

Active Packaging

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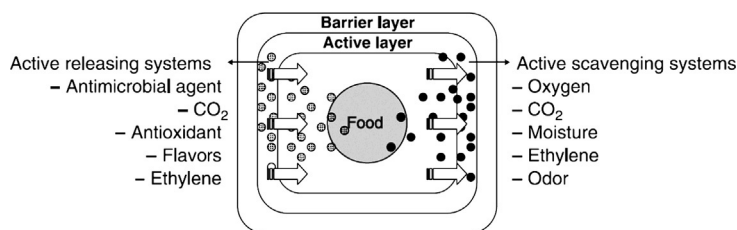
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7.1 INTRODUCTION

The traditional role of a food packaging is rather passive: protecting the food from any spoilage by acting as a physical barrier between the food product and external conditions. Over the last decades, however, consumers demand in high-quality, additive-free, nonprocessed or minimally processed and safe foods which still have an acceptable shelf life has highly increased. As a response to this need, the protective function of a packaging has been advanced over the last years leading to the development of innovative packaging technologies such as active packaging (AP) [1–6]. AP is defined in the European regulation (EC) No. 450/2009 as a packaging system that interacts with the food by “deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food” [7]. In this context, extraordinary, but vital functions, going beyond the simple barrier function of a packaging, can be realized leading to food products with an extended shelf life while ensuring their quality, safety, and integrity.

AP systems can be divided into active-releasing systems (emitters) adding compounds into the headspace or to the packaged food and active-scavenging systems (absorbers) removing undesired compounds from the food or its environment (Fig. 7.1).

AP systems, such as oxygen, moisture or ethylene absorbers and antimicrobial or carbon dioxide releasers, often come in the form of a sachet that has to be additionally added to the food packaging. Such sachets, however, have several drawbacks such as the risk of accidental breakage that could lead to involuntary consumption of the content by the consumer, the unsuitability to beverages, or the requirement of an additional packaging operation step [1,3,8]. Moreover, sachet-based applications are not well accepted by consumers in European countries, in contrast to Asia or the United States [9]. Alternatively, latest developments have aimed at directly incorporating active materials into the



■ FIG. 7.1 Active packaging systems [1].

polymer matrix of the packaging material. A big challenge in the development of such active polymer films, however, is to have high activities and capacities of active agents when being incorporated into the films as well as to preserve the initial mechanical and physical properties of the films [5,10]. Nanotechnology has the potential to overcome such challenges. The transformation of active compounds from micro to nanoscale offers a new opportunity to reduce the required amount of the active substance and may preserve the original properties of the packaging material. Furthermore, several active substances even show an enhanced activity if applied in nanoscale compared to its micro-scaled counterparts [11–14] or were even found to be active only when applied in nanoscale, such as gold [15].

In this chapter, the role of nanotechnology in active packaging is described and a wide range of nanomaterials providing active functions to food packaging are presented. Thereby, the focus is set on nanomaterials which are not “nano” by nature, such as metals and metal oxides, but are applied in nanoscale to provide/enhance active functions. Special emphasis is given to inorganic nanoparticles (NPs) expressing antimicrobial activities. The potential application of nano-carriers containing bioactive substances for antimicrobial packaging is also addressed. Furthermore, oxygen- and ethylene-scavenging systems based on active nanomaterials are presented. Special emphasis is given to publications where active packaging has been tested on food systems.

7.2 ANTIMICROBIAL PACKAGING SYSTEMS

Antimicrobial packaging systems are innovative advancements that have been designed to inhibit the growth of spoilage and pathogenic microorganisms in packaged foodstuffs and thereby reinforce, together with the physical protection, the preservative function of food packaging. Among active packaging (AP), interest in antimicrobial packaging systems has risen significantly during the last decades as it constitutes a promising complementary method to traditional preservation methods controlling undesirable microorganisms in foods [1,3,5,13].

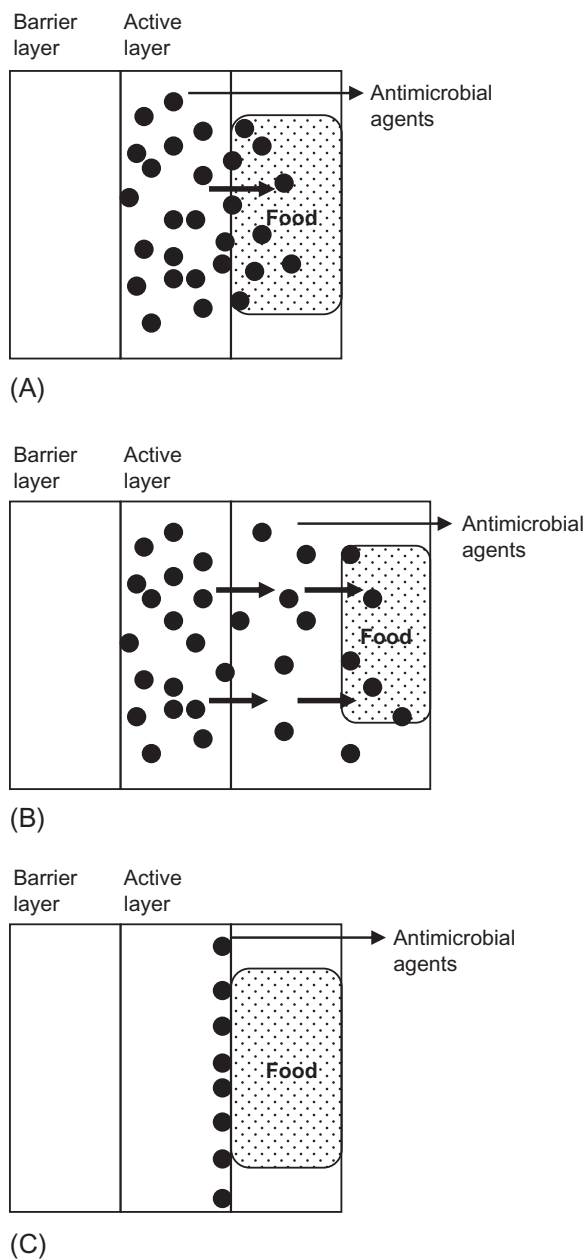
Antimicrobial activity of a packaging system can be obtained by several ways, such as by the addition of pads or sachets containing antimicrobial

volatiles; incorporation of antimicrobial agents to the packaging matrix or surface by coextrusion, immobilization, or adsorption methods; or using packaging raw materials that are inherently antimicrobial. Antimicrobial packaging systems can be categorized into three types (Fig. 7.2): (A) Systems releasing antimicrobial agents, such as organic acids, from the packaging material directly to the surface of the food where they diffuse into the food. These systems require direct food contact. (B) Systems releasing volatile antimicrobial agents, such as spice and herbs extracts, from the packaging material into the packaging headspace from where they are absorbed by the food. These systems do not require direct food contact. (C) Nonmigratory antimicrobial polymers with attached antimicrobial agent at the polymer backbone. In these systems, food contact is required as the antimicrobial agent does not intentionally migrate out. This category includes surface-modified films with antimicrobial activities or polymer films that are antimicrobial by themselves [1].

If a substance is intentionally released to the food, as it is the case for systems A) and B) earlier, it is considered as food additive and has to be declared as such [16]. Traditionally, antimicrobial substances are added directly into the food. Direct addition of such substances to the food, however, could result in an inhibition or loss of their activity due to interactions with the food matrix. Moreover, in fresh and processed food, microbial growth and food degradation mostly occurs at the surface only. Thus release of antimicrobial substances through active packaging to the surface of the product could be more effective than adding them into the whole bulk of food and may therefore decrease the amount of such substances required for the desired antimicrobial activity.

Due to its enabling nature, nanotechnology offers new possibilities to develop new antimicrobial packaging systems or to enhance antimicrobial activity of active substances. The high surface-to-volume ratio and enhanced surface activity of nano-sized antimicrobial agents may combat undesired microorganisms more effectively than their micro- or macroscale counterparts [12,14,17]. In contrast to the two latter, nanoparticles can attach to the surface of bacteria cells and thereby directly interact with them. This can cause structural changes and damage, distinctly disturbing vital cell functions, such as permeability, causing gaps and pits, suppressing enzyme activity, and finally leading to cell death [18].

Antimicrobial activity has been observed for many nanoparticles (NPs), most of all metals, such as silver (Ag) [19–21], gold (Au) [22–24], or copper (Cu) [25–27], and metal oxides, such as titanium dioxide (TiO₂) [28–30], zinc oxide (ZnO) [31–33], or magnesium oxide (MgO) [34–36]. Table 7.1 summarizes successful applications of antimicrobial food



■ **FIG. 7.2** Antimicrobial packaging systems. (A) Packaging releasing antimicrobial agent to the food; (B) packaging releasing antimicrobial agent into the headspace; (C) nonmigratory antimicrobial polymers [1].

Table 7.1 Antimicrobial Packaging Systems Containing Nanoparticles as Antimicrobial Agents

Active Substance	Packaging Material/ Medium	Microorganism	(Food) Application	Reference
Silver	Coated on PVC-PE laminate tray by inkjet printing	Total bacteria, <i>E. coli</i> , <i>S. aureus</i>	Minced beef	[21]
	Plasma-deposited PE film, acidified malt extract broth (MEB)	<i>Alicyclobacillus acidoterrestris</i>	In vitro, in vivo: apple juice	[19]
	Absorbent pad (cellulose-hybrid material)	In vitro: <i>E. coli</i> , <i>S. aureus</i> Poultry: total aerobic mesophilic and lactic acid bacteria	Poultry extrudates	[20]
	Absorbent pad (cellulose-hybrid material)	Total aerobic and lactic acid bacteria, <i>Pseudomonas</i> spp., Enterobacteriaceae	Beef meat extrudates	[37]
	Absorbent pad (cellulose-hybrid material)	Total mesophilic aerobic Bacteria, psychrotrophic microorganisms, yeasts, and molds	Fresh cut melon	[38]
	PVC film	<i>E. coli</i> , <i>S. aureus</i> , <i>B. cereus</i> , <i>P. fluorescens</i>	Chicken breast fillets	[39]
	LDPE film	Total aerobic bacteria, total yeast and molds	Fresh orange juice	[40]
	LDPE film	<i>E. coli</i> , <i>P. aeruginosa</i> , and <i>L. monocytogenes</i>	Chicken breast fillets	[41]
		<i>E. coli</i> , <i>S. typhimurium</i>	In vitro	[22]
Gold	Clinoptilolite, mordenite, and faujasite zeolites			
	Quinoa starch biofilm	<i>E. coli</i> , <i>S. aureus</i>		[24]
	Nutrient agar+ bacteriocins	<i>Micrococcus luteus</i> , <i>B. cereus</i> , <i>S. aureus</i> , <i>E. coli</i> , <i>K. pneumonia</i> , <i>Proteus mirabilis</i>		[18,23]
Copper	Chitosan film	<i>S. aureus</i> , <i>S. typhimurium</i>	In vitro	[42]
	Agar-based biofilm	<i>L. monocytogenes</i> , <i>E. coli</i>		[27]
	PLA film	In vitro: <i>Pseudomonas</i> spp.; in vivo: total mesophilic bacteria, yeast and mold	Fior di latte cheese	[26]
	Cellulose fibers	In vitro: <i>S. cerevisiae</i> In vivo: yeast and mold	Pineapple and melon juice	[25]
TiO ₂	PE film	<i>E. coli</i> , <i>S. aureus</i>	In vitro	[43]
	LDPE thin film	In vitro: <i>Pseudomonas</i> spp. and <i>Rhodotorula mucilaginosa</i> In vivo: mesophilic bacteria and yeast	In vitro: saline solution In vivo: fresh pears	[29]
	HDPE film	<i>E. coli</i> , <i>S. aureus</i>	In vitro	[44]
	Coated on oPP film	<i>E. coli</i> (in vitro and in vivo)	Fresh cut lettuce	[28]
	PET-PBS blend thin film	<i>E. coli</i> and <i>S. aureus</i>	In vitro	[30]

Continued

Table 7.1 Antimicrobial Packaging Systems Containing Nanoparticles as Antimicrobial Agents —Cont'd

Active Substance	Packaging Material/Medium	Microorganism	(Food) Application	Reference
TiO ₂ + Silver	LDPE film (+montmorillonite particles)	In vitro: <i>Botrytis cinerea</i>	Kiwifruit	[45]
	PE film (+kaolin-NPs)	In vitro: <i>Penicillium citrinum</i> (green mold)	Chinese bayberries	[46]
	PE film (+kaolin-NPs)	Visible mold growth	Strawberries, Chinese jujube (date)	[47,48]
ZnO	LDPE/LLDPE film	<i>A. flavus</i>	Rice	[49]
	HDPE film	Yeasts, molds, <i>B. subtilis</i> , <i>B. cereus</i>	Bread	[50]
	Calcium alginate film	<i>S. typhimurium</i> , <i>S. aureus</i>	Ready-to-eat poultry	[33]
	PET-PBS blend thin film	<i>E. coli</i> and <i>S. aureus</i>	In vitro	[30]
	LDPE film	<i>E. coli</i> , <i>P. aeruginosa</i> , and <i>L. monocytogenes</i>	Chicken breast fillets	[41]
	LDPE film	Total aerobic bacteria Total yeast and molds	Fresh orange juice	[40]
	Bacterial or spore suspensions in flasks	Lactic acid bacteria: <i>L. helveticus</i> , <i>L. plantarum</i> , <i>L. mesenteroides</i> ; bacterial spores: <i>Alicyclobacillus acidoterrestris</i> ; yeasts: <i>S. cerevisiae</i> , <i>C. tropicalis</i> ; fungal spores: <i>A. niger</i> , <i>P. variotii</i> , <i>Byssoschlamys</i> spp.	In vitro	[35]
	Casting bionanocomposite film: (chitosan + carboxymethyl cellulose)	<i>S. aureus</i> , <i>B. subtilis</i> , <i>B. cereus</i> , <i>P. aeruginosa</i> , <i>E. coli</i> , <i>L. monocytogenes</i> , <i>C. albicans</i> , <i>A. niger</i>	Soft white cheese	[51]
	ZnO + basil leaf essential oil	Psychrophilic and lactic acid bacteria, spoilage microorganisms	Sea bass slices	[52]
	MgO, CaO, ZnO	Lactic acid bacteria: <i>L. helveticus</i> , <i>L. plantarum</i> , <i>L. mesenteroides</i> ; bacterial spores: <i>Alicyclobacillus acidoterrestris</i> ; yeasts: <i>S. cerevisiae</i> , <i>C. tropicalis</i> ; fungal spores: <i>A. niger</i> , <i>P. variotii</i> , <i>Byssoschlamys</i> spp.	In vitro	[35]
MgO, MgO + nisin	Dispersion in glass tubes	<i>E. coli</i> O157:H7, <i>Salmonella</i> Stanley	In vitro	[36]

packaging systems where antimicrobial NPs retarded or inhibited the growth of spoilage and/or pathogenic bacteria. Apart from inorganic NPs, natural substances such as chitin/chitosan also exhibit antimicrobial activity when applied at nanoscale [51,53,54].

7.2.1 Metal Nanoparticles

7.2.1.1 Silver

Silver (Ag) has been used as an antimicrobial agent for the storage of food and beverages since ancient times and the strong antimicrobial effect of silver ions and salts is well known [15,17,55]. Despite its long history, the mechanism of antimicrobial activity of silver remains a matter of active research. In general, it can be explained that the interference of Ag ions with vital cellular processes, such as by binding to sulfhydryl or disulfide functional groups on the surfaces of membrane proteins and other enzymes; the disruption of DNA replication; and the oxidative stress through the catalysis of reactive oxygen species (ROS) formation are the main antimicrobial mechanisms [55]. However, controversy exists regarding which of these mechanisms is most important [15,17,55]. In its metal form, however, the usefulness of Ag ions and salts as antimicrobial agents is limited due to several reasons, such as interfering effects of salts in the antimicrobial mechanism, in particular the continuous release of sufficient Ag ions [15]. By the application of Ag-NPs, in contrast, such limitations can be overcome.

In medical as well as food packaging application, Ag-NPs are probably the most studied inorganic NPs and its antimicrobial activity is reported against numerous strains of bacteria, yeasts, fungi, algae, and possibly some viruses [19,20,39,50,55]. Ag-NPs incorporated into polymer matrices are a particularly attractive solution as they are chemically stable and therefore enable controlled release over long storage periods [55].

Mahdi et al. [21] investigated the antimicrobial effect of PVC-PE laminate trays which were coated with Ag-NPs by inkjet printing. The nano-Ag package was demonstrated to significantly reduce microbial growth (total bacteria counts, *Escherichia coli* and *Staphylococcus aureus*) of packaged minced beef leading to a shelf life extension from 2 days (control) to 7 days under refrigeration. In another study [19], an active PE film, where the Ag was plasma deposited in nanoscale (~90 nm) by an Ag-containing polyethyleneoxide (PEO)-like coating, was applied. The antimicrobial activity of the resulting Ag-PEO film was tested against an *Alicyclobacillus acidoterrestris* strain, a thermal and acidity resistant food spoilage bacterium, in acidified malt extract broth (MEB) as well as in apple juice. It was found that the antimicrobial activity of the active film was higher in the culture media

(MEB) than in apple juice. Based on Ag ion release tests, it was found that the efficiency of the Ag-PEO film was strictly related to the amount of Ag ions released at equilibrium, which in turn was shown to be dependent on the type of medium.

Silver-based nanomaterials have also been shown to delay microbial growth in absorbent pads of food packages. Fernández et al. [20] developed Ag-based antibacterial hybrid materials by in situ reduction of Ag nitrate adsorbed on cellulose fibers. The authors concluded that the fiber structure as well as the Ag reduction method influenced the morphology of the produced Ag-NPs and consequently their antimicrobial activity. This was demonstrated in vitro against *E. coli* and *S. aureus* where a reduction of about 4 log CFU/g was achieved. In packages containing chicken extrudates, the application of the Ag-loaded absorbent pads led to a reduction of 1.25 log CFU/g for lactic acid bacteria and 1.5–2.5 log CFU/g for mesophilic aerobic bacteria. Moreover, the application of these cellulose-Ag-NP absorbent pads was effective against aerobic and lactic acid bacteria, *Pseudomonas* spp. and Enterobacteriaceae in beef meat extrudates [37] as well as against mesophilic aerobic bacteria, psychrotrophic microorganisms, yeasts and molds in packages containing fresh cut melon [38]. Apart from the reduction of microorganisms, the ripening of the fruit was retarded leading to an improvement in visual appearance.

Azlin-Hasim et al. [39] evaluated the antimicrobial activity of Ag-NPs (in solution) against *E. coli*, *S. aureus*, *Bacillus cereus*, *Pseudomonas fluorescens* and the microflora isolated from raw chicken, raw beef, and cooked ham. They found that the Gram-negative bacteria were generally more sensitive to Ag-NPs than Gram-positive bacteria. Moreover, the microflora isolated from meat was more resistant to Ag-NPs compared to the pure culture bacteria. Highest sensitivity against Ag-NPs was observed for *P. fluorescens*. However, when the Ag-NPs were incorporated in PVC films, their antimicrobial activity was reduced. This was shown when applied to chicken breast fillets wrapped in the nanocomposite films. Although samples with the antimicrobial films retarded the lag phase of total bacteria and especially that of *P. fluorescens* (after 3 days), *P. fluorescens* was dominating after 6 days and no difference was observed between the samples wrapped in the nanocomposite film and the ones wrapped in the control PVC film. As concluded by Azlin-Hasim et al. [39], such a reduced antimicrobial activity can occur when Ag-NPs are directly inserted into polymer matrices since the majority of the NPs are not in direct contact with the food. An inhomogeneous dispersion of NPs in the film can additionally reduce the antimicrobial effect. Furthermore, food components can also affect the antimicrobial activity of the Ag-NPs, since protein functional groups

present in meat can potentially bind with Ag ions and thereby reduce the efficacy of the Ag-NPs. Such results highlight the importance of testing antimicrobial packaging not only in vitro but also in real food systems.

Ag-NPs were also applied in combination with other NPs, such as ZnO [40,41] or TiO₂ [45,47–50], that are discussed in the respective sections. Furthermore, for the combination of Ag-NPs with the bioactive polymer chitosan a cumulative antimicrobial effect is suggested [55]. The incorporation of Ag-NPs into various polymer matrices, alone or in combination with other NPs or antimicrobials, can therefore lead to an extension of the microbial shelf life of a wide range of foodstuffs.

7.2.1.2 Gold

Gold (Au)-NPs are reported to have antibacterial and antifungal activity [18,22,56,57]. To the authors' knowledge, no studies of antimicrobial packaging using gold-NPs applied to food products are available. However, several in vitro studies against foodborne pathogens have been performed. Lima et al. [22] found that gold-NPs on zeolites are excellent biocides. By dispersion of gold-NPs on different types of zeolites, best results were obtained with the faujasite zeolite where only 5%–10% of *E. coli* and *Salmonella typhi* colonies survived in culture media after 90 min. Pagno et al. [24] incorporated gold-NPs into biofilms made of quinoa starch. Besides the improvement of mechanical, optical, and morphological properties, the presence of gold-NPs in the biofilms exhibited strong antibacterial activity against foodborne pathogens showing inhibition percentages of 99% against *E. coli* and 98% against *S. aureus*. Other studies highlighted a synergistic antimicrobial effect of gold-NPs with peptides of bacteriocins produced by *Lactobacilli* as well as with the commercially available nisin, against different food-spoilage microorganisms [18,23]. Their findings revealed that the bacteriocins produced by *Lactobacilli* had more antimicrobial activity against *Micrococcus luteus* [18], *Klebsiella pneumonia*, *Proteus mirabilis* [23], *B. cereus*, *S. aureus*, and *E. coli* [18,23] when used as combination with gold-NPs than alone as well as compared to nisin combined with gold-NPs.

7.2.1.3 Copper

Copper (Cu) is a cofactor for metal-proteins and enzymes and is present in most food in the form of ions or salts [25,58]. Compared to silver, copper in bulk form shows remarkable antimicrobial properties [59–62] which are, however, lower than the potential biocidal activity of silver. Nevertheless, Cu-NPs may be preferred to Ag-NPs because of lower cost, easier mixing with polymers, and relatively more physicochemical stability [58,62].

Several studies have demonstrated the antimicrobial activity of Cu-NPs against foodborne pathogens. Cárdenas et al. [42] distributed colloidal Cu-NPs in chitosan films showing to be effective against *S. aureus* and *Salmonella typhimurium*. Shankar et al. [27] demonstrated the antimicrobial activity of environmentally friendly agar-based bionanocomposite films containing different types of copper salts. All films were shown to exhibit strong antimicrobial activity against both Gram-positive (*Listeria monocytogenes*) and Gram-negative (*E. coli*) foodborne pathogens. Cellulose/copper-composites synthesized by Llorens et al. [25] were shown to be effective in vitro against *Saccharomyces cerevisiae*. Moreover, the nanocomposite absorbent materials showed excellent antimicrobial and antifungal activity in pineapple and melon juice, reducing the loads of spoilage-related yeasts and molds about 4 log cycles. Conte et al. [26] combined the bioactivity of Cu-NPs with a biodegradable polymer matrix (PLA) providing an active packaging for fresh dairy products. The active PLA-Cu films showed delayed proliferation for *Pseudomonas* spp. (in vitro) as well as for the main spoilage microorganisms in fior di latte samples. The authors also demonstrated that the Cu-NPs did not affect the typical dairy flora preserving sensory attributes as well.

7.2.2 Metal Oxide Nanoparticles

Inorganic metal oxides such as titanium dioxide (TiO₂), zinc oxide (ZnO), or magnesium oxide (MgO) can be utilized for the production of antimicrobial packaging films. Basically, these metal oxides are used as photocatalysts deriving their catalytic activity by absorbing energy from a light source. Thereby, UV radiation leads to the generation of highly reactive oxygen species (ROS) which seems to be one of the main mechanisms of their antimicrobial activity [12,43,63]. Advantages of using inorganic oxides as antimicrobial agents can be that they contain mineral elements which are essential to humans and exhibit strong activity even when applied in small amounts [12]. Besides their strong antimicrobial activity, metal oxides have higher chemical stability than organic antimicrobial agents [64]. Generally, Gram-negative bacteria (such as *E. coli*) seem to be more resistant against metal oxide-NPs than Gram-positive bacteria (such as *S. aureus*) due to structural and polarity differences in the bacterial cell membrane [32,33].

7.2.2.1 Titanium Dioxide

Titanium dioxide (TiO₂) has attracted high attention as a photocatalytic disinfecting material in the food industry as it is inert, nontoxic, inexpensive, environmentally friendly, and has been shown to inactivate a wide variety of microorganisms in many applications [28,29,63,65,66].

Xing et al. [43] investigated the effect of TiO₂-NPs on the antibacterial properties using polyethylene (PE)-based films as matrix. They showed that the antibacterial activity to inactivate *E. coli* or *S. aureus* was significantly improved by UV irradiation resulting in an inhibition ratio of 89% for *E. coli* and 95% for *S. aureus*, respectively, compared to that of TiO₂-PE film without UV irradiation. Bodaghi et al. [29] demonstrated the photocatalytic antimicrobial effect of TiO₂-NPs incorporated in LDPE films against *Pseudomonas* spp. and *Rhodotorula mucilaginosa* (in vitro), representing the main microorganisms on fruit and vegetable crops. The effectiveness of the photocatalytic film was also proven for fruit packaging applications, showing a significant decrease in the number of mesophilic bacteria and yeast cells in packages containing fresh pears. In other studies [28,44], TiO₂-NPs were coated on the surface of packaging films. The resulting active HDPE films [44] were observed to provide a reasonable level of antibacterial activity against *E. coli* and *S. aureus* (in vitro), whereas the active oPP films [28] showed high antibacterial activity against *E. coli* in both in vitro and in food application on fresh cut lettuce.

Threepopnatkul et al. [30] compared the antibacterial properties of TiO₂ and ZnO-NPs incorporated in poly(ethylene terephthalate) (PET)/poly(butylene succinate) (PBS) blend thin films. They found that the antibacterial activity of the active films is dependent on type of filler as well as quantity and particle size of the inorganic material added to the PET/PBS thin film. Both films showed significant contribution on the inhibitory effect of *E. coli* and *S. aureus*. TiO₂-NP-containing films, however, exhibited better inhibition performance than ZnO-NP-containing films. This was explained by the fact that TiO₂-NPs were smaller than ZnO-NPs and therefore exhibiting an enhanced surface activity of antibacterial agents due to a larger surface-to-volume ratio.

Other studies investigated the combination of TiO₂-NPs and Ag-NPs. Hu et al. [45] incorporated Ag-NPs, TiO₂-NPs, and montmorillonite particles into an LDPE film and evaluated its effect on postharvest quality of kiwifruit during cold storage. Assessment of the antifungal activity of the nanocomposite-based packaging films was performed using conidial germination test of *Botrytis cinerea* (gray mold), stating one of the most common fungus on kiwifruit [45]. The obtained results demonstrated that the applied active film can effectively inhibit the germination of *B. cinerea*. Further positive effects obtained by this film are described in Section 7.4. Similarly, Li et al. [47] developed packaging films by blending polyethylene with Ag/TiO₂/kaolin nano-powder. The resulting nano-packaging films were successfully applied to inhibit mold growth of strawberries [48], Chinese jujube [47], or Chinese bayberries [46]. Moreover, Wang et al. [46]

demonstrated that a combination of nano-Ag/TiO₂/kaolin packaging films with hot air treatment resulted in a remarkably improved control of green mold (*Penicillium citrinum*) and natural decay in Chinese bayberries compared with hot air treatment or nano-package alone. Further beneficial effects of the nano-Ag/TiO₂/kaolin packaging material are described in [Section 7.4](#). Incorporation of nano-Ag/TiO₂ particles in more common polyolefin polymer matrices, such as polyethylene (PE), has also been shown to exert antimicrobial activity. Rice was inoculated with 4.84 CFU/g of *Aspergillus flavus* and packed in LDPE/LLDPE blended films containing Ag/TiO₂-NPs. Mold count increased to 5.48 CFU/g in active films compared to 7.15 CFU/g in control PE films after 35 days of storage [\[49\]](#). The application of nano-Ag/TiO₂-containing HDPE films was also shown to be effective against yeasts, molds, and bacteria in bread leading to a shelf life extension up to 6 days [\[50\]](#).

7.2.2.2 Magnesium Oxide

Magnesium oxide (MgO)-NPs were also reported to exhibit antimicrobial activity against certain vegetative bacteria [\[34,36,67\]](#) and bacteria spores [\[34,67\]](#). Moreover, the inactivation of viruses and aflatoxins has been observed when using nanoscale MgO powder possessing active forms of halogens [\[67\]](#). To the authors' knowledge, food packaging applications using MgO-NPs have not been reported in the scientific literature yet. However, few in vitro studies against foodborne pathogens have been performed using MgO-NPs alone or in combination with other antimicrobials. Thereby, it was found that MgO-NPs distort and damage the bacterial cell membrane so that intracellular contents are leaking which in turn leads to cell death [\[36\]](#).

Jin and He [\[36\]](#) demonstrated that MgO-NPs are highly effective against pathogens, achieving more than 7 log reductions in bacterial counts of *E. coli* O157:H7 and *Salmonella* Stanley. In addition, they investigated the antibacterial effect of the MgO-NPs in combination with other antimicrobials such as nisin and ZnO-NPs. Whereas by the addition of nisin a synergistic effect was observed, the combination of MgO and ZnO-NPs did not enhance the antibacterial activity against both pathogens. Other authors [\[35\]](#) investigated the antimicrobial activity of nano-assembled metallic oxides (MgO, CaO, and ZnO) against a wide range of spoilage microorganisms of fruit juices. They found that all the microorganisms tested ([Table 7.2](#)) were susceptible to at least one of the nano metal oxides clearly indicating a selective toxicity of the applied NPs. In combination, however, the authors suggested the nano metal oxides to be a promising alternative to the use of synthetic preservatives for pathogen control in fruit juices.

Table 7.2 Nano-Scaled Oxygen-Scavenging Packaging Systems

Active Substance	Package Material/Application	Potential Application/Food Tested	Reference
Iron	Fe-NPs, activated carbon, NaCl and CaCl ₂ , in sachets	Roasted sunflower seed and walnut	[11]
	HDPE and LLDPE films+ modified kaolinite	Potential for active and passive oxygen barrier	[68]
Iron-(II)-chloride and α -tocopherol	Nanoencapsulated PCL in fish gelatin film	Potential for application in retortable pouches	[69,70]
TiO ₂	Deposited on different polymer films	Potential for oxygen-scavenging packages	[71]
	Ethyl cellulose film		[72]
Palladium, platinum	FEP, PP, LLDPE, PET, nylon 6,6	Control oxygen transport through active membrane materials	[73]
Palladium	Deposited on PET film	Ham and bakery products	[74–76]
Ascorbate enzyme systems and TiO ₂ or Alumina (Al ₂ O ₃)	CaAsc/laccase, \pm oleic acid, \pm edible oils, \pm TiO ₂ -NPs, or Al ₂ O ₃ -NPs Coated or printed on PET films	Oxygen-scavenging ink formulation for the interior package surface	[77]

7.2.2.3 Zinc Oxide

In the food industry, zinc oxide (ZnO) is widely used as a supplement for zinc and it has also been incorporated into linings of food cans to prevent spoilage and preserve color. The antibacterial activity of ZnO-NP against foodborne pathogens has been thoroughly investigated [12,30,33,35,36,40,41,51]. Although the exact mechanism of the antimicrobial activity of ZnO-NPs remains unknown, the main mechanisms which have been proposed are at first, the release of antimicrobial ions, followed by an interaction of the ZnO-NPs with the microorganisms leading to a subsequent damage of the integrity of the bacterial cell as well as the formation of ROS through light radiation. In this way, ZnO-NPs can be activated by visible light or UV radiation resulting in reactive oxygen species (ROS) such as hydrogen peroxide (H₂O₂), superoxide (O₂^{•−}), or hydroxyl radicals ([•]OH) [12,32]. It has been shown that the bactericidal efficacy of ZnO-NPs (10–50nm) increases with decreasing particle size. Compared to micro-sized bulk ZnO, more ZnO-NPs are required to cover a bacterial colony (2 μ m). As a result, a larger number of ROS, released from ZnO-NPs on the surface of the colony, can be generated leading to an enhanced bactericidal activity. However, not only the higher surface-to-volume ratio of ZnO-NPs compared to micro-sized bulk ZnO, but also its rougher shape has been explained to be responsible for the enhanced bactericidal effect. Due to surface defects, ZnO-NPs are more abrasive than bulk ZnO, contributing to a greater mechanical damage of the bacterial cell membrane [12]. Additionally, synergistic effects of ZnO-NPs in

combination with other antimicrobial agents such as chitosan [51], bacteriocins [31], or other inorganic NPs [36] have been reported.

Several studies have been performed using ZnO-NPs in food packaging applications (Table 7.1). Akbar and Anal [33] loaded a calcium alginate film with ZnO-NPs (about 50 nm) and evaluated its antibacterial activity against *S. typhimurium* and *S. aureus* in ready-to-eat poultry. Thereby, the alginate-based film containing 3 mg/mL ZnO-NPs was found to be most suitable and effective for the use in active packaging. By wrapping poultry meat in the active films, challenge tests were performed at $8 \pm 1^\circ\text{C}$, resulting in a reduction of the initial number of inoculated bacteria (*S. aureus* and *S. typhimurium* 10^6 – 10^7 CFU/mL) by 2 log within the first 24 h. After 6 and 8 days of incubation, no viable cells of *S. aureus* and *S. typhimurium*, respectively, were detected whereas in poultry meat without active film no significant reduction of the inoculated bacteria was observed.

Emamifar et al. [40] prepared packages using nanocomposite LDPE films containing ZnO-NPs (0.25% or 1%, about 70 nm) or TiO₂ powder doped with Ag-NPs (1.5% or 5%, about 10 nm). The active packages were filled with fresh orange juice and had an initial microbial load of 4.9 log CFU/mL for yeasts and molds and 4.8 log CFU/mL for total aerobic bacteria. Except pouches containing 1% ZnO-NPs, all other packages kept the microbial load below the limit of microbial shelf life for fresh juice (6 log CFU/mL) during 28 days of storage. Moreover, the pouches containing 0.25% ZnO-NPs were found to have the least ascorbic acid degradation and browning development among the applied nanocomposite films. Compared to the pure LDPE control film, color loss, browning index, and ascorbic acid degradation were similar using 0.25% ZnO-NP films. However, ranking in sensory attributes (odor, taste, and overall acceptability) was significantly higher for the nanocomposite films compared to the control, and overall, it was highest for the 0.25% ZnO-NP films. Whereas the antimicrobial activity of the Ag-NP films increased by increasing the nano-Ag concentration, the opposite was observed for the ZnO-NPs. This was explained by the agglomeration of ZnO-NPs during processing of the films which increased with increasing ZnO content resulting in nanoscale aggregates up to 200 nm. Thus the results are in line with the findings of Padmavathy and Vijayaraghavan [12] that a greater particle size of ZnO-NPs decreases its antimicrobial activity.

Panea et al. [41] investigated the antimicrobial effect of the combination of ZnO-NPs and Ag-NPs in vitro and in vivo by incorporating the NPs (5 or 10 wt%, particle sizes not provided) in LDPE films. In vitro tests (5 wt% of NPs) revealed a reduction in 7.34 log CFU/cm² for *E. coli*, 6.74

logCFU/cm² for *Pseudomonas aeruginosa*, and 4.31 logCFU/cm² for *L. monocytogenes*. Packaging of chicken breasts fillets revealed that total mesophilic and Enterobacteriaceae counts were significantly higher in the LDPE control packages, after 15 days of storage at 4°C, compared to the active packages containing 5 or 10 wt% NPs. Moreover, packages containing 10 wt% NPs showed significantly lower counts of *Lactobacillus* after 21 days and also lowest total mesophilic and Enterobacteriaceae counts compared to all other samples. Thus in this application, the antimicrobial activity has been shown to be increased when increasing the amount of NPs in the nanocomposite LDPE films.

In another study [51], a casting bionanocomposite packaging film was prepared containing chitosan (CH), carboxymethyl cellulose (CMC), and ZnO-NPs. The CH/CMC/ZnO-film was evaluated for its antimicrobial activity against total bacteria, mold, yeast, and coliforms in Egyptian soft white cheese. It was shown that all of the cheese samples packed in the CH/CMC/ZnO films exhibited significantly stronger biocidal activity against Gram-positive and Gram-negative bacteria as well as mold and yeast compared to the chitosan control film (CH/CMC) leading to an increased shelf life of white soft cheese.

ZnO-NPs have also been tested in combination with essential oils which are well known for its antimicrobial effects. Thereby, Arfat et al. [52] wrapped sea bass slices in fish protein isolate/fish skin gelatin films containing 3% ZnO-NPs (20–40 nm) and basil leaf essential oil (BEO). During 12 days storage at 4°C, the fish samples wrapped in this active film resulted in lowest growth of lactic acid bacteria, psychrophilic bacteria, and spoilage microorganisms including Enterobacteriaceae, H₂S-producing bacteria, and *Pseudomonas*, compared to the BEO-containing films without ZnO-NPs, the ZnO-NP films without BEO, and the control fish protein isolate/fish skin gelatin films. Moreover, sensory evaluation of the sea bass revealed the longest shelf life for the ZnO-NP/BEO films (12 days) compared to the control (6 days). Thus the incorporation of BEO additionally provided antioxidant properties leading to a reduced lipid oxidation.

7.2.3 Bioactive Compounds

Some nanoparticles, although not having antimicrobial properties themselves, may be used as carriers of antimicrobials, especially bioactive compounds such as essential oils. They may protect food antimicrobial agents from unfavorable environmental or processing conditions as well as enable a controlled release of such substances over time [64,78].

Carbon nanotubes loaded with allyl isothiocyanate (AITC, EO occurring in mustard) and incorporated in cellulose-based films exhibited antimicrobial activity against *Salmonella choleraesuis* and reduced microbial contamination in packaged shredded cooked chicken meat [79]. Electrospinning technique was applied to produce PLA nanofibers containing a cinnamon EO/ β -cyclodextrin inclusion complex. Application of the nano-films in packaged pork meat led to a significant reduction in the growth of *E. coli* and *S. aureus* [80]. Carvacrol and thymol EOs were incorporated in LDPE/organically modified montmorillonite nanocomposite films and applied to pack strawberries inoculated with *Botrytis cinerea* (gray mold). The clay/polymer nanocomposite films could effectively inhibit the strawberry gray mold [81]. Agar-cellulose bionanocomposite films containing savory EO were shown to be effective against *L. monocytogenes*, *S. aureus*, *B. cereus*, and *E. coli* [82].

Chitosan is a natural polysaccharide, a deacetylated derivative of chitin, extracted from marine sources such as crustacean shells [54] or obtained from fungi [83,84]. It is, after cellulose, the second most abundant natural biopolymer [85]. Due to its broad applicability such as films, blends, coatings, or composites, chitosan has attracted the attention of both the scientific community and the food and packaging industry because of its nontoxicity, biocompatibility, and biodegradability. Furthermore, chitosan provides antimicrobial and antifungal activity against a wide range of foodborne pathogens; this has been thoroughly reviewed elsewhere [54,86,87]. As recently discussed by Fortunati [54], the antimicrobial effect of chitosan is still unclear to date, but several mechanisms have been proposed. According to Fortunati [54], the most widely accepted theory is based on the fact that interactions between the positively charged chitosan amine groups and the negatively charged bacterial cell membranes may lead to the leakage of low-molecular-weight materials, nucleic acids, and proteins.

It has been demonstrated that the antimicrobial effect of chitosan films was enhanced if hybrid films of the biopolymer and inorganic nano-sized clays (nanocomposite films) were produced [53,88]. Han et al. [53] prepared chitosan-montmorillonite (MMT) nanocomposites by an ion exchange reaction between water soluble oligomeric chitosan and Na^+ -MMT. Interestingly, the chitosan- Na^+ -MMT nanocomposites exhibited significantly higher antimicrobial activity against *E. coli* and *S. aureus* than it was the case for the pure chitosan and Na^+ -MMT. These results are somewhat contradictory as the positive charge of the chitosan molecules is actually neutralized through the electrostatic interaction with the anionic silicate layers of the Na^+ -MMT. Thus the observed synergistic effect in the antimicrobial activity was reasoned by the even distribution of the chitosan molecules in

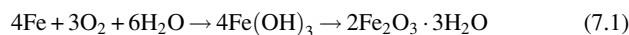
the inorganic matrix. Moreover, an enhanced thermal stability was observed for the nanocomposites. The intercalation of the biopolymer chitosan into Na^+ -MMT therefore suggests a potential application in the development of natural biopolymer-based biodegradable packaging materials with antimicrobial activity.

A further promising approach of the use of nanomaterials in bioactive packaging is offered by the nanoencapsulation of bacteriocins, such as nisin. Imran et al. [89] embedded nano-liposome-encapsulated nisin peptides (“nano” by nature) into biodegradable hydroxypropyl methylcellulose films. *in vitro* tests revealed antimicrobial activity against the foodborne pathogen *L. monocytogenes*. However, such systems are still in development state and further research is needed.

7.3 OXYGEN SCAVENGERS

Several food products are sensitive to oxygen as it can negatively affect the quality and the shelf life by oxidation of the product [90], promoting the growth of aerobic microorganisms [91,92], resulting in changes in color [93–96] or sensory properties [97–99], or causing nutritional losses [100–102]. In the food industry, oxygen-sensitive food products are packed either under MAP or using gas flushing. However, several factors such as the oxygen dissolved in the food itself being subsequently released into the headspace, oxygen permeation through the package material, insufficient evacuation during the packaging process, or poor sealing can still lead to a residual amount of oxygen in the package [3,92,96]. Therefore the application of oxygen scavengers (OS) has become one of the most important active packaging technologies as it can be used to remove oxygen from food packages as well as to improve barrier properties by acting as an active barrier [2,5,92,103].

There are several types of OS and their oxidative mode of action can be either: (a) chemical, using iron or ferrous salts [103–105], cobalt [106,107], ascorbic acid [108], gallic acid [109], photosensitive dyes [110–112], or unsaturated polymers or fatty acids [113,114]; (b) biological using immobilized yeast on a solid material [115]; or (c) biochemical through the use of enzymes [3,77,92,116,117]. Thereby, iron is the most common type of OS. Iron-based OS are activated by water and scavenge oxygen according to the following overall theoretical equations [104]:



A nano-iron-based oxygen scavenger has been developed by Mu et al. [11] (Table 7.2). Fe-NPs were mixed with activated carbon, NaCl and CaCl_2 , and filled into sachets. OS capacity of the nano-sized scavenger (110 nm average particle size) was almost 1.4 times higher compared with that of its micro-sized counterpart (about 20 μm). The authors used the nano-sized OS system to pack roasted sunflower seeds and walnuts, representing food products which are highly sensitive to lipid oxidation. Storage tests of the nuts over a period of 120 days showed that the samples containing the nano-sized oxygen scavenger possessed the lowest peroxide (PV) and p-anisidine (AnV) values in all treatments.

Busolo and Lagaron [68] evaluated a synthetic nano-iron-containing kaolinite as an oxygen scavenger additive for food packaging plastics. The corresponding polyolefin films (HDPE and LLDPE) were found to play a dual oxygen fighting role: Firstly, active performance by trapping and reacting with molecular oxygen and secondly, a passive barrier performance by imposing a more tortuous diffusion path to the permeant. Thus the authors suggest a significant potential for the use of this novel oxygen scavenger additive in food packaging applications.

Byun et al. [118] showed that α -tocopherol in combination with Fe-(II)-chloride has oxygen-scavenging capability. Thereby, oxygen free radicals were produced in the presence of a transition metal, such as iron, and were then eliminated by receiving electrons from α -tocopherol so that oxygen is successively scavenged. The authors concluded that thermal processing can accelerate this oxygen-scavenging reaction. In this context, Byun et al. [69] applied a nanoencapsulation technique to develop a heat-activated oxygen-scavenging system. Thereby, NPs of the biodegradable polyester polycaprolactone (PCL) were loaded with α -tocopherol, Fe-(II)-chloride, and water and were placed into high barrier retortable cups. The PCL coating of the NPs prevented the encapsulated α -tocopherol from reacting with oxygen free radicals. Activation of the system was achieved by means of thermal processing through disruption of the NP coating. Although the resulting oxygen-scavenging capacity and rate was not as efficient as many commercial oxygen scavengers, this oxygen-scavenging system demonstrates the use of nanoencapsulation techniques in the development of a new oxygen-scavenging system which does not require an UV activation step and showing potential for “hot-filling” applications. In a further study from Byun et al. [70], the incorporation of α -tocopherol-loaded NPs and Fe-(II)-chloride into a warm water fish gelatin film is reported. The resulting OS system, which is triggered by moisture, could scavenge oxygen effectively with an oxygen-scavenging capacity of $1969 \text{ cm}^3 \text{ O}_2/\text{m}^2/\text{mil}$ film thickness in 50 days.

TiO₂ can also be used as an oxygen scavenger [58]. For instance, Xiao-e et al. [71] developed packaging films by adding TiO₂-NPs into different polymers. They demonstrated oxygen scavenging by UV illumination of the nanocrystalline TiO₂ films in the presence of excess organic hole scavengers. Mills et al. [72] incorporated nanocrystalline titania particles in a flexible ethyl cellulose (EC) polymer film. The oxygen-scavenging rates (0.017 cm³ O₂ /h cm² over 24h) exhibited by these films were shown to compare favorably to those associated with more traditional oxygen scavengers. However, a major drawback of such TiO₂-based oxygen scavengers is the requirement of a continuous UV light source to drive the scavenging process forward [72].

Another possibility to remove residual oxygen from the headspace of food packages is the use of the catalytic activity of noble transition metals such as palladium (Pd) or platinum (Pt). If hydrogen is included in the modified atmosphere of a package, these metals can catalyze the oxidation of hydrogen into water [109,119]. Yu et al. [73] used an in situ infusion method to incorporate small amounts Pd or Pt-NPs into commercial thermoplastic polymer matrices such as fluorinated ethylene-propylene copolymers (FEP), polypropylene (PP), LLDPE, PET, and nylon 6,6. They investigated the gas transport properties of the infused polymers and found that trace amounts (~2%) of hydrogen in the purge gas were sufficient to considerably reduce the oxygen flux through the metal-infused polymer films. Thus the catalytic role of Pd and Pt resulted in a highly effective oxygen-scavenging system which was found to be independent of the chemical nature of the polymer matrix.

More recently, a Pd-based OS-film has been developed using magnetron sputtering technology [120–122]. Thereby, the nanoscaled Pd layer, deposited on a PET film, was able to remove up to 2.5 vol.% residual oxygen in food packages within a matter of minutes if hydrogen was included in the modified atmosphere [122]. This high efficiency makes the OS film particularly suitable for oxygen-sensitive food products with a short shelf life such as cooked sliced meat products where a light-induced discoloration occurs within the first hours [123,124]. In this context, Hutter et al. [74] demonstrated that by the application of the Pd-based OS film on cooked cured ham, the red color could be preserved and discoloration prevented for 21 days of storage, although packages were exposed to light 24 h/day. Contrastingly, the samples packaged without OS film lost their redness within the first 2 h after packaging. A further application of this Pd-based OS film on bakery products resulted in a 3–4 fold longer shelf life of partially baked buns, toast bread slices, and gluten-free bread slices as mold growth was retarded up to 8–10 days [75]. In samples without the OS film, mold growth was detected in all bread samples after 2 days.

Chisholm et al., Farneth et al., and Gohil et al. [125–127] developed an oxygen-scavenging ink formulation to be flexographically printed or coated onto the interior surface of a plastic film or item used for food packaging. The formulation was an ascorbate/enzyme-based system containing calcium ascorbate (CaAsc) and laccase which was activated by moisture. As for printing or coating application only very low amounts of oxygen-scavenging material can be used because it requires a very high oxygen-scavenging rate to remove the majority of oxygen from a food package, desirably within 60–100h [77]. However, this was not possible with CaAsc/enzyme systems unless a very high amount of the ascorbate would have been used. In order to increase the oxygen-scavenging efficiency of the ascorbate/enzyme system, Gohil and Wysock [77] tested a large variety of approaches by coating or printing the formulation on self-adhesive PET-carrier films which can be stuck on the inner side of a food package. They found that the addition of nano-based catalysts such as nano-TiO₂ or nano-alumina (Al₂O₃) extended the OS capacity to beyond 300h, even at lower amount of ascorbate (15% instead of 35% CaAsc). Moreover, they observed that the addition of TiO₂ or Al₂O₃ as catalysts and an edible oil to the ascorbate and laccase-based formulations induced a synergistic effect upon the rate of scavenging oxygen from the packages.

7.4 ETHYLENE SCAVENGERS

Climacteric respiration is the major metabolic process occurring in many fruits and vegetables after harvesting. [38]. Thereby, ethylene, a natural plant hormone, accelerates respiration, leading to maturity, softening the product tissues and, therefore accelerating senescence. On the other side, its accumulation can cause yellowing of green vegetables and may be responsible for a number of undesirable reactions, such as the development of bitter flavors and chlorophyll degradation. Consequently, the removal of ethylene gas from a package environment can maintain acceptable visual and organoleptic quality and thereby extend the shelf life [128–130]. The most common agent of ethylene removal is potassium permanganate (KMnO₄) [128,129,131], which oxidizes ethylene to acetate and ethanol [116]. Due to its toxicity, however, potassium permanganate cannot be integrated into packaging material with food contact and is therefore usually applied in sachets [130,132]. Ethylene can also be removed by physical adsorption on active surfaces such as zeolite, clays, or activated carbon [130,131], which may be incorporated in packaging materials.

Inorganic nanoparticles including metals such as palladium (Pd) or silver (Ag), and metal oxides, such as zinc oxide (ZnO) or titanium oxide (TiO₂), have gained interests due to their attractive physicochemical properties. A palladium (Pd)-promoted material was discovered by Johnson Matthey scientists [133]. The material consists of a palladium-impregnated zeolite giving finely dispersed Pd particles. Its ethylene adsorption capacity (4162 $\mu\text{L/g}$) at 20°C and approximately 100% RH was shown to be far superior to KmnO₄-based scavengers when used in low amounts and in conditions of high relative humidity (RH) [131,134]. The authors demonstrated that the Pd-promoted material effectively scavenged both exogenously administered and/or endogenously produced ethylene by banana or avocado (Table 7.3). As a result, a corresponding inhibition of ethylene-induced ripening of the climacteric fruits was observed. Other authors coated polyvinyl chloride (PVC) films with nano-ZnO powder and evaluated its effects on the preservation quality of fresh-cut “Fuji” apples [135]. Cutting of the apples caused an increase in ethylene level due to wound-induced ethylene production. Compared with the control (PVC film), the ethylene production was retarded by the nano-ZnO film. Moreover, it was demonstrated that samples packed in the nano-package showed significantly reduced fruit decay rate which was attributed to a decreased accumulation of malondialdehyde (MDA), maintenance of °Brix value and titratable acidity, as well as inhibition of enzyme activities.

Further NPs reported to have an influence on ethylene production are TiO₂-NPs as well as Ag-NPs. Whereas photoactive TiO₂ can oxidize ethylene into H₂O and CO₂ [58], Ag-NPs have been postulated as an ethylene inhibitor in several works [38,137,138]. For example, Luo et al. [136] reported the influence of LDPE films loaded with TiO₂-NPs on the quality of strawberries.

Table 7.3 Nano-Scaled Ethylene-Scavenging Packaging Systems

Active Substances	Matrix/Packaging Material	Food Application	Reference
Palladium	Zeolite	Avocado and bananas	[131,133,134]
ZnO	Coating a PVC film	Fresh cut apples	[135]
TiO ₂	LDPE film	Strawberries	[136]
Silver	Cellulose-hybrid materials	Fresh cut melon	[38]
Silver + TiO ₂	PE film (+kaolin)	Strawberries, Chinese jujube (date), and bayberries	[46–48]
	LDPE film (+montmorillonite)	Kiwifruit	[45]

They could demonstrate that the ethylene production of the strawberries in the nano-TiO₂ LDPE-package was significantly inhibited. Moreover, fruit decay, softening, weight loss, and titratable acid content were also reduced. In regard of Ag-NPs, Fernández et al. [38] developed cellulose-Ag-NP hybrid materials in order to control the spoilage-related microflora in absorbent pads. Experiments with these Ag-NP pads located in trays of fresh-cut melon revealed that, apart from the antimicrobial effects described in Section 7.2, the senescence of the melon cuts was remarkably retarded, indicating blocking of ethylene-mediated effects on the ripening, leading to a less ripen and juicier product. Other studies investigated the combination of TiO₂-NPs and Ag-NPs. Li et al. [47] synthesized packaging films by blending PE with nano-powder (Ag, TiO₂, and kaolin). Performance of room temperature storage tests with Chinese Jujube (date) demonstrated beneficial effects of the nano-packaging material compared with normal PE packaging material. Both physicochemical and physiological quality could be preserved during 12 days since fruit softening, weight loss, browning, and climatic evolution were significantly inhibited. Similar results were obtained when the nano-packaging material was applied to strawberries [48] or Chinese bayberries [46]. Similarly, Hu et al. [45] incorporated TiO₂-NPs, Ag-NPs, and montmorillonite particles into an LDPE film and evaluated its effect on postharvest quality of ethylene-treated kiwifruit during cold storage. The application of the nanocomposite-based packaging resulted in inhibiting ethylene production, extending organoleptic characteristics, reducing degradation of nutritional components, preventing physiologic changes, delaying ripening, and consequently in an extended shelf life of the harvested kiwifruit.

7.5 CONCLUSIONS

It has been shown that various nanoparticles can provide several active properties for food packaging materials, such as oxygen and ethylene scavenging as well as antimicrobial activity, offering great potential to maintain or improve the quality of food products. Several nanomaterials, particularly the ones used on antimicrobial packaging systems, were tested against microorganisms *in vitro* only. Food tests, however, are of great importance since the activity of the active compounds could be influenced by the food components. For successful implementation of the active nanomaterials in food packaging, the cost has to correspond to the benefit gained by the particular food product, legislative and regulatory issues must be addressed, and broad consumer acceptance is required.

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