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Relevance of Nanomaterials in Food Packaging and its Advanced Future Prospects

Pallavi Chaudhary[1] · **Faria Fatima**[1] · **Ankur Kumar**[2]

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Abstract

Biopolymers have been used in packaged foods to tackle environmental hazards due to their biodegradability and non-toxic nature. In addition to these merits, they have also several demerits such as poor mechanical properties and low resistance towards water. Nanomaterials have attracted great interest in recent years due to their phenomenal properties that makes them precedent in applications for food packaging as they enhance the mechanical, thermal and gas barriers properties, without compromising with the ability to become non-toxic and biodegradable. The most important nanomaterials used in food packaging are montmorillonite (MMT), zinc oxide (ZnO-NPs) coated silicate, kaolinite, silver NPs (Ag-NPs) and titanium dioxide (TiO_2NPs) as these, nanomaterials coated films makes a barrier against oxygen, carbon dioxide and favour compounds. They also possess oxygen scavenging capability, antimicrobial activity and tolerance towards temperature. The most difficult task related to the preparation of these nanocomposites is their complete distribution within the polymer matrix and their compatibility. Therefore, there is an increasing demand for improvement in the performance of nano-packaging materials including mechanical stability, degradability and effectiveness of antibacterial property.

Keywords Antimicrobial activity · Bio-nanocomposites · Biopolymers · Nanomaterials · Packaging · Preservation

1 Introduction

After its introduction by Richard Feynman in 1959, nanotechnologies have been a challenging field of research and development [1]. According to Persistence Market Research report in 2014, it was estimated that up to 400 companies in the world are making use of nanotechnology [2]. At the heart of research, this area involves the synthesis, characterization, modelling and applications of novel materials known as nanoparticles (NPs) with nanometre-scale ranging from approximately 1 to 100 nm [3]. The threshold value of these NPs gets lower due to its smaller size, resulting in the processed material being entirely different from the properties of macro-scale materials. These nanomaterials also exhibit novel optical, physical, and chemical features [4, 5]. Moreover basic properties of materials such as flexibility, durability, flame resistance, barrier properties, or recycling properties can be further modified with the addition of different nanomaterials [6] due to which they are getting advanced with their wide applications in electronic, optical, magnetic devices, biology, medicine, energy, defence and so on. Additionally their developments in food packaging sector are also growing day by day [7, 8]. Recently, studies based on their mode of synthesis, characterisation, applications and evaluations have encouraged scientific advancement to expand and alter the entire food sector [9, 10]. Although it is a newly emerging technology, it is forecast to develop steadily in the coming era [11].

2 Nanomaterials

From the ancient time, the nanomaterials were naturally implemented as well as intentionally added by man i.e., arises either from naturally occurring or from engineered material sources [12]. For example, in animals, nanoscale components like casein micelles produce in milk showed dimensions of 300 to 400 nm [13, 14], while in plants

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✉ Faria Fatima
fatimafaria45@gmail.com

[1] Department of Agriculture, IIAST, Integral University, Kursi Road, Lucknow, Uttar Pradesh, India

[2] Department of Horticulture, Sardar Vallabh Bhai Patel University of Agriculture and Technology, Meerut, Uttar Pradesh, India

they contain pectin nanostructures in fruit show polymer chain length about 100 to 400 nm [15]. The food industry, on the other hand, is experiencing a variety of engineered nanomaterials in development. For example, nanometer salt grains were developed to reduce the consumption of salt by increasing its surface area and, as a result, a small amount of nanosalt may give the same original savoury taste to humans [16]. They are used to include nutrients in food, drinks, and supplements without altering their taste or appearance. In addition, one of the main benefits of nanomaterials is that it also acts as carriers for vitamins or minerals via encapsulation process. Nanocapsules already transmit vitamins via the human stomach through the bloodstream [17].

It was reported that nanomaterials with stronger packaging barriers maintain food quality during shipping, prolong fruit and vegetable freshness during storage, and sustain meat or poultry from pathogenic microbes. Thus due to their exceptional barrier, mechanical and heat resistance properties, they represent a novel alternate solution of additives to improve the polymeric properties of food packaging materials [18, 19].

3 Materials Used in Food Packaging

Packaging is a key component of each stage of the food industry, but its permeability is the main defect in traditional food packaging materials as there are no packaging materials that are fully atmospheric and water vapour resistant [20]. In addition, participants together with the food supply chain are seeking cost-effective, innovative, environmentally friendly and resourceful food packaging alternatives to protect and monitor the quality of packaged foods, which can only be made possible by committed food safety, quality and its durability. As a result, several main factors drive the continuous discovery of innovative food packaging materials [21, 22] that facilitate the handling, transportation, and protection from environmental contamination, and also influence the increased demands of consumers for nutritious and high-quality food products [23, 24]. Till date, the maximum use of plastics, glass, and metals in packaging applications serves as non-biodegradable materials which have raised anxieties about atmospheric pollution thus suggesting a serious problem on the universal environment [25]. Consequently, some bionanocomposite materials can be developed having different functional characteristics used in food packaging. This green packaging growth, including plant extracts, biodegradable edible materials and nanocomposite materials, has established potential for reducing the negative environmental impacts. The products used for foodstuff packaging are given.

3.1 Biopolymers

Biopolymers have been introduced as renewable packaging materials and alternatives for petroleum-based polymers, including polysaccharides (starch and cellulose derivatives, chitosan, and alginates), lipids (bees and carnauba wax, and free fatty acids), proteins (casein, whey, and gluten), poly hydroxyl butyrates (PHB), polylactic acid (PLA), poly caprolactone (PCL), polyvinyl alcohol (PVA), poly butylene succinate and their biopolymer blends. Due to the development of precursors, the glycolic acid, the polyglycolic acid (PGA) has received particular attention via natural metabolic path [26]. Their mechanical strength and the properties of oxygen and moisture barriers can be adapted for packaging applications on the basis of efficient compounding and processing [27]. Most biopolymers can have problems with their handling due to their relatively high molecular weight, viscosity, hydrophobicity, crystallization activity, fragility or melting nature, which uncertainly delays their maximum industrial use. As a consequence, it is found to be effective in conjunction with other biopolymers, plasticizers and compatibilizers. Nonetheless, the barrier properties and mechanical rigidity/strength of native biopolymer films are often inferior for packaging applications and should be modified by grafting or coating mechanisms by means of physical cross-linking or surface modifications [28].

3.2 Paper as Packaging Materials

Paper is commonly used to label foodstuffs. In general it reflects as the most beneficial choice as packaging materials because of its low price and weight, comprehensive availability, printability and strong mechanical properties. Its key downside is exposure to humidity and moisture absorption [29]. Interestingly, the paper products were increasingly treated in combination with a layer of biopolymer coating to enhance their barrier properties hydrophobicity, and functionality [30] that can be done by surface treatment of mixing biopolymers [31].

3.3 Glass and Metals as Packaging Materials

Glass and metals and are also fully resistant to gasses and vapours, thus providing an effective barrier to the exchange of materials between the air inside the kit and the external atmosphere [32]. Gasses and vapours can move within the packaging material either through molecular diffusion or through pores and holes present. Thus coatings using deposition of atomic layers will enhance the barrier properties of bio-based packaging materials while resistance to humidity should be enhanced by hydrophobic surface treatments [33].

4 Advancement of Nanomaterials over Synthetic Chemicals

Currently, a wide range of engineered nanomaterials have been introduced in food packaging as functional additives including silver NPs (AgNPs), nanoclay, nano-zinc oxide (nano-ZnO) [34] nano-titanium dioxide (nano-TiO_2), titanium nitride NPs (nano-TiN) etc. [35]. Due to the variations in characteristics and chemical structure, each nanomaterial possesses different properties for the host material, resulting in different practical applications for packaging [36]. Several nanomaterials like zinc oxide and titanium dioxide are often used as photocatalyst agent to degrade organic molecules and microorganisms whereas AgNPs, nano-clays, layered silicates can be used as antimicrobial agents [37]. The photocatalytic reaction of nano-ZnO and nano-TiO_2 contributes to reactive oxygen species (ROS) production, resulting in cytoplasm oxidation of bacterial cells and resulting in cell death (Fig. 1) [38]. It was also reported that ZnO is relatively more efficient and attractive over AgNPs due to its less toxicity and cost effectiveness [39]. Nano-TiN, a food contact material approved by the European Food Safety Authority (EFSA 2012), is usually synthesized in a nitrogen-containing gas at high temperature with heating of TiO_2 particles [40]. This nanomaterial is widely used for mechanical strength and processing aid particularly for polyethylene terephthalate (PET) [41].

5 Nanomaterials Used in Food Packaging

5.1 Silver NPs (AgNPs)

Silver has been used as an antimicrobial agent for protection of food and beverages for many years. In ancient times, wine and water were placed in silver barrels, and at the bottom of the bottles were mounted silver dollars or silver spoons to preserve liquids like milk or water for travellers [3]. AgNPs are usually metallic silver intended for sterilization and possess antimicrobial, anti-yeasts, anti-fungal, and anti-viral activities as they have a larger surface area per mass compared to micro-scale silver particles or bulk silver content [42–45]. Additionally, AgNPs can bind to the surface of the cell and degrade lipo-polysaccharides, thus forming a pit within the cell membrane. The integration of AgNPs into plastic polymers for packaging can be implemented in several different methods. For example, silver ions can be deposited or trapped in the porous zeolite, and these materials can then be applied to plastics. It has been reported that AgNPs and ZnO-NPs containing low density PE (LDPE) can preserve and prolong the shelf life of orange juice. This active-nanocomposite has been shown to be highly effective as antimicrobial nanomaterial in combination with heat treatment [46].

5.2 Nanoclay

Nanoclay was the first material to appear on the market among the polymer of nano-composites and has been the most commonly used nanomaterials in food packaging [47]. It is commonly used for improving the physical properties

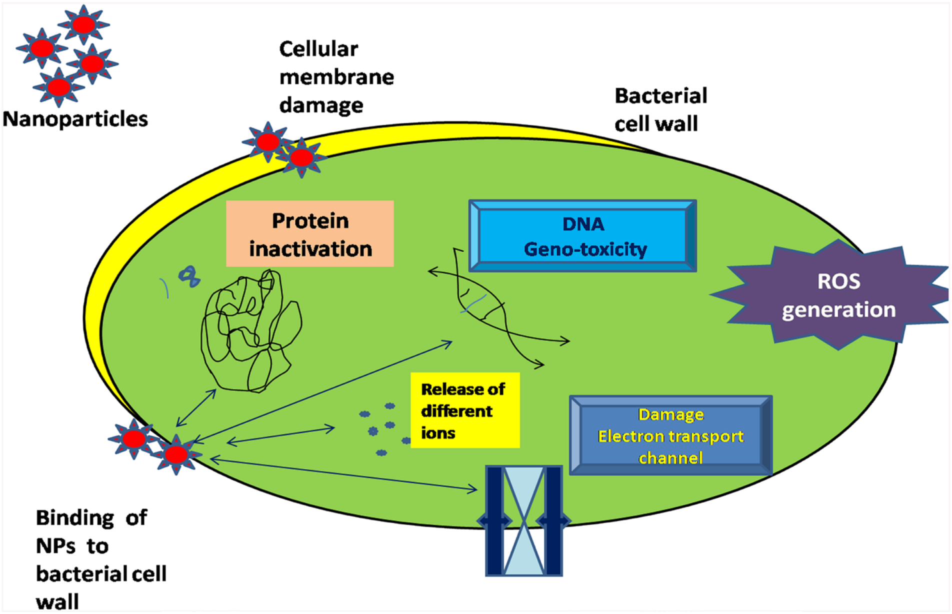

Fig. 1 Schematic representation of antimicrobial mechanisms of NPs

of plastic packaging and its barriers to gas and moisture. An example of nanoclay, Montmorillonite (MMT) consists of an octahedral edge-shaped sheet of aluminium hydroxide among dual layers of tetrahedral silica. Due to its excellent cation exchange efficiency, wide surface area and good swelling behaviour, it has been extensively used in polymer composites [48]. MMT is derived from volcanic ash and rocks, and is therefore readily available in nature and fairly cheap [49]. They are usually produced in the form of platelet clusters. Thus, high shear or sonication techniques are required to disaggregate them and evenly distribute them within the polymer matrix. The pattern of nanoclay dispersion in the polymer matrix is classified into three categories: tactoid, intercalated, or exfoliated. Nevertheless, due to its poor compatibility with polymers, it is unusual to find a tactoid structure inside a nanocomposite. Additionally, the agglomeration of clay platelets with a tactoid structure results in a low aspect ratio and a high barrier structure [50]. Normally, nanoclay composites have an intercalated or exfoliated pattern, depending on the degree of NPs dispersion in the polymer matrix. Exfoliated nanoclay clusters readily lose their tendency to agglomerate and are separated into single flakes, thereby facilitating dispersion of the NPs in a polymer matrix. The intercalated method makes only a moderate level of dispersion of clay into the polymer matrix. Therefore, exfoliated NPs show the best barrier properties and reinforcement [51]. Nanoclay is generally recognized as an essential filler for bio-based polymer reinforcements as it can enhance barrier properties, frame, creep resistance and provide mechanical strength of bio-polymer with very low clay content while biodegradability remains intact [52, 53]. It has been described bio-composite films prepared with Agar and Nanoclay (Cloisite-Na$^+$) and demonstrated that nanoclay greatly influences tensile strength, water vapor permeability, and hydrophobic behavior of agar films [54]. Nanopaper that consists of montmorrilonite nanoclay, nanofibrillated cellulose and chitosan were also developed [55]. As a result, this nanocomposite material, due to the molecular clay platelet, showed low oxygen transmission rate, excellent mechanical properties (i.e., modulus, strength and toughness) and fire retardancy.

The application of nanoclay to food packaging began in the 1990s [56]. One of the examples of commercial nanoclay composites is Durethan® KU2-2601, which is the trade name of a nanoclay-engineered polyamide film developed by Bayer [57] and commercialized under Lanxess Deutschland [58]. It is used in variety of markets and applications including medical and food packaging films. Durethan® KU2-2601 is comprised of clay platelets distributed throughout the polymer matrix that act as a barrier [59].

Due to its superior characteristics, it is extensively used for beverage packaging as well. In the past, plastic bottles did not adequately retain the gas and the flavour of beer or soda because of their poor gas barrier property. However, this challenge has been overcome by integrating nanoclay into the polymer matrix. Voridian, a division of *Eastman Chemical* that specializes in the manufacture of PET, in collaboration with Nanocor, a subsidiary of Illinois-based AMCOL International that specializes in nanoclay material, has developed Imperm® which is composited with nanoclay and MXD6 resin (nylon6 polymer from Mitsubishi Gas Chemical Company, Inc. [60]. This new resin has been produced as mono- and multi-layer films, as well as multilayer co-injection PET bottles for sensitive beverages such as beer, 100% juices, flavored alcoholic beverages and specialty waters [61].

5.3 Nano Zinc-Oxide (ZnO-NPs)

ZnO-NPs also exhibit diverse morphologies and shows robust inhibition against growth of broad-spectrum bacterial species [62]. ZnONPs are widely used in cosmetics, medical devices, medication delivery and atmospheric processed (MAP) packaging. It has been reported that ZnO nanostructures perform better against *E. coli, Bacillus atrophaeus*, and *Salmonella aureus* than other metal oxides [63]. Compared to AgNPs, ZnO-NPs is particularly attractive for packaging applications because it is more affordable and less toxic to animals and humans [39]. Moreover, under UV irradiation, ZnO can produce a great amount of hydrogen peroxide, which can cause oxidative stress in bacterial cells. Mizielinska [64] studied the effect of UV rays on the mechanical and antimicrobial properties of PLA/ZnONPs films against tested pathogenic microorganisms. Several experiments indicate that zinc ions playa a major role in inhibiting the growth of bacteria, i.e. bacteriostatic, rather than destroying bacteria, i.e. bactericidal [65].

Song-Sing Nano Technology Co, Ltd. (Taiwan) plastic wrap containing ZnONPs is intended for food and beverage packaging [66]. Additionally, several researchers are researching the effectiveness of these NPs for applications in packaging of food products. It has been reported that the antibacterial activity of ZnO-NPs on *Salmonella typhimurium* and *Staphylococcus aureus* in ready-to-eat poultry meat [67] and the potential activity of these nano-ZnO-NPs can protect the food from bacterial contamination [68]. Furthermore, to assess the decay rate of fresh cut apples, several indices are also used such as malondialdehyde (MDA), ethylene, polyphenol oxidase activity, and pyrogallol peroxidase (POD) activity. Under UV irradiation, ZnONPs can oxidize ethylene into H_2O and CO_2 and reduce accumulation of MDA, polyphenol oxidase activity and POD activity. By this mechanism, MAP with PVC–ZnO-nano-composite films can be used to extend the shelf life of commodities.

5.4 Titanium NPs (TiO_2-NPs/TiN-NPs)

TiO_2-NPs are among the most explored materials, are considered as valuable metal oxide nanomaterials with thermo-stability and inertia. The material also has the ability to modify the properties of biodegradable films, cheap, nontoxic, and photo-stable. Since TiO_2 became approved by the USFDA in 1996 as a food additive and for food contact material [69], food packaging uses it routinely as a whitener or photo catalyst for economic and environmental fields such as water and air purification, antimicrobial, self-cleaning structures and water filtering [70]. Although, TiO_2 is inert and non-toxic to human, it can oxidize the unsaturated poly-phospholipid component of a microbial cell membrane, thereby resulting in a biocidal effect. Several studies performed on the antimicrobial effects of TiO_2 suggested that, under sunlight or ultraviolet light, TiO_2 also generates reactive oxygen species such as superoxide anions, hydrogen peroxide, and hydroxyl radicals, which directly damage microbial cell walls [71, 72].

Another function of TiO_2 typically applied in food packaging is as a pigment and coating additive. The white TiO_2 particles effectively scatter visible light, thus giving the coated object whiteness, brightness, and power. For pasteurized milk packaging, PET and co-extruded HDPE bottles are usually combined with TiO_2NPs to reduce the adverse effects of light on milk quality [73]. As a thin coating in solid form, TiO_2 is non-volatile, non-flammable, completely inert and totally insoluble in all foods and food substances [74]. As of May 2011, the European Food Safety Authority (EFSA) has licensed one of the most popular titanium-based products, titanium nitride (TiN), for use in certain food contact plastics (European Food Safety Authority, 2012). Nano-TiN is typically found in PET bottles and PET thermoforming trays as nucleating agents or reheat additive. By adding its very small amounts, PET can accelerate its crystallization rate, while larger amounts can improve the abrasion resistance and impact resistance [75].

5.5 Nano-Starch

Starch is a natural, renewable, biodegradable, and non-toxic polysaccharide and has been widely involved in food, paper-making, pharmaceuticals, rubber, plastic, and packaging materials due to its low cost, environmental friendliness, and abundant supply [76]. In general, starch occurs in the form of discrete and partially crystalline granules mostly composed of two glucosidic macromolecules, named linear amylose and branched amylopectin. To produce nanostarch, it is important to separate crystalline starch from the amorphous and crystalline complexes. Several methods are used for processes of amylose extraction, such as enzyme hydrolysis [77], acid hydrolysis [78], precipitation [79], and mechanical micro-fluidizer treatment [80].

In the cycle of acid hydrolysis, the starch is incubated at a level below the starch gelatinization point in mild acid. The acid molecules target the amorphous regions because these areas are hydrolysed more rapidly than that of the crystalline domains. As a consequence, an almost pure crystalline residue is extracted which is used in platelet implementations on a nanoscale [81]. Particularly, starch nano-crystals proved to be promising fillers for flexible food packaging because they impart enhanced mechanical and barrier properties as it is highly susceptible to hydration [82]. These undesirable behaviours of starch can be reduced or eliminated by reorganizing the structure of the starch granules, there-by enhancing their physico-chemical properties. As a natural and low-cost binder, starch nano-crystals are promising alternatives to synthetic emulsion latex. The starch-based nano-biopolymer binder can be made from cationic starch, which is generally used in wet-end processes to replace synthetic dry strength resins (e.g., glyoxalated poly acrylamide).

5.6 Nano-Scaled Cellulose

Nano-scaled cellulose is also called cellulose nano-fibers, micro-fibrils or cellulose nano-whiskers [48]. Generally, it consists of alternating crystalline and amorphous strings. Crystalline region is formed with the firm hydrogen bonds network that gives cellulose a relatively stable polymer. This complex system of hydrogen bonds makes cellulose chains rather high axial stiffness, which is a prerequisite property for a filler to be composited [83]. Therefore, they are being common additives for reinforcement fibers because their properties and performance far exceed compared with conventional fillers. Due to the high aspect ratio only a small percentage of nano-cellulose can increase the effectiveness and rigidity of a polymer. Cellulose nano-whiskers was prepared from delignified coconut husk fibers by hydrolysis method [84] while designed soy protein-based green composite by using micro/nano-sized bamboo fibers showing significant improvement in Young's modulus and fracture stress [85]. These outstanding properties with excellent biodegradability suggest that nanocellulose is a promising alternative to traditional petroleum based materials.

5.7 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) have been recently composed into polymers such as polyvinyl alcohol (PVOH), polypropylene (PP), nylon, polylactic acid (PLA), etc., and have been studied for packaging purposes, especially antimicrobial and intelligent sensors. There are two types of CNTs: single atom thick nanotubes and several concentric nanotubes. Both provide an extraordinarily high elastic modulus and tensile strength when added to the polymer matrix. Bacteria such as *E. coli* are toxic to extremely pure single-walled carbon nanotubes (SWCNTs) with minimal metal residue. Furthermore the Technische Universität München, Germany, suggested the concept of integrated intelligent packaging [86]. Such packets are sprayed with CNT-based gas sensors in order to produce a thin, transparent film embedded with wireless chips. This packaging would be able to communicate to the customer or market manager when an element or compound has reached a defined threshold and the meat or fresh food is about to spoil.

5.8 Nano-Silica

Nano-silica is primarily used during hydrophobic coatings, particularly for materials which are self-cleaning. A non-adhesive coating can turn food into a free-flowing material inside containers or jars [87, 88]. Products that benefit from this technology include beer, wine, and powdered soup [89]. Development super hydrophobic paperboard by coating Aerosil® silica NPs showed prominent capability of water resistance resulted from lotus-like surface created by nano-sized silica [87]. Some articles specifically analyzed a number of nanomaterials that are currently used or researched for food packaging.

6 Different Methods of Nanoparticles Synthesis

The nanoparticles can be synthesized by different methods, which are categorized as either bottom-up or top-down approaches. Table 1 represents a simplified description of the processes.

6.1 Bottom-Up Method

Bottom-up or productive method is structural building from atom to cluster to nanoparticles. Sol-gel, spinning, chemical vapor deposition (CVD), pyrolysis, and biosynthesis have been the most commonly used techniques for the processing of nanoparticles.

6.1.1 Sol–Gel

A colloidal mixture of solids suspended in a liquid form constitutes the sol. The gel is usually defined as a solid macromolecule that was dissolved in a solvent. Sol–gel is the most recommended bottom-up method owing to its efficiency and as most of the nanoparticles can be synthesised from this method. It is a wet-chemical procedure, containing a chemical solution that acts as a precursor to interconnected discrete interacting particles. Metallic oxides and chlorides are the commonly used components in sol-gel synthesis of nanoparticles [89]. The components are distributed in a host fluid either by stirring, spinning or sonication where the resultant system comprises a liquid and a solid phase. Further, a phase separation is conducted to retrieve the nanoparticles by alternative techniques such as sedimentation, ultra filtration or by centrifugation, while the humidity is furthermore removed by drying mechanism.

6.1.2 Chemical Vapour Deposition (CVD)

Chemical vapor deposition [CVD] is the precipitations of a thin layer of gaseous reactants it onto substrate. The deposition is taken out in a reactor system at room temperature by mixing gas molecules. A chemical reaction takes place when the cumulative gas comes into contact with a heated substratum. This reactivity creates a thin film of product, which is further recovered and used on the surface of the material. The major determining factor in CVD is the substratum temperature. CVD has highly pure, consistent, hard and strong nanoparticles as its advantages while its disadvantages includes as it requires specialized equipment and the gaseous by-products are highly toxic in nature [90].

Table 1 Different methods to prepare nanoparticles

Category	Method	Nanoparticles
Bottom-up approach	Sol-gel method	Carbon, metal and metal oxide based
	Chemical vapour deposition (CVD) method	Carbon and metal oxide based
	Spinning method	Organic polymers
	Pyrolysis method	Carbon and metal oxide based
	Biosynthesis method	Organic polymers and metal based
Top down approach	Thermal decomposition method	Carbon and metal oxide based
	Nanolithography method	Metal based
	Mechanical milling method	Metal, oxide and polymer based
	Sputtering method	Metal oxide based
	Laser ablation method	Carbon and metal oxide based

6.1.3 Spinning

A rotating disc reactor (SDR) performs the synthesis of nanoparticles by rotating. It includes a rotating disk inside a chamber/reactor where it is possible to control physical conditions such as temperature. Usually, the reactor is filled with nitrogen or other inert gasses to remove oxygen inside and prevent chemical reactions. The disk is rotated at various rates, under which the liquid, for example the precursor, is pumped in and in water. The spinning allows the particles or atoms to bind together and is precipitated, stored, and dried. The different operating parameters like liquid flow rate, disk rotation speed, liquid / precursor ratio, feed location, disk surface, etc. determine the synthesized nanoparticles attributes [91].

6.1.4 Pyrolysis

Pyrolysis is the most frequently used method for the production of nanoparticles in large-scale industries. It involves burning a flaming precursor. The precursor would either be liquid or vapor that is supplied into the furnace through a small opening where it burns at atmospheric temperatures. In order to retrieve the nanoparticles, the combustion or by-product gases are then called air. In order to recover the nanoparticles, the combustion or by-product gases are then air classified. Some of the furnaces utilise laser and plasma to produce high temperature for convenient evaporation, instead of flames. The benefits of pyrolysis are fast, reliable, cost-effective and elevated-yield, continuous processes [92].

6.1.5 Bio-Assisted Methods

Biological mode of synthesis is a green and environmentally sustainable approach to the preparation of different nanoparticles that are nontoxic and degradable in nature. These methods involve natural products, bacteria [93], viruses, actinomycetes, fungi [94], yeast, plants [95] etc. along with the analogues to produce nanoparticle instead of convention chemicals for bio-reduction and capping purposes. The biosynthesized nanoparticles have special and improved properties that turn their attention in both food and biomedical applications. The mechanism involved where the metallic ions were first captured on the surface of biological cells via., electrostatic interactions between ions and negatively charged cell wall enzymes. Then, these metallic ions were further bio-reduced into their respective nanoparticles. The two important aspects in the biosynthesis of nanoparticles are NADH (nicotinamide adenine dinucleotide) and NADH-dependent nitrate reductase. It was demonstrated that the nitrate reductase was responsible for the production of bioreduced metallic nanoparticles by several biological organism like *B. Licheniformis*, *Fusarium oxysporum*, actinomycete *Thermomonospora* sp., *Verticillium* sp., *Brassica juncea* (Indian mustard), *Medicago sativa* (Alfalfa), and *Helianthus annuus* (Sunflower) [94]. However, these processes of biosynthesis linked to the formation of metal salt ions and the resultant metallic nanoparticles by microorganisms remain unmapped.

6.2 Top-Down Method

Top-down or destructive approach requires nanometric-scale reduction of a bulk material to components. Mechanical milling, Electron Beam lithography, laser ablation, sputtering, and thermal decomposition are among the most frequently used technique of nanoparticles synthesis.

6.2.1 Thermal Decomposition

Thermal decomposition is a heat-generated endothermic chemical process of breaking down the chemical bonds within the compound. The exact temperature at which an element breaks down chemically is the temperature of the decomposition. The nanoparticle that forms by breaking down the metals at different temperatures undergoes a chemical compound that creates secondary products [96].

6.2.2 Nanolithography

Nanolithography is the analysis of the manufacture of nanoscopic-scale structures with a size range of approximately one dimension from 1 to 100 nm. Various nanolithographic processes include optical, electron beam, multiphoton, nanoimprint and scanning probe lithography, for example, Lithography is generally the procedure of printing a considered necessary shape or structure onto a light-sensitive material that preferentially removes a portion of the sample to create the desired shape and configuration. The key advantages of nanolithography are to create a cluster of desired shape and scale, from a single nanoparticle. The drawbacks include cost associated complex equipments [97].

6.2.3 Mechanical Milling

In 1970, John Benjamin developed oxide dispersion reinforced alloys that are strong enough to withstand high temperature and pressure. This method becomes a reliable and energy-efficient strategy of synthesizing nanoparticles with highly variable sizes and dimensions. It involves moving of balls that transfer their kinetic energy to the material being milled that results in the breakage of their chemical bonds and rupturing the milled materials into tiny particles. Mechanical friction is commonly used during synthesis for the milling and post-annealing of nanoparticles where different components are milled in an inert environment.

For mechanical milling, the determining factors are plastic deformation that leads to particle size distribution, fracturing leads to reduced particle size and cold-welding leads to increased particle size [98].

6.2.4 Sputtering

Sputtering is mainly the accumulation of nanoparticles on a surface by extinguishing particles by colliding with ions. It is usually a thin film deposition of nanoparticles that is followed by annealing process. The shape and size can be determines by the thickness, annealing duration, temperature, and the type of substratum used [99].

6.2.5 Laser Ablation

It is a common method to generate nanoparticles from diverse solvents. The radiation exposure of a metal which is submerged by a laser light in a liquid solution condenses a plasma plume which produces different nanoparticles [100]. It is a robust top-down approach that provides nanoparticles based on metal synthesis with an alternative solution to traditional metallic chemical reduction. It is a ‘natural’ method because it offers a balanced synthesis of nanoparticles in organic solvents and water that does not need any stabilizing agent or chemicals.

7 Mechanisms of Antibacterial Action

The antibacterial component must be capable of attaining essential molecular target spots that are implicated in microbial cell physiology, such as cell wall development, replication and protein synthesis. Nanoparticles have special properties physical, chemical, biological, dielectrical, electrical, thermal, mechanical, magnetic, and optical [101]. Despite of these characteristics the use of metal oxide nanoparticles as possible antimicrobials is of great concern. It has been documented that several naturally/chemically engineered nanomaterials have an effective antibacterial efficacy through various mechanisms including the formation of reactive oxygen species which can disrupt enzyme activity, damage internal cell organelles, and interrupt DNA synthesis [102, 103] (Fig. 1). Nanoparticles possess significant positive zeta potential that facilitates their interaction with cell membranes that could really leads to cellular membrane disruption influencing the proper transmission channel via plasma membrane and lead to cellular death [104]. The positive charge on the surface of nanoparticles and the negative charge on the bacterial cell membrane have been studied to make it important for antibacterial efficacy as ions impact the respiratory enzymes present on the surface causing an efflux-influx of ions within the cell leading to cell death. In addition, signalling cascade occurs when nanoparticles come into contact with microbial cell membranes such as respiratory enzyme oxidation, reactive oxygen species production which eventually affect cell physiological function and ultimately promote damage to DNA.

In mitochondria, ATP synthesis involves the reduction of molecular oxygen via an electron -proton transmission cycle that results in the production of superoxide anionic radicals, hydroxyl radicals, hydrogen peroxide (H_2O_2) that proves lethal for microbes [105]. It is well-known that the generation of ROS can lead to per-oxidation of cellular constituents, oxidative stress, damage of communication channels and cellular constituents, generation of protein radicals [106], lipids peroxidation [107], DNA-strand breaks, modification of nucleic acids [108], modulation of gene expression through activation of redox-sensitive transcription factors [109] and modulation of inflammatory responses through signal transduction [110], that lead to cytotoxicity and genotoxicity effects [111]. Several studies have also demonstrated that NPs of titanium dioxide affects the formation of biofilms adhesion rate of bacteria and affect D-alanine metabolism related with the growth of *S. mutans* biofilm [112]. Considerable evidence CuO-NPs also inhibit the enzyme activity of nitrate reductase and nitrite reductase leading to severe inhibition in *Paracoccus denitrificans* .machinery The proteomic studies showed that CuO-NPs regulate proteins that are involved in electron transport and nitrogen metabolism. Due to the expressions of NADH dehydrogenase and cytochrome which are key electron-transfer proteins were suppressed by the CuO NPs action, adversely affecting electrons transfer for denitrification [113].

8 Challenges and Risk Assessment of Nanomaterials

Recent reports and methodologies analyzed in previous research outline the overall risk assessment characteristics of NMs. These characteristics are based on the defining components of the NPs which are strongly attributable to their methods for the nanoparticle synthesis [114]. The properties of NPs and their impact in inhibiting challenges and toxicity risks are summarized in Table 2. Production, use, disposal, and waste treatment of products containing nanoproducts are the prime reasons for the environmental release of nanoparticulates in the original or modified forms. The adverse effects triggered by NPs exposure include the formation of reactive oxygen species, protein denaturation, mitochondrial disconcertion and phagocytosis function disruption. The general properties of NPs used to classify them are dimensionality, structure, composition, aggregation, and uniformity.

Table 2 Nanomaterial toxicity and risk factors associated with it

Properties of nanomaterial	Risk factors associated
Size and its reactivity	Reactivity and agglomeration of NPs is mostly dependent on their particle size. It is well known that the process of agglomeration will happen at slower rates in smaller particles. After the synthesis of the NPs, it is impossible to retain their original size. Hence, encapsulation becomes highly inevitable in NP synthesis. The exceptional size-dependent chemistry of NPs is distinguished from classical colloid chemistry by categorizing NPs according to their particle size [115]. NPs can be charged either by functionalization or spontaneous degradative reactions [115]
Agglomeration or aggregation	Poor corrosion resistance, high solubility and phase change of NMs leads to deterioration and the structure maintenance becomes challenging [116]
Impurity, contaminant dissociation and its recycling and disposal	Due to their high reactivity, NPs interact with impurities due to which encapsulation is required that provide stability to the NPs while the contamination of residual impurities in the NP is considered as a major risk factor [117, 118]. The potential toxicity issues are still under question. Hence, the uncertainty of a nanomaterials effect is yet to be developed for permanent disposal and recycling policies.

9 Ethical Issues, Safety Features and Toxicokinetics in Food Packaging

The commencement of novel nanomaterials applications in food packaging has largely focused on providing healthier, safer and quality products for better eating and living. The advantages of nanofoods have been widely documented, but the health implications with it are still in the process of feasibility and verification studies, while the employment in the field of food packaging has yet to be accepted with regard to their safety concerns, which may arise from the transfer of nanomaterials from packaging to food matrix [119]. The size dependent properties of nanomaterials and their miniaturisation together offer valuable scope for nanotechnological innovation. Nevertheless, some of these materials' characteristics can lead to toxicological results during their association with cellular cells, tissues and organs through nanofoods and food contact materials The risks associated with the inhalation, ingestion and skin absorption of engineered NPs of unknown toxicity urgently demands the development of reliable analytical tools to conduct a safety risk evaluation of nano-food products [120]. Before inclusion of NPs within foods, safety approaches are being developed to classify and quantify NPs in food matrices for potential regulatory testing regarding the distribution and migration of engineered particles in food stuffs. This would greatly improve consumer trust in goods based on NPs so as to ensure quality control and protection of shelf goods. Efforts to develop strategies and instrumentation through food analysis have met a lack of analytical evaluation tools in this field. This field will require further investigation, however, regulatory authorities can impose restrictions on the use of NPs in food components. One such invention involves an apparatus designed to assess engineered NPs in a substrate. The study defines a means of identification, size and its distribution that should be noninvasive and unrestrictive, detecting and quantifying food embedded NPs [121]. The approach is focused on the use of a substrate loaded by NPs as a reference material, when combined with imaging and analytical systems, focussing on screening techniques such as dynamic light scattering (particle size distribution), mass spectroscopy (test material composition), spectroscopy (NPs size), positron emission tomography (radio-tracing) and optical emission spectrometry (trace level elemental analysis) for collecting regulatory information. Another, patented method for food monitoring of harmful substances describes a sensor system composed of nano-structured surfaces or NPs in solution capable of responding to changes in metal roughness (electromagnetic signal enhancement) and changes in the adsorbate electronic states (chemical signal enhancement) that result from the chemi-sorption of the analysis at the NPs surface of the biosensor [122]. A food safety detection system termed Raman Nano Chip™ [123] uses nanorods to collect test samples by adsorption of molecules onto the nano surface structure through specific interactions. For broader applicability and utility, sensors may be coated with a colloidal suspension of NPs in the form of metallic, oxide or polymeric materials. A reliable system to detect migration of NPs from food contact materials such as packaging into food will be an important safety criterion in the future.

10 Future Trends and Conclusion

Through improved outlook of nanomaterials and the realisation of their potential in the food industry, the influx of nanotech foods will provide solutions for persisting problems associated with foods and will offer long-term economic benefits. Globally, nations will be benefitted from increased food productivity with cost effective returns, innovative products with tuneable properties to deliver smarter and healthier foods and equally intelligent packaging systems having enhanced storage properties for better food protection. In conclusion nanomaterials in foods will have a huge impact on sustainability and will be accompanied by health and environmental benefits if regulated properly. However, as the challenge in assessing the safety of nanofoods and nanopackaging becomes more complex with the arrival of novel nanomaterials for use in the food industry. Therefore there is a need for greater collaboration to ensure that social and environmental interests are not undermined as new products are introduced. In conclusion, the pace of introducing food technology must be sufficiently slowed to allow potential risks to be identified and assessed for a safer future. This essentially means that innovation must be balanced by regulatory guidelines through the availability of reliable and robust risk-assessment tools which currently do not exist for nanofoods as if nanofoods are to be implemented successively in our food cycle, the benefits of nanotech foods must be accompanied by greater transparency of the risks of such foods publicly to build consumer confidence and acceptance of nanoprocessed foods. In this way, nanomaterials can be allowed to work better in the food preservation and packaging sector. However, identification of novel detection methods will give a justified evaluation on using these NPs, considered as a warranty for the humans to enjoy high technology products safely within the food industry.

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Compliance with Ethical Standards

Conflict of interest No potential conflict of interest was reported by the authors.

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