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Review

Metallic-based micro and nanocomposites in food contact materials and active food packaging☆

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Metallic-based micro and nano-structured materials are incorporated into food contact polymers to enhance mechanical and barrier properties, and to prevent the photodegradation of plastics. Additionally heavy metals are effective antimicrobials in the form of salts, oxides, and colloids, complexes such as silver zeolites, or as elemental nanoparticles. They are incorporated for food preservation purposes and to decontaminate surfaces in industrial environments. Other relevant properties in active food packaging, such as the capability for ethylene oxidation or oxygen scavenging, can be used to extend food shelf-life. Silver based nano-engineered materials are currently the most commonly used in commodities due to their antimicrobial capacity. Copper, zinc and titanium nanostructures are also showing promise in food safety and technology. The antimicrobial properties of zinc oxide at the nanoscale will provide affordable and safe innovative strategies. Copper has been shown to be an efficient sensor for humidity, and titanium oxide has resistance to abrasion and UV-blocking performance. The migration of cations from the polymer matrices is the key point to determine their antimicrobial effectiveness; however, this cation migration may affect legal status of the polymer as a food-contact material.

Introduction

Social changes, globalization, packaging life cycles, and the requirement for strict safety measures are increasing the pressure to produce new packaging systems able to transport food items and that also allow the traceability along the food distribution chain. Consumers have increasing interest in ready-to-eat commodities with fresh-like and healthy attributes, thus raising the commercialization of minimally processed foods. But those foods have high risk of surface dehydration, moisture loss, oxidation, or browning, and cross-contamination through cutting boards, knifes, working surfaces, equipments or the processing environment. Biofilm forming microorganisms are an additional potential danger for the consumer in many food types, and may cause toxiinfections (Donlan, 2002). The growth potential of foodborne pathogens such as *Salmonella*, *Campylobacter*, *Listeria* and *Escherichica coli* 0157:H7 needs to be minimised, and this leads to the necessity for the implementation of Food Safety Management Systems (Luning, Bango, Kussaga, Rivira & Marcelis, 2008).

Many applications, including food production and storage, might benefit from the incorporation of safe, economical, and wide spectrum long-lasting biocides into polymers, paints, or working surfaces (Appendini & Hotchkiss, 2002; Fernández, Cava, Ocio, & Lagarón, 2008). Certain metal ions, such as copper, silver, zinc, palladium, or titanium, occur naturally and; in some cases, are essential minerals. These ions do not have adverse effects on eukaryotic cells below certain concentrations and may be good candidates for the implementation of novel safety measures. In this context, the antimicrobial, photocatalytic, oxidizing, and UV protecting properties of highly innovative inorganic nanostructured materials (Fig. 1) are being investigated and exploited in numerous applications (Table 1). In this article,

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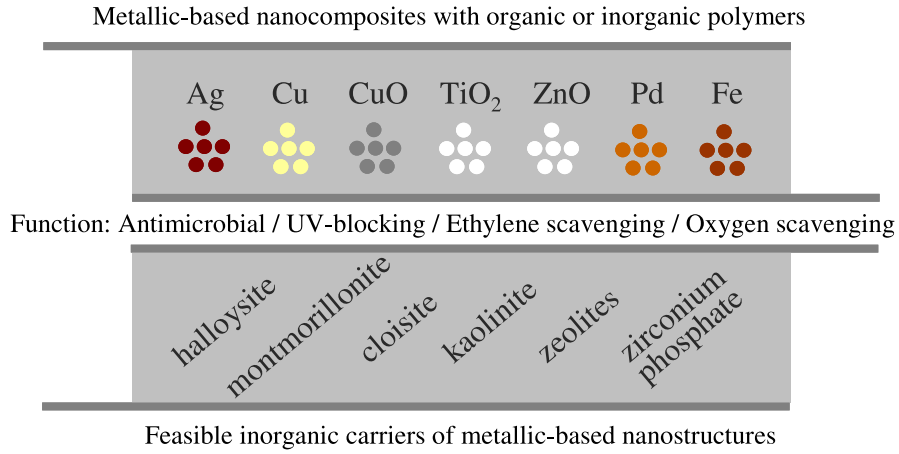

Fig. 1. Potential for the development of metallic-based nanocomposites in active food packaging.

we overview the latest developments concerning the implementation of metallic-based micro- and nanocomposites into food packaging strategies, taking into account the limits established by food regulations.

Metal based composites with antimicrobial activity

Silver

Among metallic cations, ionic silver is known to have the greatest antimicrobial capacity against a broad range of

Table 1. Antimicrobial metallic-based micro and nonocomposites in food packing.

Metal	Size	Carrier	Microorganism	Log reduction	Food items	References
Ag Zeolites	Micro	Stainless steel	*Bacillus* spp.	3 $\log_{10}$ CFU/mL	-	Galeano *et al.*, 2003
Ag Zeolites	Micro	Stainless steel	*E. coli*; *P. aeruginosa*; *S. aureus*	>6 $\log_{10}$ CFU/mL	-	Cowan *et al.*, 2003
AgNPs clusters	90 nm	PE	*Alicyclobacillus acidoterrestris*	2 $\log_{10}$ CFU/mL	Apple juice	Del Nobile *et al.*, 2004
Ag-clays, AgNPs Ag-zeolite	Nano Micro	Chitosan	*E. coli; Listeria; S. aureus; Salmonella*	Inhibition zones	-	Rhim *et al.*, 2006
AgNPs	15–25 nm	Polyvinylpyrrolidone	Psychrotrophic	10 days shelf-life increase	Asparagus spears	An *et al.*, 2008
AgNPs	5–35 nm	Cellulose	*K. pneumoniae*	>5 $\log_{10}$ CFU/mL	-	Pinto *et al.*, 2009
AgNPs	5–35 nm	Cellulose	*E. coli*; *S. aureus;* Mesophilic	1–3 $\log_{10}$ CFU/mL	Meat, melon cuts	Fernandez *et al.*, 2010a, b
Ag-montmorillonite	Nano	Zein, agar, poly (ε-caprolactone)	*Pseudomonas* spp.	>2 $\log_{10}$ CFU/mL	-	Incoronato *et al.*, 2010
CuNPs	20–60 nm	Cellulose	*E. coli*	Inhibition zones	-	Mary *et al.*, 2009
CuNPs	10 nm	Chitosan	*S. aureus; Salmonella*	3–4 $\log_{10}$ CFU/mL	-	Cardenas *et al.*, 2009
ZnO	200–400 nm	PVC	*E. coli*; *S. aureus*; Psychrotrophic	Inhibition zones, low decay	Apple cuts	Li *et al.*, 2009a, 2011
Cu or ZnO	Nano	Hydroxyapatite	*E. coli*; *S. aureus; C. albicans*	1–2 $\log_{10}$ CFU/mL	-	Stanic *et al.*, 2010
TiO_2	Nanophase	Stainless steel	*E. coli*	Inhibition zones	Meat exudates	Verran *et al.*, 2010
TiO_2	20 nm	EVOH	*Bacillus* spp.; *E. coli*; *L. plantarum*, etc.	Self-sterility	-	Cerrada *et al.*, 2008
TiO_2	20 nm	Stainless steel	Biofilms of *Listeria*	3 $\log_{10}$ CFU/mL	-	Chorianopoulos *et al.*, 2011
TiO_2	0.7–0.9 μm	Glass	*E. coli; Listeria; S. aureus; Salmonella*	2.8 $\log_{10}$ CFU/mL	Lettuce	Kim *et al.*, 2009
TiO_2	7 nm, 5 μm	Oriented PP	*E. coli*	1 $\log_{10}$ CFU/mL	Lettuce	Chawengkijwanich & Hayata, 2008
ZnO, nisin	Nano	PLA on Glass	*Salmonella enterica*	3–4 $\log_{10}$ CFU/mL	Liquid egg	Jin & Gurtler, 2011
AgNPs, TiO_2, ZnO	Nano	LDPE	Mesophilic	Shelf-life stable 28 days	Orange juice	Emamifar *et al.*, 2010
AgNPs, TiO_2, kaolin	Nano	PE	-	Better quality preserved	Jujube	Li *et al.*, 2009b
AgNPs, TiO_2, kaolin + hot air	Nano	LDPE	*P. citrinum*; yeasts and moulds	Decay decrease	Bayberries	Wang *et al.*, 2010

Gram+ and Gram− microorganisms; it has long-term biocide properties and low volatility, but low toxicity to eukaryotic cells. Furthermore, in recent years, silver has gained popularity because of the spread of antibiotic resistant *Staphylococcus aureus* strains (Deurenberg & Stobberingh, 2008), being resistance to silver considered sporadic with a low clinical incidence (Chopra, 2007; Percival, Bowler, & Russell, 2005). Consequently, the development of antimicrobial surfaces, aseptic food containers, and active packaging systems based on a sustainable release of Ag^+ ions is seen as promising. Low amounts of silver, around 50−100 μg Ag^+/kg (Galeano, Korff, & Nicholson, 2003), are required to achieve biocidal effects in low buffered systems or in water; but the antimicrobial capacity of silver decreases rapidly in the presence of proteins, and about 10−100 mg Ag^+/kg are required in realistic food applications (Fernandez, Picouet, & Lloret, 2010a). Standardization of methods to determine MIC values in complex matrices remains a main problem; inconsistent results may lead to wrong claims. Molecular basis of resistance to silver have been documented (Silver, 2003), showing particularly concerns associated to the overuse of silver which should also be considered in technological applications.

Different mechanisms of action have been described for ionic silver. Silver ions interact significantly with cytoplasmatic components and nucleic acids, and alter the enzymatic activities after chelation by the thiol groups of proteins (Holt & Bard, 2005). They interact with the ribosomes, thus inhibiting the expression of enzymes, and interfere with the membrane permeability. Low concentrations of silver ions induce a massive proton leakage through the membrane and hinder the respiratory chain and the mechanisms related to energy production in the cell.

Generally, silver-based antimicrobial additives consist of silver ions integrated into inert matrices such as ceramic, glass, or zeolites (Matsumura, Yoshikata, Kunisaki, & Tsuchido, 2003). Other additive types, silver salts or metallic silver, may be incorporated into thermoplastic polymers, such as polyethylene, polypropylene, polystyrene, butadiene styrene, or nylon (Del Nobile *et al*., 2004).

Silver nanotechnology

The bioactivity of nano-sized silver particles (AgNPs) is an area of growing scientific interest. Nano-sized elemental particles with a diameter below 100 nm exhibit optical and chemical properties that vary with particle size, shape, surface functionalization, and boundary conditions. Metallic silver nanoparticles interact with oxygen, boosting their antimicrobial activity when compared to the bulk solid or to silver oxide. Henglein (1998) obtained partially oxidized silver nanoparticles with chemisorbed Ag^+ and demonstrated that the oxidation state of silver atoms taking part of the AgNPs is a key point to achieve antimicrobial properties. This was confirmed by Lok *et al.* (2007). Zero-valence AgNPs did not exhibit biological activity, but partially oxidized AgNPs seemed to have antibacterial properties mediated only by the silver ions chemisorbed in the surface of the AgNPs. The antimicrobial activity of the AgNPs themselves was postulated by Sondi and Salopek-Sondi (2004) and the nanoparticle shape was found relevant for the interaction with *E. coli* membranes (Pal, Tak, & Song, 2007). The leakage of intracellular materials due to the association of silver nanoparticles with the membrane of Gram- *E. coli* bacteria was interpreted from TEM imaging. Energy dispersion X-ray analysis provided evidence for the incorporation of AgNPs in the bacterial membranes. The antimicrobial activity of the AgNPs is, however, a highly controversial subject, mainly due to the small dimensions required to achieving antimicrobial activity, the necessity of having an oxidized surface, and the subsequently feasible exchange of silver ions. Regarding the size of AgNPs, Morones *et al.* (2005) and Fernandez *et al.* (2009) confirmed that optimal antimicrobial activity falls between 1 and 10 nm of well distributed non-aggregated nanoparticles. Concerning surface oxidation, especially oxygen availability and the boundary conditions (pH and ionic strength) need to be considered (Henglein, 1998), which is expected to lead to the sustained release of silver ions. Antimicrobial activity in food contact applications could be consequently achieved without silver nanoparticle migration, acting polymeric matrices as carriers of silver nanoreservoirs.

A number of methods have been developed to synthesize non-agglomerated-regular in shape AgNPs. Those include the use of polymeric matrices as carriers of antimicrobials, biological macromolecules, mesoporous inorganic materials, and hydrogels (Mohan, Lee, Premkumar, & Geckeler, 2007). Silver nanoparticles are synthesised by the reduction of silver ions from a silver containing salt, being silver nitrate the most frequently used. Reducing agents are physical (mainly heat or UV radiation), chemical (borohydride, D-glucose, L-ascorbic acid, lactic acid, etc.), or mixed (hydrothermal). In addition, nano-sized metal particles (silver, copper, gold) are produced from appropriate salts (silver nitrate, copper sulphate, gold nitrate) in the cultivars of different types of microorganisms, such as bacteria, fungi, or algae. The nano-sized silver particles may enhance, for example, the biological activity of antifungal molecules, such as fluconazole (Gajbhiye, Kesharwani, Ingle, Gade, & Rai, 2009).

Nano-sized silver particles are being immobilized in food packaging polymers intended for food packaging applications. Biobased polymers, and those coming from renewable sources, are being used as carriers of silver nanoparticles. Biobased polymers are sensitive to humidity and strongly plasticized due to water sorption, which induces the uncontrolled release of immobilized active substances; however surface oxidation due to contact with oxygen and the ionic exchange are mandatory to achieve the release of metal ions trapped in nanoparticles. Consequently, the high water sorption created by the hydrophilic nature of biobased matrices, promotes the antimicrobial activity of the AgNPs. Chitosan, a polycationic biopolymer derived from chitin by alkaline deacetylation, has been proposed in several studies as carrier polymer or as reducing agent. Most of the studies suggest methods with direct applicability in the textile industry,

biomedical materials and devices, or in tissue engineering. A few authors have explored the potentiality for technological applications related to food science. Rhim, Hong, Park, and Ng (2006) demonstrated the effectiveness of chitosan-based nanocomposites containing silver nanoparticles against *E. coli, S. aureus* and *Listeria monocytogenes*. Sanpui, Murugadoss, Prasad, Ghosh, and Chattopadhyay (2008) utilized chitosan as stabilizer and reducing agent, and generated antimicrobial silver/chitosan nanocomposites. Another study showed the reduction of silver atoms from silver nitrate in an aqueous chitosan acetic acid solution by 35 kGy gamma irradiation producing 20–25 nm nanoparticles (Yoksan & Chirachanchai, 2010), which were incorporated in rice starch to produce a silver based antimicrobial chitosan/starch film. These silver loaded chitosan matrices were effective in the inhibition of the growth of Gram+ and Gram- microorganisms, and were suggested as components of food packaging polymers. Ali, Rajendran, and Joshi (2011) also generated 165 nm chitosan-silver nanoparticles by ionic gelation with tripoliphosphate, and after the subsequent loading with silver ions, they showed antimicrobial activity against *S. aureus*.

In addition, other food contact polymers and some typical GRAS (Generally Recognized as Safe) hydrogels have been suggested as carriers of silver nanoparticles. This is the case for highly swelling hydrogels of silver/collagen or silver/alginate, which produced inhibition zones in contact with microorganisms. Their effectiveness is, however, limited in biomedical applications due to chelation (Cavanagh, Burrell, & Ndworny, 2010). Cellulose acetate phthalate films filled with nano-sized silver particles showed antimicrobial properties against *E. coli* and *S. aureus* (Necula *et al.*, 2010), and electrospun nanofibres of cellulose acetate containing 20 nm silver nanoparticles showed strong antimicrobial activity (Son, Youk, & Park, 2006).

Taking into account aspects relevant for food safety, Del Nobile *et al.* (2004) focused on the antimicrobial activity of a silver-containing polyethyleneoxide-like coating on a polyethylene layer. The 90 nm size plasma deposited silver clusters showed high bactericide capacity against *Alicyclobacillus acidoterrestris*, and the material prolonged the shelf-life of apple juice. An, Zhang, Wang, and Tang (2008) were also able to lengthen the shelf-life of asparagus by about 10 days at 2 °C, when the product was coated with chemically reduced silver nanoparticles dispersed in polyvinylpyrrolidone; the nanoparticles were on average 15–25 nm. Nanocomposites of low density polyethylene filled with a powder containing 95% titanium oxide doping 5% metal-nanosilver (10 nm) were useful to extend the shelf-life of orange juice during 28 days, without impairing juice relevant quality attributes, such as colour or ascorbic acid content (Emamifar, Kadivar, Shahedi, & Soleimanian-Zad, 2010). And Li, Li *et al.* (2009) evaluated the capacity of a blend of polyethylene with a powder containing nano-Ag, nano TiO_2 and kaolin on the shelf-life of Chinese jujube, finding positive effects on the physicochemical parameters and the sensory quality of the product.

The porous structure of cellulose has been proposed as nanoreactor to help in the formation of AgNPs of a regular shape. Pinto *et al.* (2009) and Fernandez *et al.* (2009) studied different silver loaded cellulose materials. Silver loaded fluff pulp cellulose, bacterial cellulose, and EFTec™ nanostructured cellulose (Engineered Fibres Technology, Shelton, USA) showed differential properties, but a reasonably good antimicrobial activity against *Klebsiella pneumoniae*, *E. coli*, *S. aureus* and spore forming *B. subtilis* in protein rich cultivation media. A concentration of 60 mg Ag^+/kg was necessary to reduce the microbial load 1 $\log_{10}$ CFU/mL in absorbent pads in contact with beef meat. Natural chelating agents in food matrices, especially proteins, counteract the antimicrobial power of silver ions. This strongly limits the feasibility of this promising technology in food contact applications. In contrast, a higher antimicrobial activity may be expected in the presence of juices with low protein content, such as vegetable or fruit juices (Fernandez, Picouet, & Lloret, 2010b).

Silver exchanged inorganic materials

Silver and zinc ions have been trapped in zeolite type microporous inorganic ceramics, and their use has expanded the applications of silver in diverse fields. Alkaline or alkaline earth metal ions complexed with aluminosilicates are partially replaced with silver or zinc ions by ionic exchange mechanisms. The silver exchanged zeolites have shown antimicrobial activity mediated by the release of silver ions. In addition, inorganic clays have been postulated as carriers of silver ions or silver nanoparticles. The platelet clays swell in water and generate a stable network that interacts and stabilizes the exchanged Ag^+ ions. Oya, Banse, Ohashi, and Otani (1991) confirmed the antimicrobial properties of silver exchanged montmorillonite.

Silver-substituted zeolites are the most common antimicrobials incorporated into diverse food contact polymers in Japan, and Sinanen Zeomic Co. zeolites can be kneaded to numerous resins. In the USA, zeolite based technologies are listed under the FDA Food Contact Substance Notification for use in all types of food-contact polymers (FDA, 2007). The European Food Safety Agency released a positive opinion in 2005 concerning the use of two zeolites containing Ag^+ ions in food contact surfaces. In Europe, silver migration into food matrices is, however, highly restricted since only 50 μg Ag^+/kg of food is authorized. Companies willing to commercialize food contact polymers, are required to prove that silver containing materials do not have any effect on food shelf-life.

The bactericidal action of the silver zeolites is affected by inorganic salts and ion chelators, and seems to follow mechanisms similar to the action of silver nitrate. The bactericidal effect seems to be related to the transfer of the Ag^+ ions to the cell, and the generation of reactive oxygen species. In a similar view, and although the main antimicrobial activity is probably due to silver release, zinc ions are believed to reinforce the antimicrobial activity of silver by interfering

with proton transfer and inhibiting nutrient uptake (Galeano *et al*., 2003). Silver-zinc zeolites are already being widely used in diverse applications, such as the decontamination of surfaces in industrial environments, the disinfection of medical devices, and for food preservation purposes. For example, Cowan, Abshire, Houk, and Evans (2003) demonstrated the effectiveness of those silver zeolites coating on stainless steel surfaces against bacteria typically implied in foodborne illnesses. Relatively high concentrations of zeolite were required, up to 3.13 mg/mL, and a silver concentration up to 39 mg/mL to eliminate fully *Pseudomonas aeruginosa, E. coli*, and *S. aureus*. Remarkably, *P. aeruginosa* was resistant to many antimicrobials, but sensitive to silver exchanged zeolites, present as powders or coatings.

Silver-doped zeolites have also been incorporated in polymers for use in food packaging (Fernandez, Soriano, Hernandez-Muñoz, & Gavara, 2010; Kamişoğlu, Aksoy, Hasirci, & Bac, 2008; Pehlivan, Balköse, Ülku, &, Tihminliolu, 2005). These silver-doped zeolites, in most cases, have shown an increase in polymer crystallinity, low effects upon mechanical properties, and low rate polymer degradation for the low silver concentrations. However, some interface incompatibility may cause defects in the distribution of the zeolites into polypropylene or in polylactic acid. Polyurethane composites (Hiyama *et al*., 1995), polyethylene (Kamişoğlu *et al*., 2008), and polylactide (Fernandez, Soriano *et al*., 2010) with silver-doped zeolites showed antimicrobial activity against *E. coli* and *S. aureus*. In those materials, the migration of silver ions was sensitive to the processing methodology, such as the ionic strength and the ion concentration. Chitosan composites with zeolites silver-doped (Rhim *et al*., 2006) showed antimicrobial properties against *E. coli*., but also showed an increase in mechanical and water vapour barrier properties due to the filler.

In natural montmorillonites, sodium cations were replaced by Ag^{+} from silver nitrate, forming antimicrobial nanocomposites (Incoronato, Buonocore, Conte, Lavorgna, & Del Nobile, 2010). Those silver/clay nanoparticles were embedded in biobased hydrogels such as agar, zein, and poly(epsilon-caprolactone). Zein was the polymer matrix showing lower water sorption and lower antimicrobial activity against *Pseudomonas* spp. On the other hand, the best antimicrobial activity was obtained with agar due to ionic exchange favoured by the high water sorption. Incoronato, Conte, Buonocore and Del Nobile (2011) showed the effectiveness of the agar/silver montmorillonite nanoparticles to prolong the shelf-life in Fior di Latte cheese. In a similar study, Busolo, Fernandez, Ocio, and Lagaron (2010) reported the limited ionic exchange and the subsequent low silver release from polylactic acid nanocomposites containing a silver exchanged montmorillonite, thus confirming the results of Fernandez, Soriano *et al*. (2010) with a silver zeolite in the same matrix. Recently, halloysite and kaolinite were also attached to polymethacrylic acid (PMA) silver-capped nanoparticles *via* an electrostatic interaction. The results showed high molecular weight compounds adsorbed on the clay platelets surface, with typical layer-by-layer assembly morphology (Burridge, Johnston, & Borrmann, 2011).

Copper

Copper is an essential element and is present in most food in the form of ions or salts at levels, in most cases, below 2 mg Cu^{2+}/kg (meat, fish, pecans, green vegetables, etc.), but up to 39 mg Cu^{2+}/kg in cocoa and liver (Aaseth & Norseth, 1986). At low concentrations copper is a cofactor for metalloproteins and enzymes, and it also shows remarkable antimicrobial properties. In this context, in February 2008 the U.S. Environmental Protection Agency (EPA) approved the registration of copper alloys based on the claim that they reduce bacteria linked to potentially fatal microbial infections, and confirmed the antimicrobial efficacy of copper against *E. coli* O157:H7, *S. aureus*, *Enterobacter aerogenes* and *P. aeruginosa* (http://www.epa.gov/pesticides/factsheets/copper-alloy-products.htm, consulted 03.05.2011).

Although copper is typically applied to keep uncontaminated medical devices, and surfaces free of contaminant microorganisms, direct applications in food safety have also been reported for copper salts. Copper cast alloys were evaluated in food processing work surfaces and diminished the risks associated to *E. coli* O157:H7, although the presence of beef residues was a limiting factor for the achieved growth inhibition (Noyce, Michels, & Keevil, 2006). The growth of *Salmonella*, *E. coli* O157:H7 and *Cronobacter* spp.could be impaired by subletal concentrations of copper (II) ions (50 mg/kg) combined with other antimicrobials, such as lactic acid, in infant formula (Al-Holy, Castro, & Al-Quadiri, 2010) and carrot juice (Ibrahim, Yang, & Seo, 2008).

Compared to silver, the potential biocidal activity of copper is lower (about 10 mg Cu^{2+}/kg in water is necessary to kill 10^{6} cells of *Saccharomyces cerevisiae*). However copper ions can be easily mobilized due to oxidation. Antimicrobial nanoparticles (CuNPs) of elementary copper or copper oxide can be generated by different procedures. Elementary copper nanoparticles can be formed under thermal or sonochemical reduction from copper hydrazine carboxylate complexes in aqueous media (Dhas, Raj, & Gedanken, 1998). Reduction with borohydride mainly produces copper oxide (Kotelnikova, Vainio, Pirkkalainen, & Seriman, 2007), which can be easily oxidized to provide antimicrobial activity in ammonia containing media. The ion copper utility has been exploited in different nanocomposites. Copper has been embedded, for example, in high-pressure polyethylene (Ushakov, Ul'zutuev, & Kosobudskii, 2008). In addition, various biobased polymers have been used as carriers of antimicrobial copper. Cotton fabrics have been impregnated with nano-sized copper particles as colloidal solution (Chattopadhyay & Patel, 2010). Colloidal copper nanoparticles were also regularly distributed in chitosan films intended for food packaging applications (Cardenas, Diaz, Melendrez, Cruzat, & Garcia Cancino, 2009). And copper nanoparticles were immobilized on chitosan covalently attached to cellulose fibres after reduction with borohydride

(Mary, Bajpai, & Chand, 2009). The nanoparticles were effective against *E. coli* in wound dressings, and could be useful for preserving hygienic conditions in food retail packaging and display cases.

Zinc oxide

Zinc is a ubiquitous trace metal and essential for a large number of metalloenzymes. Nano-sized ZnO particles present biocidal activity and have some advantages compared to AgNPs, such as their lower cost, white appearance and UV-blocking properties (Dastjerdi & Montazer, 2010). They also present high versatility, and inorganic carriers, such as hydroxyapatite, can also be doped with zinc oxide providing novel structures with antimicrobial activity against *E. coli*, *S. aureus,* and *Candida albicans* (Stanic *et al*., 2010).

The feasibility of ZnO incorporated in polymer nanocomposites intended for food packaging has been tested. For instance, Li, Xing, Jiang, Ding, and Li (2009) coated poly (vinyl chloride) films with zinc oxide nanoparticles, and reported antimicrobial activities against *E. coli* and *S. aureus*. In a more recent work, Li *et al*. (2011) verified also the potential of the nano-packaging containing ZnO nanoparticles during the storage of Fuji apple cuts, observing a better preservation of quality indicators such as ascorbic acid and polyphenol content, and lower counts of typical altering microorganisms. Emamifar *et al*. (2010) reported on the antimicrobial activity of nanocomposites of low density polyethylene (LDPE) containing AgNPs and ZnO, showing a significant impact of the proposed nano-packaging on the shelf-life of orange juice. Additionally, combinations of allyl isothiocyanate, nisin and zinc oxide nanoparticles coated on glass jars were able to inactivate effectively *Salmonella* in liquid egg albumen (Jin & Gurtler, 2011).

Titanium dioxide

Titanium oxide has been positively evaluated as a food additive (Directive 94/36/EC, 1994). Nano-sized TiO_2 particles show photocatalytic properties, being useful as self-cleaning and antibacterial agents and against UV light (Nordman & Berlin, 1986). The photocatalytic activity of TiO_2 is strongly related to the crystal structure, which is related to the characteristic band gap. Titanium dioxide can be found in three different forms (rutile or anatase, tetragonal, and brookite, orthorhombic), with different reactivity depending on their characteristic band gap. Titanium dioxide irradiation at higher energies than the band gap induces the formation of electron−hole pairs, giving rise to redox reactions. Negative electrons generate O^{2-}, and positive electric holes generate hydroxyl radicals. Reactive oxygen species oxidize organic molecules, and kill bacteria and viruses.

Nano-sized TiO_2 particles are produced following different methodologies with sol-gel processing the most commonly used (Ibrahim & Sreekantan, 2011). TiO_2 nanoparticles (anatase or rutile) have also been attached to cellulose (Daoud, Xin, & Zhang, 2005). TiO_2 nanotubes can be formed hydrothermally at 180 °C, heating titanium oxide with NaOH. The best antimicrobial activity results are achieved in the presence of UVA light or black-light bulbs (Chorianopoulos, Tsoukleris, Panagou, Falaras, & Nychas, 2011).

TiO_2 photocatalytic activity has been found particularly useful to decontaminate water, also wash water, used for cleaning minimally processed products (Chaleshtori, Masud, & Saupe, 2008). In food processing, one of the most promising applications of nano-sized titanium dioxide particles as antimicrobial is to diminish the risks associated to biofilms in food contact surfaces (eg.: biofilms of *L. monocytogenes*, Chorianopoulos *et al*., 2011), or to improve cleanability of stainless steel (Verran, Packer, Kelly, & Whitehead, 2010). The biocide capacity of TiO_2 nanocomposites with typical packaging materials has also been tested. For example, EVOH (copolymer of ethylene and vinyl alcohol)-TiO_2 nanomaterials with 2−5% TiO_2 were acceptably well dispersed and adhered, and mechanical properties were enhanced. They were efficient against Gram+ and Gram− microorganisms, and kept self-sterility (Cerrada *et al*., 2008). TiO_2 nanotubes filling chitosan produced UV-blocking semitransparent films (Diaz-Visurraga, Melendrez, Garcia, Paulraj, & Cardenas, 2010); without UV-excitation, discrete bactericidal activity against *E. coli*, *S. enteric*a and S*vit-gedcie-d-mio-c,*

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