and produce neurotoxicity in brain tissues, causing apoptosis, which is one of the main mechanisms of their material toxicity. Moreover, the toxic effects of nanoparticles are also related to their size and encapsulation materials, and different sizes of nanoparticles have different effects on cells, which may enhance the release rate of lactate dehydrogenase, change the permeability of cell membranes, and cause damage to cell membranes. Therefore, although nanomaterials have demonstrated their

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unique advantages in food packaging, more in-depth studies on their potential toxicity and migration issues are needed to ensure their safe application [21].

5. Conclusion

This paper focuses on the research progress of nanomaterials as food packaging materials. The paper first explores the characteristics of nanocellulose and other organic nanomaterials in terms of structure and properties. Secondly this paper describes the structure and properties of nano metal oxides, nano silicon dioxide and other inorganic nanomaterials. After discussing their properties, the paper then goes on to explain in detail the properties that differentiate them from conventional packaging materials in food packaging and the reasons why they have such properties. Finally, it is shown that the use of nanomaterials in food packaging still has potential toxicological issues that need to continue to be investigated and addressed. This paper reveals that nanomaterials show great potential for application in food packaging due to their unique physical, chemical and biological properties. They have high specific surface area, excellent mechanical properties and chemical stability, as well as good biocompatibility and environmental friendliness. However, research on nanomaterials still faces environmental health risks, technical challenges and cost issues that need to be further overcome. This paper does not cover the types of nanomaterials comprehensively enough to give a complete picture of the properties of each nanomaterial and their applications in food packaging. It is hoped that future research will contribute to nanomaterials in future research.

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