pISSN 1229-1153 / eISSN 2465-9223 J. Food Hyg. Saf. Vol. 34, No. 4, pp. 317~324 (2019) https://doi.org/10.13103/JFHS.2019.34.4.317

Review



Application of Nanoparticles in Food Preservation and Food Processing

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(Received February 4, 2019/Revised March 21, 2019/Accepted July 4, 2019)

ABSTRACT - This study focuses on the role of nanotechnology in the field of food industries. Bioactive components with antimicrobial activity against food pathogens are encapsulated into nanoparticles (NPs) to improve and extend their efficiency in food preservation. However, these NPs should be biocompatible and nontoxic for humans. Advancement in this field has resulted in the development of NPs for food packaging in some industries. The most commonly used group of NPs in the food industry is metal oxide. As metal oxide NPs such as zinc oxide and titanium dioxide exhibit antimicrobial activity in food materials, the NPs can be used for food preservation with enhanced functional properties. The application and effects of nanotechnology in correlation with the nutritional and sensory properties of foods were briefly discussed with a few insights into safety regulations on nano-based food formulation and preservation.

Key words : Nanotechnology, Nanoparticles, Food pathogens, Antimicrobial activity, Food preservation

The term "Nano" a prefix meaning "one billionth" is derived from the ancient Greek language. In 1974, the word "nanotechnology" was coined for the first time in the scientific world by Taniguchi (1974) at the International Conference on Industrial Production in Tokyo. He was a professor in Tokyo University of Science¹⁾. Nano science is the study of nanometer size materials that are below 1 micrometer $(1 \ \mu m)$ size. The nanoscale is measured in nanometers $(10^{-9}m)^{2}$. In recent years, nanotechnology is the most active research field as it has the ability to control and manipulate matter in the nano-size³⁾. Nanotechnology combines knowledge from the fields of physics, chemistry, biology, medicine, engineering, and informatics⁴⁾. Nanosized materials change their characteristic properties like conductivity, ionic structure, freezing, melting, and color, within 1-100 nm range. According to size, the materials can be categorized as macro- (50-200 µm size), micro- (1-50 µm size), and nanomaterials (1-1000 nm size)⁵⁾. Nanomaterials are used for many applications because at this scale, unique optical, magnetic, electrical, and other properties emerge⁶. Nanotechnology deals with synthesis and characterization of nanomaterials. These materials are synthesized and characterized by various methods. Nanotechnology is very fast as growing field in upcoming years, and the application of nanoparticles (NPs) on other field of biotechnology leads biomedical application⁷⁾ In addition the nanotechnology can be mainly applied as drug target and delivery, skin regeneration, etc. Naturally, existing, NPs such as minerals, catalysts and some porous materials have same different properties, particularly because of the nanoscale features⁸⁾. Most of the nano-material were extracted naturally but some of them were artificially synthesized and applied for diverging applications⁹.

Synthesis methods for nanomaterials

There are several methods for synthesis of nanomaterials, including hydrothermal synthesis, sol-gel synthesis, wet chemical synthesis, physical vapor deposition (PVD), and chemical vapor deposition (CVD)¹⁰.

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Hydrothermal synthesis

The hydrothermal technique is one of the most popular synthesis techniques. Hydro means water and thermal means heat. This technique includes water and heating process. The reaction of water at high temperature and pressure is bringing changes in nanomaterials. Water is one of the important solvent in this process. Advantage of using water in hydrothermal technique is environment-friendly and cheap. As water evaporate quickly, it can be easily removed from the product. Another advantage of this process is to be able to, get clear crystal morphology and easily reduce the particle size¹¹⁾. Autoclave is used for this synthesis (Fig. 1).

Sol gel synthesis

Sol-gel synthesis includes chemical and physical processes correlated with hydrolysis, polymerization, drying and densification of the precursors. This process generally starts with the mixing of metal oxides or salts in water or in a relevant solvent at atmospheric or slightly high temperatures¹².

Wet chemical synthesis

Wet chemical process is commonly used to synthesis the inorganic molecules. Advantage of this process is to, produce large scale of nanomaterials¹³. Wet chemical analysis, known as wet chemistry analysis, is modeled on chemically fluid stages. This method is used to reduce the particle size, since wet chemical analysis is done on a liquid samples¹⁰.

Biological applications of nanotechnology

In recent years, nanomaterials are being used in many applications. This study analyzes specifically about biological applications of nanotechnology. A list of some specific biological applications of nanotechnology has provided in Fig. 2.

Cancer therapy

Cancer is one of the major causes of death in the world. We have only limited cancer treatments like chemotherapy, radiation, and some surgery. Using nanomaterial is one of the greatest ideas for cancer therapy¹⁴⁾. Drug targeting, selectivity and greater delivery efficiency are the major challenges in cancer therapy. A therapeutic drug would be selectively targeted to cancer cell, which will enhance the treatment of cancer with small damage to normal tissues¹⁴⁾. The nanomaterials are used as the drug carrier to the cancer cells and used to reach easily to the affected cells. Another advantage is to avoid drug delivery to normal sites and reduce the side effects¹¹⁾.

Smart drug delivery system

In drug delivery system, one may design different delivery systems for enriched therapeutic efficiency without side effects. Smart drug delivery system has several advantages compared to other drug delivery systems¹⁵⁾. The other drug release systems are based on the predetermined drug release rate irrespective of the environmental condition at the time of application. But Smart drug delivery system is based on the release-on-demand strategy. The major advantages on drug Nano based delivery system (Fig. 3), depends on low dosage, specific target¹⁶⁾.

Magnetic resonance imaging (MRI) contrast enhancement

In MRI scan, magnetic NPs have been used as a contrast agent^{17,18}). NPs are used to improve the quality of the image. NPs made up of the elements like iron (Fe), gadolinium (Gd) or manganese (Mn) are currently used as a contrast agent in MRI¹⁸). MRI scanners regenerate images from the electromagnetic signals.

Gene therapy

The use of nanotechnology in gene therapy is currently used to replace virus vectors. The transfer of genes can introduce ethical products successfully. The use of NPs has lot of advantages in gene therapy. Normally NPs retain genetic leap for a long time when compared to other vehicles¹³.

Nanoparticles for food preservation

Silver nanoparticles

Using leafs of Protiumserratum, silver nanoparticles (AgNPs) are synthesized. Bryaskova et al. showed effective antibacterial activity against foodborne pathogens like Pseudomonas aeruginosa (IC₅₀=74.26±0.14 mg/mL), Escherichia coli (E. coli) (IC₅₀=84.28±0.36 mg/mL), and Bacillus subtilis $(IC_{50}=94.43\pm0.42 \text{ mg/mL}^{19-21})$. Mohanta et al. reported the antioxidant activity of AgNPs based on the 1,1-diphenyl-2picryl-hydrazil (DHHP) is IC₅₀=6.78±0.15 mg/mL and hydroxyl radical assay (IC₅₀=89.58±1.15 mg/mL²²⁾. The biocompatibility activity of AgNPs do not inhibit fibroblast cell line (L-929) at lower concentration but increase in concentration result in cell viability decline²³⁾. The IC_{50} values against normal cell line L-929 is 600.28±0.75 µg/ml and it does not show any cytotoxicity activity against cell Line L-929. The above results suggested that AgNPs can be used in food package and preservation along with pharmaceutical and biomedical application²⁴⁾. AgNPs were synthesized using aqueous extract of Jatropha curcas (Jc-AgNPs) and it showed potential activity against foodborne pathogens such as E. coli (ZOI: 23 mm, MBC: 0.010 mg/ mL), Staphylococcus aureus (ZOI: 14.66 mm, MBC: 0.041 mg/mL), Salmonella enterica (ZOI: 16.66 mm, MBC: 0.041 mg/mL)²⁴⁾. Silver nanoparticles were synthesized from white radish (Raphanussativus var. aegyptiacus) and it is exposed to snails (Eobaniavermiculata) and solid matrix in laboratory experiments which results in reducing the viability of land snails (about 20% of snails dies when treated with silver nanoparticles). It also reduced the fungal population in a solid matrix⁶. Using culture supernatant of Serratia sp. BHU-S4, silver nanoparticles were synthesized and it showed potential antifungal against Bipolarissorokiniana, the spot blotch pathogen of wheat²⁵⁾. The three main important advantage of nanomaterials are 1) size less than 100 nm. 2) Small size particles with unique properties 3) Controlling the structure, function and composition we can control the properties. Size and surface area will change depending on solvent used.

Nanomaterials in food packing

Using targeted nano-carriers, we can reduce the toxicity and the efficiency of distribution²⁶. Micelles size of about 5-100 nm diameter (sphericalshape) has the capacity to encapsulate the nonpolar molecules like lipids, flavorings, antimicrobial, antioxidant and vitamins²⁷. The use of nanoparticles can develop the mechanical and heat resistance properties of food packaging and this lead to increase in the shelf-life by disturbing water vapor or gas permeability. For examples, polymers are not naturally impermeable to water vapor or gas but polymer silicate nanocomposites have the ability to develop gas barriers, the heat resistance and the mechanical strength properties of food packaging¹⁹⁻²¹.

The addition of montmorillonite (3-5%) into nanocomposite construction makes plastic lighter, more thermal stability, increased barrier properties of oxygen, carbondioxides, moistures, and volatiles. The addition of nanoclays into poly (lactic acid) biopolymers and into ethylene vinyl alcohol copolymer increases barricade properties of oxygen and water vapor which lead the increase the shelflife period of food products²⁸⁾. In recent days, lipids, carbohydrates, and proteins are used for creating films and coatings. This Nano-laminates (which consist of 2 or more layers of nanomaterials that physically or chemically bonded to each other) are used as coating materials on the surface of food because of their maximum thin nature that makes them very fragile²⁹⁻³¹.

Carbon based nanomaterials

Huang et al. have described the function of carbon

nanotubes for crystallization of proteins and building of bioreactors and biosensors³³⁾. Deposition of silver on nanoparticles of titanium dioxide boosts its bactericidal effects against *E. coli*³⁴⁾. Since nanomaterials have high surface area, it can easily bind to the food packing. Food industries use nanomaterials for application like against food spoiling microorganisms. For packaging nanomaterial like reduced Graphene oxide are used in food industries. Titanium dioxide combined with carbon nanotubes considerably enhances disinfectant properties against Bacillus cereus spores³⁵⁾. Nanotubes can are also used in food industry for analytical functions such as membrane separation of biomolecules (proteins, peptides, vitamins, or minerals) and molecular detection (enzymes, antibodies, various proteins, and DNA)^{36,37)}.

Zinc oxide nanoparticles

Tayel et al. synthesized zinc oxide nanoparticles and analyzed their antibacterial activity against foodborne pathogens³⁸⁾. Two different antimicrobial tests such as Determination of the Minimal Inhibitory Concentrations and Paper Disc Diffusion Assay. ZnO nanoparticles inhibit *Salmonella typhimurium* (22 mM), and inhibit *S. aureus* (10 mM). Increase in zinc oxide nanoparticles increases the probability of nanoparticles attaching to *S. typhimurium* and *S. aureus* cells.

Silver nanoparticle in food packaging

Nishimaet et al. synthesized the sodium benzoate functionalized silver nanoparticle from silver nitrate³⁹. As compared to sodium benzoate, sodium benzoate functionalized silver nanoparticles show high antibacterial activity against foodborne pathogenic bacteria such as *E. coli, S. aureus, S. typhimurium type 2, Bacillus cereus.* So these can be used for food packaging by applying permutable concentration of sodium benzoate functionalized silver nanoparticle silver nanoparticle. These can lead to high yield as well as easy to produce with low cost.

Munish et al., synthesis one pot synthesis of sodium acetate functionalized silver nanoparticles from silver nitrate by using capping as well as reducing agent of sodium acetate⁴⁰. These have good antimicrobial agent for food preservative by using permitted concentration of silver nanoparticle against different bacteria like *E. coli*, methicillin-resistant *S. aureus* (MRSA), *P. aeruginosa*, and *Klebsiella pneumonia*. These are food borne pathogens. These can be characterized using UV-Visible absorption spectroscopy, dynamic light scattering, zeta potential, fourier transform infrared (FT-IR) spectroscopy, and transmission electron microscopy (TEM).

The natural nanoparticles are mainly used to control the growth of food spoiling pathogen. Silver nanoparticles play a remarkable role in bio-textiles, electrical appliances, refrigerator, and kitchenwares. The ions present in silver nanoparticles have a capacity to suppress the diverse range of biological process in bacteria⁴¹⁾.

The zinc nanoparticles synthesized from leaf extract of *Moringaoleifera*showed effective antibacterial activity against certain bacterial strains like *S. aureus, B. subtilis, P. aeruginosa, Proteus mirabilis, E. coli* and fungal strains such as *Candida albicans* and *Candida tropicalis.* Zone of inhibition is maximum for *S. aureus* of about 23.80.76 when compared to others⁴²⁾. Zinc nanoparticles synthesized from *Partheniumhysterophorus* shows strong antifungal activity against plant fungal pathogens such as *Aspergillus flavus* and *Aspergillus niger*. The maximum zone of inhibition is 275 nm⁴³⁾.

Zinc nanoparticles synthesized from leafs of Catharanthusroseus (L.) showed potential antibacterial activity against gram negative bacteria E. coli (ATCC 25922), P. aeruginosa (ATCC 15442), gram positive S. aureus (ATCC 6538) and B. thuringiensis (ATCC 10792). The result suggested that P. aeruginosa was more susceptible and *B. thuringiensis* was highly resistant to zinc nanoparticles^{44,45)}. The antibacterial activity of zinc nanoparticles demonstrated against gram positive bacteria such as B. subtilis and S. aureus reveals that they are sensitive to this nanoparticle⁴⁶. Xieet al., showed that zinc nanoparticles are highly potential antibacterial against certain gram negative bacteria like P. aeruginosa, C. jejuni and E. colt⁴⁷⁾. Zinc nanoparticles also showed potential antifungal activity against **Botrvtis** cinerea and Penicilliumexpansum in higher concentration than 3 mmol/ L. This result suggests that P. expansum is more sensitive than *B*. $cinerea^{47}$.

Titanium dioxide having a particle size of not more than 100 nm is extensively used as an antimicrobial agent and food additive for storage containers and food packaging⁴⁸⁾. Silver nanoparticles are potentially used as antimicrobial agents in food packaging, storage containers, chopping boards and refrigerators and also as a health supplement⁴⁹⁾. Zinc and zinc oxide are effectively used as antimicrobial agents in food packaging and also as nutritional additives⁵⁰⁾. Ana Raquel Madureira et al used chitosan nanoparticles against for food pathogens⁵¹⁾. He prepared chitosan nanoparticles coated with polyphenols and used for antioxidant, antibacterial activity. Chitosan nanoparticles have shown to affect bacterial cell wall.

Silicon dioxide and carbon having a particles size of few hundred nm in size are used as food additives and for food packaging⁵²). Platinum and gold nanowires are broadly used as biosensors for advanced food analysis⁵³. Zou et al.,

confirmed that the effective use of nisin loaded liposomal nanoparticles antibacterial activity against L. monocytogenes and S. aureus⁵⁴⁾. Prombutara et al., 2012 also the studied the antimicrobial activity of nisin free and nisin loaded lipid nanoparticles⁵⁵⁾. Their result revealed that strong and stable antimicrobial activity was seen in nisin load nanoparticles against L. monocytogenes DMST 2871 compared to free nisin, representing that nisin is released from the nanoparticles throughout the storage periods. Naturally occurring phenolic compound delivered by nanoparticles confirmed to be an effective antibacterial agent against L. monocytogenes in raw and cooked meat system⁵⁶). Improved antibacterial activity of nano-dispersed eugenol against E. coli O157:H7 and L. monocytogenes was observed in bovine milk. Thymol containing nano-dispersed also have an effective role in food application against food borne pathogen⁵⁷⁾.

Enzymes incorporated with gold nanoparticles are effectively used in detecting microbes and gas in order to observe the food condition. Nano fibril of berylline-based fluoro pores plays a potential role in indicating the meat and fish spoilage by detecting gaseous amines. For the detection of the volatile organic compound, zinc oxide and titanium oxide nano composites are used. For the tagging and security purpose nano-barcodes are used58). Commercial names like nanoceuticals and nutrition-be-nanotech are marketed for supplements. In order to increase the absorption of nutrients, nano-sized powders are used. Nano cochleae are used as a potential tool for nutrient delivery into the cell without losing the color and taste of food products. Vitamin sprays disperse Nano droplets are essential for better absorption of nutrients. Encapsulation techniques with iron and zinc Nano structured capsule are mostly involved in supplement aspects which are essential for probiotic and other products targeted at the human systems^{59,60)}. Ruengruglikit et al., has created an electronic tongue which consists of several nano sensors that are extensively used to detect the gases emitted by the spoiled food⁵⁷⁾. This spoiled food causes sensor strips to change the color that indicates whether food is fresh or not. Using nanotechnology, an analytical technique called reflective interferometry was developed and used for the food quality assurance by detecting the E. coli in food sample by measuring and detecting light scattering by mitochondria⁵⁷⁾. Colorimetric assays, based on the fact that aggregated AuNPs are blue in color while dispersed solutions of AuNPs display a red color were developed for the monitoring of S. typhimurium⁵⁵⁾ and multiple drug resistant S. typhimurium DT10455).

The Piezoelectric biosensor is developed from the electric properties of gold nanoparticles which are used for the realtime detection of foodborne pathogens like *E. coli* 0157:H7. The principle behind this sensor is to target specific ssDNA- functionalized Au NPs bound firstly to the target DNA and subsequently to a complementary probe immobilized onto the piezoelectric biosensor surface resulting in a frequency shift of the piezoelectric biosensor. Concentrations as low as of 1.2×10^2 CFU/mL of *E. coli* O157:H7 were detectable⁴⁵⁾. Quantum Dots have been used as fluorescent labels in numerous assays for the detection of food borne pathogens such as *L. monocytogenes*⁵⁷⁾, *C. jejuni*⁵⁸⁾, *E. coli* O157:H7⁴⁶⁾, *S. typhimurium*⁶⁰⁾, *S. aureus*⁵⁴⁾ and *Shigella flexneri*⁵⁷⁾.

Yiping et al. synthesized magnesium oxide nanoparticles with small particle size, with high antibacterial activity against some food pathogens⁶⁰. Micro plate assay is used for measuring growth zone in magnesium oxide nanoparticles. It showed growth inhibition for different concentration and different bacteria, 10^4 CFU/mL of *C. jejuni, E. coli* O157:H7, and *S.* Enteritidis were determined to be 1, 2, and 0.5 mg/mL, respectively. To completely inactivate 10^{8-9} CFU/mL bacterial cells in 4hrs, a minimal concentration of MgO nanoparticles was required 2 mg/mL for *C. jejuni* whereas that was required at least 8 mg/mL for *E. coli* O157:H7 and *S.* Enteritidis.

Biosensors

The detection and quantification of glucose, an electrochemical glucose biosensor is used. The biosensor is nanofabricated by layer-by-layer self-assembly of polyelectrolyte⁶¹⁾. Liposome nano-vesicles are extensively applied for detecting peanut allergenic protein in chocolate⁶²). An immunogenic sandwich assay and universal G-liposomal nano-vesicles are potentially used for the detection of E. coli O157:H7, Salmonella spp., and L. monocytogenes⁶³. Quantum dots (fluorescence marker) coupled with immune magnetic separation is used as a sensitive and rapid method for the detection of E. coli O157:H764).

An electronic nose is a device which is used for detection of diverse types of odors. The device majorly consists of gas sensors that are composed of zinc oxide nanowires⁶⁸. Using polydimethylsiloxane (PDMS) chip coupled with fluid bilayer membrane is potentially used for immune-sensing of *Staphylococcus* enterotoxin B (SEB) in milk. Antibodies to the enterotoxin were attached to the bilayer membrane in PDMS channels from a biosensor⁶⁵⁾. A gold nano particle coated quartz crystal microbalance based DNA sensor has been reported for the detection of *E. coli*. The use of nanoparticles amplifies the signals and improves the detection limit of pathogenic bacteria⁶⁶⁾.

Nanoparticles have a number of applications in biology¹⁹⁾. Researchers have developed nanomaterial based sensor using nanoparticles like metal oxide, quantum dots and carbon nanotubes to detecting for

foodborne pathogens. It can easily detect food contamination induced by bacteria or any microorganisms. These nanoparticle easily bind with the microorganisms by using sensors. PalanivelVelmurugan et al synthesized silver and gold nanoparticles with 10-20 nm of particle size using and ginger rhizome extract, for antibacterial activity and in deducting for food pathogens⁶⁷⁾. In the synthesis of Au and Ag nanoparticles, different parameters like pH, temperature, reaction time are controlled for adjusting the size and shape of the nanoparticles. These nanoparticles have antibacterial activity at the concentration of 30 ± 14.3 and $20\pm12.8 \ \mu g/mL$ against spp. respectively, however, no inhibition was observed against Bacillus spp.

The role of metallic nanoparticles in the food industries

Silver nanoparticles (AgNPs) were synthesized using aqueous extraction method from corn waste (corn leaf of Synthesized nanoparticles Zea mays). showed antibacterial activity against foodborne pathogens such as B. cereus, L. monocytogenes, S. aureus, E. coli, and S. Typhimurium. The minimum inhibitory concentration (MIC) and MBC of AgNPs against the foodborne pathogens are about 12.5 to 100 µg/ml. When antibiotics (kanamycin and rifampicin) and AgNPs are used to study the synergistic antimicrobial activity, the zone of inhibition ranges 10.62 to 14.33 mm in diameter against all pathogens. Similarly, antibacterial agent and AgNPs were used to investigate the synergistic antibacterial activity, which showed 9.74 to 14.75 mm of inhibitory zone against several Candida species such as C. albicans, C. glabrata, C. geochares, and C. saitoana⁶⁷).

Conclusion

This study reviewed applications of nanoparticles used in the food industries. Mainly metal oxide nanoparticles are used to prevent food contamination for the reduction of food pathogens. Nanoparticles with high surface area and size modification can be used for multiple applications. Some nanoparticles are used for sensor application to detect food pathogens. They easily detect food contaminating microorganisms. We can use nanoparticles and thin film for biosensor to easily detect the foodborne pathogens. Different nanoparticles like gold, silver, zinc oxide, titanium oxide, graphene oxide are used in commercial products to control foodborne pathogens. Biosensors made of thin films are also used for the detection of food pathogens. 322 Prakash J. et al.

Acknowledgement

The author acknowledges Department of Nanotechnology, SRM University and Crystal Growth Centre, Anna University for the support.

국문요약

본 리뷰 논문은 식품 산업에서 나노 기술의 활용에 관 한 보고이다. 식품 병원균에 대한 항균 활성을 갖는 생리 활성 성분은 식품 보존시 효율성을 향상시키고 보존성을 증진시키기 위해 나노입자(NPs)로 캡슐화된다. 그러나, 이 러한 NPs는 인간에게 생체 적합성과 무독성을 지녀야 된 다. 식품 보존분야의 발전은 일부 산업 분야에서 식품 포 장용 NPs의 개발을 가져왔다. 식품 산업 분야에서 식품 포 장용 NPs의 개발을 가져왔다. 식품 산업 분야에서 가장 일 반적으로 사용되는 NPs 그룹은 금속 산화물이다. 산화 아 연과 이산화 티타늄 같은 금속 산화물 NPs는 식품 재료에 서 항균 활성을 나타내기 때문에, NPs는 강화된 기능적 특 성으로 식품 보존에 사용될 수 있다. 식품 영양과 관능적 특성과 관련된 나노 기술의 적용은 나노 기반 식품 제조 및 보존에 관한 안전규제를 중심으로 간략하게 정리하였다.

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