REVIEW PAPER

Current advancements in applications of chitosan based nano-metal oxides as food preservative materials

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ABSTRACT

Objective(s): A remarkable growing effort has been conducted by several researchers to fabricate food packaging materials which are able to protect foodstuffs and enhance their shelf-life from food-borne pathogens and fungal attack which causes great damage to the food industries. Recent studies has focused on the potential applications of nano-metal oxides in food packaging area.

Methods: This study reviews the latest trends and research results concerning the application of chitosan films containing some important nano-metal oxides as appropriate materials for food applications.

Results: Nano-metal oxides including zinc oxide, magnesium oxide, titanium dioxide, copper oxide, iron oxide, silicon dioxide, and silica are the most common nano-metal oxides that incorporated into the chitosan film for improving its antimicrobial, physical, mechanical, and thermal properties.

Conclusions: The reviewed nano-metal oxides may have positive implications for food industries, particularly in the area of food packaging based on nanoparticles to improve the physic-mechanical properties and also quality shelf-life parameters of foodstuffs.

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INTRODUCTION

A remarkable growing effort has been conducted by several researchers to fabricate food packaging materials which are able to protect foodstuffs and enhance their shelf-life from food-borne pathogens, spoilage-related microorganisms and fungal attack which causes great damage to the food industries [1-3]. In this regard, biodegradable/biocompatible polymers from natural renewable resources have been under extensive evaluation as appropriate alternatives to the synthetic petroleum-based polymers [4]. However, natural biopolymers are deficient in vital properties necessary to meet industrial standards [3].

Certain physicochemical and thermal properties of the chitosan (CH) need to be improved in order to make biopolymer based wrapping ingredients reasonable, moderate, and economical in contrast to the petroleum-based synthetic materials [5]. CH (Fig. 1) is a natural polysaccharide consisting of randomly distributed unites namely (1 → 4)-2-acetamido-2-deoxy-β-D-glucan (N-acetyl-D-glucosamine; NAG) and (1→4)-2-amino-2-deoxy-β-D-glucan (D-glucosamine) linked by β (1→4) linkages and is considered as the largest biomaterial after cellulose [6]. It can be obtained by partial alkaline deacetylation or enzymatic hydrolysis of chitin (Fig. 2), the structural element found in the exoskeleton of crustaceans e.g., tortoise, lobster, crab, and shrimp [7]. Moreover, it is naturally occurs in the exoskeleton of arthropods, internal structures of invertebrates, and cell walls of some living microorganisms such as fungi [8, 9].

CH and its derivatives have a broad range of applications in the medical and pharmaceutical fields, food industry, cosmetics, water treatment, and agricultural sector due to environment

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friendly nature, biodegradability, biocompatibility, edibility, non-toxicity, and serving as a compound carrier [4, 8]. Moreover, the US Food and Drug Administration (US FDA) lists CH as a "Generally Recognized as Safe-GRAS" [10]. CH has a various functional specialties due to the abundant hydroxyl groups, acetylamine and free amino groups in its structure. For this reason, it has been found to have antibacterial (Fig. 3), antifungal, antiviral, antioxidant, antihypertensive, anticoagulant, anti-allergic, anti-inflammatory, anticancer, antiinhemostatic, and mucoadhesive activities [6, 7, 11]. These properties are particularly amenable to a wide variety biomedical and pharmaceutical purposes including wound healing [7], gene delivery carrier [12, 13], tissue engineering [14], and drug delivery applications [9]. For aforementioned applications, CH is mainly processed in to gels, nanofibers, beads, microparticles, and nanoparticles composites and films [4, 11].

Nanotechnology is highly interdisciplinary involving the exploitation of materials with one or more dimensions that are less than 10 nm [15]. Recent studies has focused on the potential application of nano-metal oxides in wide ranging of food industry area including improving supplements, new food packaging polymers based on nano-metal oxides, extending the range of food textures, colors and tastes, increasing the application of liquid filters, and cooking oil catalysation. Due to their nano-sized dimensions, these materials possess very large surface-to-volume ratio and surface activity. When added to compatible polymers, the nanomaterials can

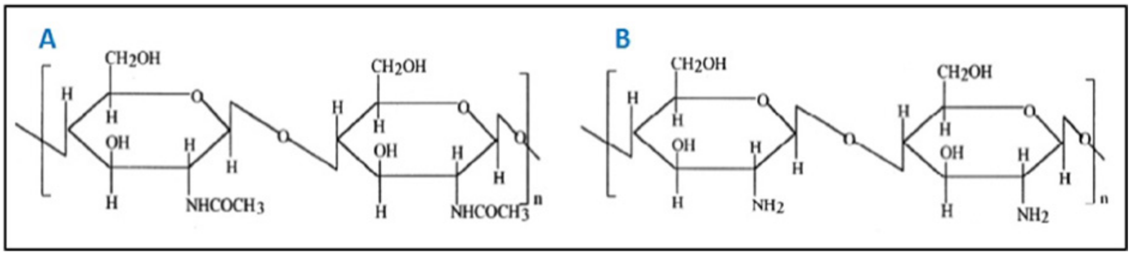

Fig. 1. Chemical structure of chitin (A) and chitosan (B) [65].

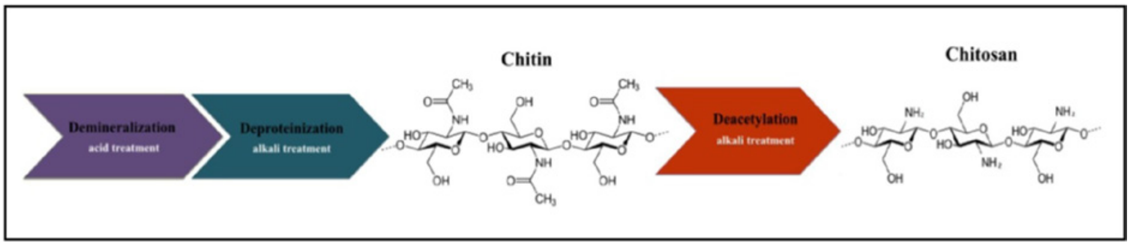

Fig. 2. Extraction process of chitin and chitosan [65].

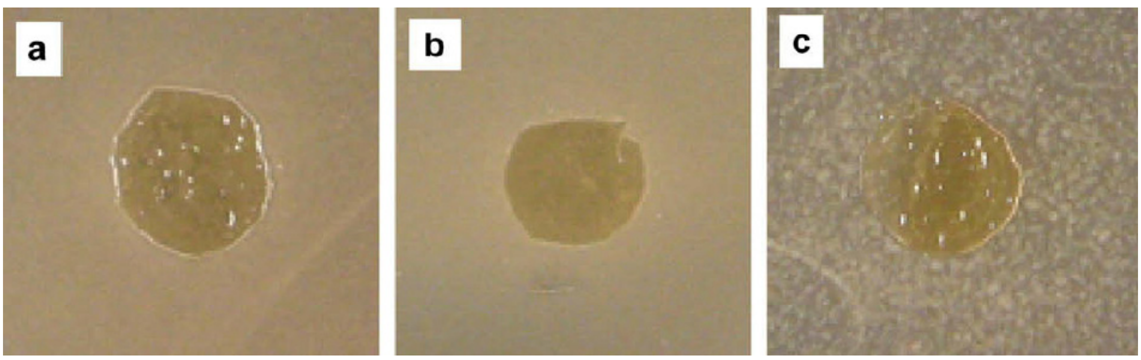

Fig. 3. Inhibitory effect of chitosan film against (a) *E. coli*, (b) *S. aureus*, and (c) *B. Subtilis* [5].

dramatically enhance the material properties of the resulting nanocomposites, such as improved mechanical strength, enhanced thermal stability, and increased electrical conductivity [7]. Therefore, nanomaterials are promising approach for increasing the mechanical and barrier properties of food packages, as well as the development of advanced structures for active and intelligent applications. This study reviews the latest trends and research results concerning the application of CH films containing some important nano-metal oxides as appropriate materials for food applications.

FUNCTIONAL PROPERTIES OF CHITOSAN

The backbone of CH is β-(1→4) glycosidic linkages with various degrees of N-acetylation of glucosamine residues. In addition, the hydroxyl group at C-2 position of the cellulose is replaced by an acetsmide group. Therefore, CH is composed of two repeating unites namely (1 → 4)-2-acetamido-2-deoxy-β-D-glucan (N-acetyl-D-glucosamine; NAG) and (1→4)-2-amino-2-deoxy-β-D-glucan (D-glucosamine) [12]. It can be obtained from chitin by partial alkaline N-deacetylation using concentrated sodium hydroxide solution or thought enzymatic hydrolysis of chitin in the presence of chitin deacetylase under relatively mild condition [16]. CH derived from chitin of crustacean shells is the most commercially used product due to its low cost and ready availability. In the first step of CH production, a linear chain of chitin composed of N-acetyl-D-glucosamine and 2-acetamido-2-deoxy-β-D-gluconopyranose joined together by β (1→4) bond, deproteinated using dilute aqueous sodium hydroxide, and then calcium carbonate was removed from shells of crustaceans by dilute hydrochloric acid. In the second step, chitin was deacetylated using 40-60% aqueous sodium hydroxide at 110-115 ºC for several hours. When the number of N-acetyl-glucosamine unites exceeds 50%, the biopolymer is termed as CH.

The antimicrobial property of CH was recently published in previous studies [17-19]. The antibacterial activity of CH depends on numerous parameters such as molecular weight, percentage of CH deacetylation, composite formulation, procedure of CH production, and release degree of its bio-active structure [20]. It has been concluded that the CH mechanism is attributed to interactions between its amino groups (NH_2) and negatively charged bacterial cell phospholipids, which is subsequently resulted in the leakage of essential constituents including cellular proteins and electrolytes, and finally microbial cell death [21].

The molecular weight and amino groups of CH have significant effects on its preservative/antimicrobial property. Roberts and Greenwood, [22] has evaluated the antibacterial property of CH and found that CH with low and high molecular weight of 4.7×10^5 g/mol and 1.1×10^6 g/mol were significantly control the growth of *L. monocytogenes* on the surface of ready-to-eat roast beef. No et al., [23] evaluated six CH oligomers with different molecular weights against four gram-negative (*Escherichia coli*, *Pseudomonas fluorescens*, *Salmonella typhimurium,* and *Vibrio parahaemolyticus*) and seven gram-positive bacteria (*Listeria monocytogenes*, *Bacillus megaterium*, *B. cereus*, *Staphylococcus aureus*, *Lactobacillus plantarum*, *L. brevis,* and *L. bulgaricus*) in different food models and *in-vitro* condition. They reported that CH remarkably inhibited the growth of investigated microorganisms, but the inhibitory effect was differed with regard to the molecular weight of CH and the type of bacterium. Devlieghere et al., [24] examined the antimicrobial effect of CH with high deacetylation degree and low molecular weight against several psychrotrophic food-borne pathogens and spoilage microorganisms. Based on their findings, *Brochotrix thermosphacta* and *B. cereus* were very sensitive to the applied CH while *L. monocytogenes* and lactic acid bacteria were less susceptible.

CHITOSAN SUPPLEMENTED WITH NANO-METALS

Zinc oxide (ZnO) nanoparticles

Among nano-metals, zinc oxide (ZnO) is one of the most commonly used compounds in numerous area owing to its excellent antimicrobial, non-toxicity, good UV absorbance, high stability, and photocatalytic attributes [25]. It is currently considered as a safe material for human beings by the US FDA [26], and have been applied as a food preservative, sunscreen, coating, paint, packaging material, and in water purification [27]. Moreover, it has been regarded in food packaging films/coatings to keep food color, prevent the growth of spoilage related microorganisms and pathogenic bacteria, and enhance packaging material properties, including mechanical strength, thermal stability, barrier properties, and stability [28]. Premanathan et al., [29] found that ZnO nanoparticles possessed a more inhibitory effect against gram-positive (*S. aureus*) than gram-negative (*E. coli* and *P. aeruginosa*) bacteria, and the bactericidal efficacy was recorded to extend by reducing the particle size of ZnO. There are some studies about the application of CH and ZnO nanoparticles for antimicrobial food packaging. Rahman et al., [30] indicated that the fabrication of antimicrobial/antioxidant CH-ZnO nano-composite pouches could increase the shelf life time of raw beef meat. Razak et al., [31] confirmed that the incorporation of nano ZnO in to CH enhanced the antimicrobial property and decreased the water vapor transmission rate, compared to straight CH films. Ummartyotin et al., [32] reported that ZnO-dispersed CH film had excellent resistance to against *E. coli* and *S. aureus*. Sarojini et al., [33] have reported nano ZnO incorporated CH-Mahua oil based polyurethane composite films for food packaging application. Indumathi et al., [34] have fabricated CH-ZnO nano composite film, which had appropriate antimicrobial property against several pathogenic bacteria including *E. coli*, *S. aureus*, *Bacillus subtilis*, and *P. aeruginosa* in black grape fruits. Similar findings were reported by Applerot et al., [35], indicating glass coated with ZnO nanoparticles (diameter = 300 nm) possessed good antibacterial activity *E. coli*, *B. subtilis*, *S. aureus,* and *Lactobacillus plantarum* with an 76-89% reduction in population. Noshirvani et al., [25] indicated that CH + ZnO nanoparticles at concentrations of 0.5, 1 and 2% decreased the number of yeasts and molds in sliced bread during 15 days. The antimicrobial mechanism of ZnO nanoparticles is still unclear, but several authors indicated that ZnO nanoparticles can disrupt the microbial cell membrane and change the cell structure owing to oxidative stress produced by reactive oxygen species (ROS) and accumulation of the nanoparticles on the bacterial cell membrane due to electrostatic forces [36, 37].

Magnesium oxide (MgO) nanoparticles

Magnesium oxide (MgO), as a reproducible, colorless, and crystalline mineral, is a widely applied metal oxide, which might easily be produced using economical approaches with low-cost raw materials such as brines, magnesium salts, and magnesium bearing minerals including dolomite and magnesite [38]. Nano-MgO has numerous noticeable properties such as antimicrobial ability, chemical inertness, thermal stability, photo-stability, electrical insulation, non-toxicity, good biocompatibility and biodegradability, large surface area-to volume ratio, low cost, UV blocking ability, and photocatalytic activity [39]. Therefore, it has been used in a wide filed area such as food packaging, pharmaceutics, and medical sciences [40]. Regarding food application of MgO nanoparticles, Zhao et al., [41] fabricated MgO nanoparticles and applied them as a nano-filler to reinforce CH film. Accordingly, the elastic modulus and tensile strength increased by 78% and 17%, respectively, with the incorporating MgO 1%. De Silva et al., [40] concluded that CH-MgO nanoparticles showed noticeable thermal stability, flame retardant properties, UV shielding, and water barrier properties, which could critically add value to the food packaging matrix. Based on the results of Sanuja et al., [42], the MgO nanoparticles affected thermo-mechanical, physical, and antimicrobial properties of CH based films. Sawai et al., [43] have concluded that MgO nanoparticles incorporated to the CH film have remarkable antimicrobial activity against *E. coli, S. aureus, Candida albicans*, *Saccharomyces cerevisiae*, *Aspergillus niger,* and *Rhizopus stolonifer* under *in-vitro* condition. Stoimenov et al., [44] found that MgO nanoparticles are very effective against *E. coli* and *Bacillus megaterium* bacteria as well as spores of *B. subtilis.* It has been suggested that active oxygen, such as superoxide, available on the surfaces of MgO nanoparticles was one of the important parameters that significantly affect their antimicrobial ability [44].

Titanium dioxide (TiO_2) nanoparticles

Titanium dioxide (TiO_2), a metal oxide semiconductor, is a novel photocatalyst owing to its remarkable catalytic ability, chemical stability, low toxicity, and low cost [45]. TiO_2 nanoparticles possessed appropriate adhesiveness and antimicrobial properties [46] and has been regarded as a generally recognized as safe by US FDA as a chemical additive in human food, drugs, cosmetics, medical devices, biomaterials, and food contact material [26]. However, the commercial applications of TiO_2 nanoparticles are limited because of its unstable thermodynamic activities and trend to agglomerate [47]. The photocatalytic activity of nano-TiO_2 is activated by UV light in the presence of oxygen and water molecules, and it lead to the development of reactive oxygen species and hydroxyl radical that resulted for the antibacterial and anti-fungal properties [48]. It might be applied for a degradation and mineralization of a widespread pollutants such as or organic and inorganic compounds in water and environment [49]. It is well known for exhibition of great photocatalytic antimicrobial effect against a broad spectrum of food-borne pathogens [50]. The antimicrobial effect of this compound might be related to the high redox potential of ROS generated by the photo-excitation [51]. Foster et al., [51] reported that TiO_2 nanoparticles are able to death viruses including poliovirus-1, hepatitis B virus, herpes simplex virus, and MS2 bacteriophage. Lin et al., [48] found that nano-composite based CH-TiO_2 decreased *E. coli* population by 6 log after 24 h of incubation, and had an minimum inhibitory concentration (MIC) value of 0.38 mg/ml during the fruit storage at refrigerated condition. Al-Taweel et al., [52] reported that TiO_2-CH nano-composite based films by crosslinking agent and applied it for meat preservation for 14 days at refrigerated storage condition.

Copper oxide (CuO) nanoparticles

Copper is a critical element and is available in most food products (2-39 mg/kg) such as meat, fish, pecans, green vegetables, cocoa, and liver. Copper oxide (CuO) is listed as a GRAS by the US FDA [26]. It is a cofactor for metalloproteins and enzymes, and it also possess significant antimicrobial activity *E. coli* O157:H7, *S. aureus*, *Enterobacter aerogenes,* and *P. aeruginosa* [53]. Although CuO nanoparticles are commonly used to maintain uncontaminated medical devices, and surfaces free of contaminant microorganisms, and direct usage of CuO nanoparticles or incorporation into bio-based polymers have been reported [54]. The growth of *Salmonella* spp., *E. coli* O157:H7 and *Cronobacter* spp., can be significantly reduced in infant formula [55] and carrot juice [56]. Previous studies have been done to evaluate the antibacterial activity of CuO nanoparticles when incorporated in a range of CH material [57, 58]. Their results showed that incorporating CuO nanoparticles into the CH films could increase the mechanical, antibacterial properties, and reduce both water solubility and UV transition with the lowest effect on the transparency of the films.

Iron oxide nanoparticles

Iron oxide (Fe_3O_4) nanoparticles are becoming popular compounds in foods, bioengineering and biomedical owing to their capability to act at cellular and molecular level, stability against photo-chemical corrosion, superparamagnetic, biocompatibility, crystalline structure, non-toxicity, monodispersity, water soluble and cost effective [59]. Nehra et al., [59] reported that CH coated with Fe_3O_4 nanoparticles are effective as an antimicrobial agent against *E. coli*, *B. subtilis*, *Candida albicans*, *Aspergillus niger* and *Fusarium solani*. Shrifian-Esfahni et al., [60] reported that CH-Fe_3O_4 nanoparticles film had excellent inhibitory effect against *E. coli* and *P. aeruginosa* under *in-vitro* condition. It has been suggested that apart from ROS production by Fe_3O_4 nanoparticles, physical damage to the bacterial cell membrane might be the most important factor for the recorded high decreasing for nanorod structures of the bacteria [36].

Silicon dioxide and silica nanoparticles

Silicon dioxide (SiO_2) and silica nano-particles have good antimicrobial property, quite stable and cannot be digested by the digestive tract. These compounds have been recently approved as food additives by US FDA [26]. At present, SiO_2 and silica nano-particles was strict in application of food processing and preservation in terms of direct addition and incorporating to the biodegradable and un-degradable polymers and related information must be marked in label [61]. Kou et al., [62] reported that a composite CH/nano-silica/sodium alginate composite film could prolong the shelf life of post-harvested winter jujube for approximately 1 month, while the abscisic acid treatment induced ripening and reduced the quality. Tian et al., [63] found that the addition of nano-SiO_2 particles into the CH film increased the physic-mechanical properties of the composite films including tensile strength, water-vapor and gas permeability. CH film supplemented with nano-SiO_2 particles could significantly decrease the decay rate, shrinkage rate, respiration rate, ethylene production rate, electrolyte leakage rate, superoxide anion production rate, and the accumulation of malondialdehyde (MDA) content in *Ginkgo biloba* seeds.

PHYSIC-MECHANICAL PROPERTIES OF CHITOSAN FILM CONTAINING NANO-METALS

There are general agreement about the physic-mechanical properties of CH film containing nano-metals [32]. In general, mechanical properties of films supplemented with nano-metals including tensile strength, puncture force, puncture deformation, and elongation at break were significantly increased compared to the films without nano-metals, which could be attributed to the strong polymer–polymer interactions between metals and film matrices [32]. It is believed that this phenomenon can increase the intermolecular force, resistance, and flexibility to fracture of polymer materials [64]. Moreover, films containing nano-metals have better water and oxygen barrier properties than straight films. This phenomenon could be attributed to more intermolecular interactions between film matrices and metal nanoparticles [32].

CONCLUSION

The reviewed nano-metal oxides may have positive implications for food industries, particularly in the area of food packaging based on nanoparticles to improve the physic-mechanical properties and also quality shelf life parameters of foodstuffs. It is obvious that this new packaging materials, if managed and regulated correctly, can play a critical role in environment about synthetic petroleum-based polymers. Regarding functional properties of CH film blended with nano-metals including its physic-mechanical, rheological, water vapor permeability, antioxidant and antibacterial characteristics, CH can be considered as a remarkably promising packaging material for preserving and improving the shelf-life of foodstuffs.

CONFLICT OF INTEREST

The author declares no conflict of interest.

REFERENCES

1. Nouri Ala MA, Shahbazi Y. The effects of novel bioactive carboxymethyl cellulose coatings on food-borne pathogenic bacteria and shelf life extension of fresh and sauced chicken breast fillets. LWT. 2019;111:602-11.
2. Shahbazi Y, Karami N, Shavisi N. Effect of Mentha spicata essential oil on chemical, microbial, and sensory properties of minced camel meat during refrigerated storage. Journal of Food Safety. 2017;38(1):e12375.
3. Mujtaba M, Morsi RE, Kerch G, Elsabee MZ, Kaya M, Labidi J, et al. Current advancements in chitosan-based film production for food technology; A review. International Journal of Biological Macromolecules. 2019;121:889-904.
4. Elgadir MA, Uddin MS, Ferdosh S, Adam A, Chowdhury AJK, Sarker MZI. Impact of chitosan composites and chitosan nanoparticle composites on various drug delivery systems: A review. Journal of Food and Drug Analysis. 2015;23(4):619-29.
5. Dutta PK, Tripathi S, Mehrotra GK, Dutta J. Perspectives for chitosan based antimicrobial films in food applications. Food Chemistry. 2009;114(4):1173-82.
6. Yuan G, Chen X, Li D. Chitosan films and coatings containing essential oils: The antioxidant and antimicrobial activity, and application in food systems. Food Research International. 2016;89:117-28.
7. Patrulea V, Ostafe V, Borchard G, Jordan O. Chitosan as a starting material for wound healing applications. European Journal of Pharmaceutics and Biopharmaceutics. 2015;97:417-26.
8. Kakaei S, Shahbazi Y. Effect of chitosan-gelatin film incorporated with ethanolic red grape seed extract and Ziziphora clinopodioides essential oil on survival of Listeria monocytogenes and chemical, microbial and sensory properties of minced trout fillet. LWT - Food Science and Technology. 2016;72:432-8.
9. Usman A, Zia KM, Zuber M, Tabasum S, Rehman S, Zia F. Chitin and chitosan based polyurethanes: A review of recent advances and prospective biomedical applications. International Journal of Biological Macromolecules. 2016;86:630-45.
10. USFDA. GRAS notice inventory. GRN, No. 397, www.fda.gov. 2013.
11. Jayakumar R, Menon D, Manzoor K, Nair SV, Tamura H. Biomedical applications of chitin and chitosan based nanomaterials—A short review. Carbohydrate Polymers. 2010;82(2):227-32.
12. Saranya N, Moorthi A, Saravanan S, Devi MP, Selvamurugan N. Chitosan and its derivatives for gene delivery. International Journal of Biological Macromolecules. 2011;48(2):234-8.
13. Jayakumar R, Chennazhi KP, Muzzarelli RAA, Tamura H, Nair SV, Selvamurugan N. Chitosan conjugated DNA nanoparticles in gene therapy. Carbohydrate Polymers. 2010;79(1):1-8.
14. Madhumathi K, Binulal NS, Nagahama H, Tamura H, Shalumon KT, Selvamurugan N, et al. Preparation and characterization of novel β-chitin–hydroxyapatite composite membranes for tissue engineering applications. International Journal of Biological Macromolecules. 2009;44(1):1-5.
15. Mihindukulasuriya SDF, Lim LT. Nanotechnology development in food packaging: A review. Trends in Food Science & Technology. 2014;40(2):149-67.
16. Prashanth KH, Kittur F, Tharanathan R. Solid state structure of chitosan prepared under different N-deacetylating conditions. Carbohydrate Polymers, 2002;50 (1):27-33.
17. Tsai G-J, Su W-H, Chen H-C, Pan C-L. Antimicrobial activity of shrimp chitin and chitosan from different treatments and applications of fish preservation. Fisheries Science. 2002;68(1):170-7.
18. Gómez-Estaca J, López de Lacey A, López-Caballero ME, Gómez-Guillén MC, Montero P. Biodegradable gelatin–chitosan films incorporated with essential oils as antimicrobial agents for fish preservation. Food Microbiology. 2010;27(7):889-96.
19. Chamanara V, Shabanpour B, Gorgin S, Khomeiri M. An investigation on characteristics of rainbow trout coated using chitosan assisted with thyme essential oil. International Journal of Biological Macromolecules. 2012;50(3):540-4.
20. Fernández-Saiz P, Sánchez G, Soler C, Lagaron JM, Ocio MJ. Chitosan films for the microbiological preservation

of refrigerated sole and hake fillets. Food Control. 2013;34(1):61-8.
21. Nowzari F, Shábanpour B, Ojagh SM. Comparison of chitosan–gelatin composite and bilayer coating and film effect on the quality of refrigerated rainbow trout. Food Chemistry. 2013;141(3):1667-72.
22. Roberts D, Greenwood M. Practical food microbiology. Massachusetts: John Wiley & Sons; 2008.
23. No HK, Park NY, Lee SH, Meyers SP. Antibacterial activity of chitosans and chitosan oligomers with different molecular weights. International Journal of Food Microbiology, 2002;74 (1-2):65-72.
24. Devlieghere F, Vermeulen A, Debevere J. Chitosan: antimicrobial activity, interactions with food components and applicability as a coating on fruit and vegetables. Food Microbiology. 2004;21(6):703-14.
25. Noshirvani N, Ghanbarzadeh B, Mokarram RR, Hashemi M, Coma V. Preparation and characterization of active emulsified films based on chitosan-carboxymethyl cellulose containing zinc oxide nano particles. International Journal of Biological Macromolecules. 2017;99:530-8.
26. FDA. Code of Federal Regulations 21CFR73.575 for listing of color additives exempt from certification. Title 21, Volume 1. Revised as of April 1, 2014. 2014.
27. Franklin NM, Rogers NJ, Apte SC, Batley GE, Gadd GE, Casey PS. Comparative Toxicity of Nanoparticulate ZnO, Bulk ZnO, and ZnCl2to a Freshwater Microalga (Pseudokirchneriella subcapitata): The Importance of Particle Solubility. Environmental Science & Technology. 2007;41(24):8484-90.
28. Al-Naamani L, Dobretsov S, Dutta J. Chitosan-zinc oxide nanoparticle composite coating for active food packaging applications. Innovative Food Science & Emerging Technologies. 2016;38:231-7.
29. Premanathan M, Karthikeyan K, Jeyasubramanian K, Manivannan G. Selective toxicity of ZnO nanoparticles toward Gram-positive bacteria and cancer cells by apoptosis through lipid peroxidation. Nanomedicine: Nanotechnology, Biology and Medicine. 2011;7(2):184-92.
30. Rahman PM, Mujeeb VMA, Muraleedharan K. Flexible chitosan-nano ZnO antimicrobial pouches as a new material for extending the shelf life of raw meat. International Journal of Biological Macromolecules. 2017;97:382-91.
31. Razak SRA, Basri H. Chitosan-Zinc Oxide Composite for Active Food Packaging Applications. International Journal of Engineering & Technology. 2018;7(4.30):253.
32. Ummartyotin S, Pechyen C. Physico-Chemical Properties of ZnO and Chitosan Composite for Packaging Material. Journal of Biobased Materials and Bioenergy. 2017;11(3):183-92.
33. Indumathi M, Rajarajeswari G. Mahua oil-based polyurethane/chitosan/nano ZnO composite films for biodegradable food packaging applications. International Journal of Biological Macromolecules, 2019;124:163-174.
34. Indumathi MP, Saral Sarojini K, Rajarajeswari GR. Antimicrobial and biodegradable chitosan/cellulose acetate phthalate/ZnO nano composite films with optimal oxygen permeability and hydrophobicity for extending the shelf life of black grape fruits. International Journal of Biological Macromolecules. 2019;132:1112-20.
35. Applerot G, Perkas N, Amirian G, Girshevitz O, Gedanken A. Coating of glass with ZnO via ultrasonic irradiation and a study of its antibacterial properties. Applied Surface Science. 2009;256(3):S3-S8.
36. Yemmireddy VK, Hung Y-C. Using Photocatalyst Metal Oxides as Antimicrobial Surface Coatings to Ensure Food Safety-Opportunities and Challenges. Comprehensive Reviews in Food Science and Food Safety. 2017;16(4):617-31.
37. Xie Y, He Y, Irwin PL, Jin T, Shi X. Antibacterial Activity and Mechanism of Action of Zinc Oxide Nanoparticles againstCampylobacter jejuni. Applied and Environmental Microbiology. 2011;77(7):2325-31.
38. Duncan TV. Applications of nanotechnology in food packaging and food safety: Barrier materials, antimicrobials and sensors. Journal of Colloid and Interface Science. 2011;363(1):1-24.
39. Chatterjee D, Dasgupta S. Visible light induced photocatalytic degradation of organic pollutants. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 2005;6(2-3):186-205.
40. De Silva RT, Mantilaka MMMGPG, Ratnayake SP, Amaratunga GAJ, de Silva KMN. Nano-MgO reinforced chitosan nanocomposites for high performance packaging applications with improved mechanical, thermal and barrier properties. Carbohydrate Polymers. 2017;157:739-47.
41. Zhao Y, Liu B, You C, Chen M. Effects of MgO whiskers on mechanical properties and crystallization behavior of PLLA/MgO composites. Materials & Design. 2016;89:573-81.
42. Sanuja S, Agalya A, Umapathy MJ. Studies on Magnesium Oxide Reinforced Chitosan Bionanocomposite Incorporated with Clove Oil for Active Food Packaging Application. International Journal of Polymeric Materials and Polymeric Biomaterials. 2014;63(14):733-40.
43. Sawai J, Yoshikawa T. Quantitative evaluation of antifungal activity of metallic oxide powders (MgO, CaO and ZnO) by an indirect conductimetric assay. Journal of Applied Microbiology. 2004;96(4):803-9.
44. Stoimenov PK, Klinger RL, Marchin GL, Klabunde KJ. Metal Oxide Nanoparticles as Bactericidal Agents. Langmuir. 2002;18(17):6679-86.
45. Jiménez M, Ignacio Maldonado M, Rodríguez EM, Hernández-Ramírez A, Saggioro E, Carra I, et al. Supported TiO2solar photocatalysis at semi-pilot scale: degradation of pesticides found in citrus processing industry wastewater, reactivity and influence of photogenerated species. Journal of Chemical Technology & Biotechnology. 2014;90(1):149-57.
46. Kääriäinen ML, Kääriäinen TO, Cameron DC. Titanium dioxide thin films, their structure and its effect on their photoactivity and photocatalytic properties. Thin Solid Films. 2009;517(24):6666-70.
47. Kim B, Kim D, Cho D, Cho S. Bactericidal effect of TiO2 photocatalyst on selected food-borne pathogenic bacteria. Chemosphere. 2003;52(1):277-81.
48. Lin B, Luo Y, Teng Z, Zhang B, Zhou B, Wang Q. Development of silver/titanium dioxide/chitosan adipate nanocomposite as an antibacterial coating for fruit storage. LWT - Food Science and Technology. 2015;63(2):1206-13.
49. Hur J-S, Oh S-O, Lim K-M, Jung JS, Kim J-W, Koh YJ. Novel effects of TiO2 photocatalytic ozonation on control of postharvest fungal spoilage of kiwifruit. Postharvest Biology and Technology. 2005;35(1):109-13.
50. Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO2

Surfaces: Principles, Mechanisms, and Selected Results. Chemical Reviews. 1995;95(3):735-58.
51. Foster HA, Ditta IB, Varghese S, Steele A. Photocatalytic disinfection using titanium dioxide: spectrum and mechanism of antimicrobial activity. Applied Microbiology and Biotechnology. 2011;90(6):1847-68.
52. Al-Taweel SS, Saud HR, Kadhum AAH, Takriff MS. The influence of titanium dioxide nanofiller ratio on morphology and surface properties of TiO2/chitosan nanocomposite. Results in Physics. 2019;13:102296.
53. Llorens A, Lloret E, Picouet PA, Trbojevich R, Fernandez A. Metallic-based micro and nanocomposites in food contact materials and active food packaging. Trends in Food Science & Technology. 2012;24(1):19-29.
54. Noyce JO, Michels H, Keevil CW. Use of Copper Cast Alloys To Control Escherichia coli O157 Cross-Contamination during Food Processing. Applied and Environmental Microbiology. 2006;72(6):4239-44.
55. Al-Holy MA, Castro LF, Al-Qadiri HM. Inactivation ofCronobacterspp. (Enterobacter sakazakii) in infant formula using lactic acid, copper sulfate and monolaurin. Letters in Applied Microbiology. 2010;50(3):246-51.
56. Ibrahim SA, Sreekantan S. Effect of pH on TiO_2 Nanoparticles via Sol-Gel Method. Advanced Materials Research. 2010;173:184-9.
57. Nouri A, Yaraki MT, Ghorbanpour M, Agarwal S, Gupta VK. Enhanced Antibacterial effect of chitosan film using Montmorillonite/CuO nanocomposite. International Journal of Biological Macromolecules. 2018;109:1219-31.
58. Cioffi N, Torsi L, Ditaranto N, Tantillo G, Ghibelli L, Sabbatini L, et al. Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties. Chemistry of Materials. 2005;17(21):5255-62.
59. Nehra P, Chauhan RP, Garg N, Verma K. Antibacterial and antifungal activity of chitosan coated iron oxide nanoparticles. British Journal of Biomedical Science. 2017;75(1):13-8.
60. Shrifian-Esfahni A, Salehi MT, Nasr-Esfahni M, Ekramian E. Chitosan-modified superparamgnetic iron oxide nanoparticles: design, fabrication, characterization and antibacterial activity. Chemik, 2015;69 (1):19-32.
61. Yu Y, Zhang S, Ren Y, Li H, Zhang X, Di J. Jujube preservation using chitosan film with nano-silicon dioxide. Journal of Food Engineering. 2012;113(3):408-14.
62. Kou X, He Y, Li Y, Chen X, Feng Y, Xue Z. Effect of abscisic acid (ABA) and chitosan/nano-silica/sodium alginate composite film on the color development and quality of postharvest Chinese winter jujube (Zizyphus jujuba Mill. cv. Dongzao). Food Chemistry. 2019;270:385-94.
63. Tian F, Chen W, Wu CE, Kou X, Fan G, Li T, et al. Preservation of Ginkgo biloba seeds by coating with chitosan/nano-TiO2 and chitosan/nano-SiO2 films. International Journal of Biological Macromolecules. 2019;126:917-25.
64. Khezrian A, Shahbazi Y. Application of nanocompostie chitosan and carboxymethyl cellulose films containing natural preservative compounds in minced camel's meat. International Journal of Biological Macromolecules. 2018;106:1146-58.
65. El Knidri H, Belaabed R, Addaou A, Laajeb A, Lahsini A. Extraction, chemical modification and characterization of chitin and chitosan. International Journal of Biological Macromolecules. 2018;120:1181-9.