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Recent developments in synthesis of nanomaterials utilized in polymer based composites for food packaging applications

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ABSTRACT

Foodborne diseases are a global public health issue. So, the demand for a new efficient and economical technology to control foodborne pathogens has increased in the recent years. Nanoparticles based food packaging plays an important role in controlling foodborne pathogens, inhibiting or retarding microbial growth on food surfaces, extending food shelf life etc. The nanotechnology involves the manufacture and the use of materials with size up to 100 nm in one or more dimensions. Major studies over the last decades have shown that nanoparticles could be used as fillers to improve mechanical and barrier properties of biocomposites, many times used in packaging. Nanocomposite consists of nanoparticle and polymeric film. Larger surface area of nanoparticles as compared to their micro-scale counterparts enhance the filler–polymer matrix interactions and hence the performance of the resulting packaging material. The objective of this review is to summarize published data regarding the recent developments in the main synthesis methods of organic and inorganic nanoparticles (NPs), which are currently listed as a generally recognized safe material by Food and Drug Administration. This review also presents the mechanism of action of the nanoparticles and their applications in polymer matrices, used in food packaging applications.

Keywords: *Nanoparticle, polymer, synthesis, nanocomposite, food packaging.*

INTRODUCTION

Foodborne diseases are a global public health issue. So, the demand for new efficient and economical technologies to control foodborne pathogens has increased in the recent years. Food processing and packaging are the two important phases of operations to control the foodborne pathogens. Processing includes the thermal processing and non-thermal processing. In thermal processing, the combination of temperature and time plays a significant role in eliminating the desired number of microorganisms from the food product without compromising its quality. Non-thermal processing methods such as PEF (Pulsed Electric Field), UV (Ultraviolet), and Ozone yield products with more ‘fresh-like’ flavor than those produced by traditional thermal processes due to fewer chemical and physical changes, although they are not completely effective in reducing the microbial activity (Dunne C.P. and Kluter R.A., 2001). Since there is an abundance of literature dealing with the above scientific processing techniques and methods, we prefer to concentrate on trends in packaging and the use of nanomaterials in food packaging. The packaging protects food from environmental conditions, such as light, oxygen, moisture, microbes, mechanical stress and dust. Packaging has also a more significant role in the preservation of food and in ensuring the safety of food in order to avoid wastage and food poisoning and to reduce allergies. Various terms for new packaging methods can be found in the literature, such as active, intelligent packaging. According to the definitions, active and intelligent packaging is:

- Active packaging changes the condition of the packed food to extend shelf life or to improve safety or sensory properties, while maintaining the quality of the packaged food.

- Intelligent packaging systems monitor the condition of packaged foods to give information about the quality of the packaged food during transport and storage.

The definition of intelligent packaging includes indicators used for quality control of the packed food. Intelligent food packaging gives information such as the origin of food, contents and consumption-date expiration. It can also track a product in the food supply chain, be anti-theft and damage proof. Active packaging plays a role in determining the shelf life of packaged food which is affected by physiological processes (e.g., respiration of fresh fruit and vegetables), chemical processes (e.g., lipid oxidation), physical processes (e.g., staling of bread, dehydration), microbiological aspects (e.g., spoilage by microorganisms) and infestation (e.g., by insects) (Silvestre *et al.*, 2011). Due to such applications, active packaging technologies have started to receive a great deal of attention since the last decade. So, active packaging is considered in this study.

Mainly, the use of nano-scale fillers is leading to the development of "active packaging" which consists of a biopolymer or synthetic polymer matrix reinforced with particles (nanoparticles) having at least one dimension in the nanometer range (1 to 100 nm) (Kumar *et al.*, 2011).

Size, shape and loading level of nanoparticles and ultimate tensile strength, elastic modulus of polymer affects physical, mechanical and other properties of the biopolymer/synthetic polymer nanocomposites (Choudalakis and Gotsis, 2009; Moghbelli *et al.*, 2009). High surface area to volume ratio and hence more interaction between nanoparticle and biopolymer/synthetic matrix leads to the formation of composites with higher mechanical, thermal and barrier properties) in comparison to their conventional microcomposite counterparts. Bionanocomposites have recyclability along with low density and transparency as compared to synthetic based nanocomposites (Avella *et al.*, 2005; Sorrentino *et al.*, 2007; Kristo and Biliaderis, 2007a).

Thus, there is an abundance of literature dealing with the synthesis of food packaging along with the synthesis of nanoparticles. There are several methods that are available for the synthesis of specific nanoparticles. So, it is difficult for researchers to select the best method for the synthesis of specific nanoparticles.

Therefore, in this review, we have discussed several methods and suggested the best method for the synthesis of specific nanoparticle. This review paper is also concerned with the properties and applications of organic and inorganic nanomaterials with good potential of reinforcement activity that can be incorporated into biopolymer/synthetic polymer based packaging materials as 'nano-additives'.

DIFFERENT TYPES OF NANOMATERIAL USED IN FOOD PACKAGING

Nanomaterials have three categories i.e. nanoparticles having three dimensions of particulates in the order of nanometers (e.g. silica and metal oxides like TiO_2, ZnO), nanotubes having two dimensions in the nanometer scale (e.g. Titania nanotubes (TiNTs)) and nanolayers having only one dimension in nanometer scale. Engineered nanoparticles have regular shapes while both natural (e.g. minerals) and incidental nanoparticles (e.g. diesel exhaust, coal combustion) may have irregular or regular shapes (Bouwmeester *et al.*, 2009).

The top down approaches and the bottom-up approaches (Figure 1) are mainly used to synthesize the engineered nanoparticles. The ''top-down" approach involves the size reduction of bulk materials using milling, nanolithography. The ''bottom-up" approach involves the built of nanoparticles from individual atoms or molecules through crystal growth or chemical synthesis (Azeredo, 2009; Cushen *et al.*, 2013a).

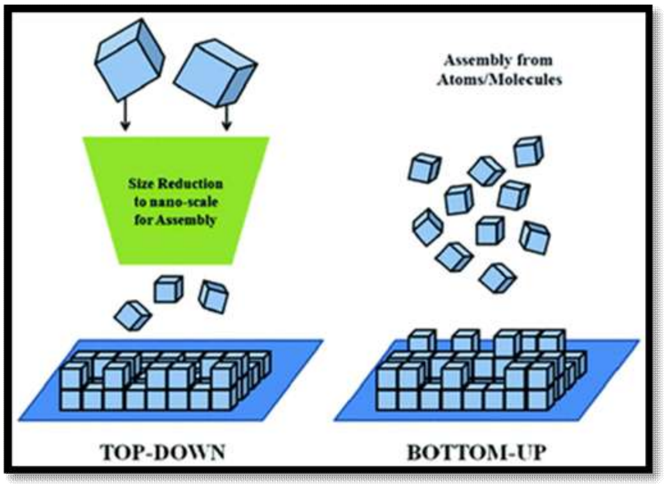

Figure 1. Top-down and bottom up approach for synthesis of nanoparticle.

The inorganic nanoparticles include titanium dioxide, silver, zinc oxide, nano-silica, copper, zirconium phosphate and organic nanoparticles include chitosan and starch nanocrystal. However, each one has a special concept, architecture and properties. All these nanoparticles have application in food packaging. All applications of each nanoparticles will be mentioned in the subsequent sections while discussing their synthesis methods. This part should contain complete, correct and detailed information regarding employed materials, interventions and analytical methods, in order to ensure the reproducibility of all experiments.

MECHANISM OF A NANOMATERIAL ACTIVITY IN FOOD PACKAGING

The principles behind active packaging are based either on the intrinsic properties of the polymer matrix used as packaging material itself or on the introduction of a specific nanomaterial inside the polymer (Dainelli *et al.*, 2008). A nanomaterial can be incorporated inside the packaging material or onto its surface, in multilayer structures or in particular elements associated with the packaging material. The nature of the nanomaterial can be metal oxides, enzymes, bactericides, fungicides, natural extracts, ions, ethanol etc. There are also different types of nanostructured materials which can give only one function either active or ‘‘smart” properties to the packaging system (e.g., antimicrobial activity, biosensing, etc). Some nanoparticles can show multiple properties which can overlap and give multiple application (e.g. titanium dioxide which can act as reinforcing and antimicrobial material (Sozer and Kokini, 2012). The mechanism for each nanoparticle activity has been described in the Table 1.

Thus, it is clear from the existing literature in Table 1 that research in the area of antimicrobial food packaging materials has significantly increased during recent few years as an alternative method for controlling microbial contamination of foods by the incorporation of antimicrobial substances in or coated onto the packaging materials (Chalier *et al.*, 2007). Much research is devoted to the design of antimicrobial packaging containing antimicrobial agents for specific or broad microbial inhibition depending on the nature of the agents used or on their concentration. The general mechanism for antimicrobial activity of nanoparticle is shown in Figure 2.

Recent studies also show that nanoparticles can be tailored for both controlled release and/or specificity in the action of the active agent having moisture or temperature as triggering mechanisms (second generation of nanostructured materials). As for any other new technology that is coming into the stage of application, a sound evaluation and a risk-benefit analysis needs to be carried out.

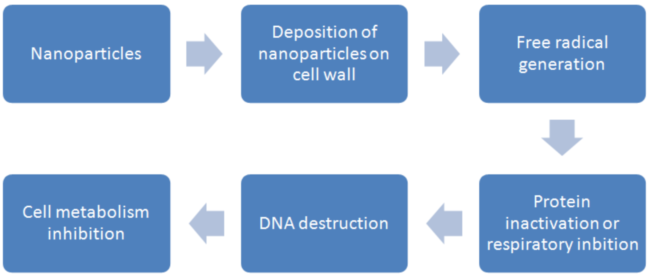

Figure 2. Mechanism for antimicrobial activity of nanoparticles.

In this context, nanostructures are generated by one or two dimensional nano-additives being the other dimension more in the conventional micro-size, thus resulting in a reduced potential mobility.

Therefore, these nanocarriers can be considered of less safety concern than other nanoparticles. On the other hand, the high surface developed by nanoparticles can potentially bind unwanted substances that could be otherwise released in contact with foods. The full understanding of the effects on food safety of the introduction of nanostructures has still to be ascertained.

Table 1. Summary of different activity of the main nanomaterials used in active food packaging systems.

Nanomaterials	Polymer matrix	Type of packaging	Working principle/mechanism	References
Copper Nanoparticles	Polylactic acid, Low density polyethylene (LDPE)	Antifungal/antibacterial application	Nanoparticles attach to the surface of cell membrane disturbing the permeability and respiration function of the cell. The damage to the cell may be caused by the interaction of nanoparticles with phosphate or sulfur-containing compounds such as DNA.	(Bruna *et al.*, 2012; Lee *et al.*, 2013; Longano *et al.*, 2012; Ramyadevi *et al.*, 2012)
Nano-silica (SiO2)	Bovine Gelatin	Hydrophobic Packaging with improved mechanical properties	Coupling between thetremendous surface area of the nano-silica and the polymer matrix. Strong affinity between polymer and nano-silica. Large aspect ratio of the nano-silica leads to improvement in the mechanical properties of nanocomposite films.	(Chaudhry and Castle, 2011; Voon *et al.*, 2010)
Silver Nanoparticles	Polyethylene, low density polyethylene (LDPE), polyvinyl chloride (PVC)	Antimicrobial packaging for shelf life of apple, orange juice.	The three most common mechanisms of antimicrobial properties are: (1) uptake of free silver ions followed by disruption of ATP production and DNA replication, (2) silver nanoparticle and silver ion generation of ROS, and (3) silver nanoparticle direct damage to cell membranes.	(Cushen *et al.*, 2013b; Emamifar *et al.*, 2010; Fortunati *et al.*, 2012; George *et al.*, 2014; Marambio-Jones and Hoek, 2010; Zhou *et al.*, 2011)
	Bacterial Cellulose, polylactic acid (PLA)	Biobased moisture resistance and transparent antimicrobial packaging		
TiO_2 Nanoparticles	Polypropylene, polyethylene	Antimicrobial coating with increased tensile strength and elongation at break of PE film	The antimicrobial activity is due to attack of reactive oxygen species like hydroxyl radicals (OH•) and superoxide anions (O2•¯) when TiO2 directly contacts to cells. Improve tensile strength and water vapor resistance is due to the filling of TiO2 nanoparticles into the interstice of polymer chains.	(Chawengkijwanich and Hayata, 2008; Kim *et al.*, 2012; Xing *et al.*, 2012; Zhou *et al.*, 2009)
	Whey protein isolate (WPI)	Biodegradable antimicrobial packaging		
Zirconium Phosphate (ZrP)	Pea Starch, rice starch, potato starch, Polyvinyl Alcohol (PVA)	Water resistance packaging	Zirconium Phosphate forms hydrogen bonds between the molecules of base polymer, decreasing the number of –OH groups available for interaction with migrating water molecules.	(Wu *et al.*, 2009; Yang *et al.*, 2009)
Zinc Oxide Nanoparticles (ZnO)	Glass, LDPE, polystyrene, polypropylene, chitosan and polyvinyl alcohol	Antimicrobial packaging	Antimicrobial activity is due to mechanical damage to the cell membrane caused by the abrasive surface of nanoparticles.	(Espitia *et al.*, 2012)

Nanomaterials	Polymer matrix	Type of packaging	Working principle/mechanism	References
			Antimicrobial activity is due to the generation of ROS such as hydroxyl radical (•OH), hydrogen peroxide (H2O2) and superoxide (O2 •−), which are the result of ZnO nanoparticle activation by visible light and UV.	

SYNTHESIS OF NANOMATERIALS

Copper Nanoparticles

Synthesis of copper Nanoparticles

Copper nanoparticles (CuNP) are very attractive due to their heat transfer properties, high surface area to volume ratio, low production cost, antibacterial potency, catalytic activity, optical and magnetic properties as compared to precision metals such as gold, silver or palladium. Copper ions can destroy microorganisms and viruses, and copper is indispensible for life as a constituent of metallic enzymes (Longano *et al.*, 2012). Copper is considered relatively safe since it is not concentrated by animals and thus has few adverse effects on higher animals. A polymer based nanocomposite loading stabilized copper nanoparticles with antifungal and bacteriostatic properties has been proposed for the food packaging application (Llorens *et al.*, 2012a).

However, copper is not generally used in food packaging industry since it is regarded as toxic in contact with food and it would accelerate biochemical deterioration with foods due to its catalytic action of oxidation. Chemical reduction has been used for the synthesis of copper nanoparticles. Biological or biosynthesis techniques are also considered chemical methods. Here, copper nanoparticles are prepared by the reduction of copper salts by various reducing agents at different conditions, as shown in Table 2.

Thus, it can be concluded from Table 2 that CuNP production using chemical reduction method gives good results, but the use of hazardous reducing, costly and protecting agents makes the process toxic in some cases. To avoid the toxicity and to prepare CuNP in green environment, many authors have used ascorbic acid in the chemical reduction process. Ascorbic acid works both as a reducing and protecting agent, which makes the process economical, nontoxic and environment friendly (Umer *et al.*, 2014). The use of more naturally occurring plant extract for reduction of copper salts also make the process nontoxic and environment friendly.

Application of copper nanoparticles in nanocomposites

Several nanocomposites were prepared by combining copper nanoparticles of two sizes (10 nm and 45 μm) with different polymer i.e. polypropylene (PP), polyamide 6 (PA6) and high density polyethylene (HDPE) (Palza *et al.*, 2015). Nanocomposites of polypropylene with nanoparticles displayed larger antimicrobial activities against *Staphylococcus aureus* and *Pseudomonas aeruginosa* bacteria than microcomposites. More copper ions release from nanoparticles than microparticles was attributed to higher antimicrobial activity of the nanocomposite than the microcomposite.

Shankar *et al.*, 2014 reported no change in mechanical and water barrier properties of agar based bionanocomposite by adding copper nanoparticles. This was probably due to the addition of nanoparticles that reduced the interaction between polymer chains, thereby making more availability of free hydroxyl groups to absorb water. The agar bionanocomposite films showed profound antibacterial activity against both Gram-positive and Gram-negative foodborne pathogenic bacteria. It was expected due to the nano-size of the CuNPs, relatively high surface area and high dispersion of CuNPs in agar matrices interact closely with the bacterial cells leading to inhibition of bacteria.

Silver nanoparticles

Synthesis of Silver nanoparticles

Among the numerous nanoparticles used for functionalizing polymeric materials, silver nanoparticles have been one of the most widely used for the development of innovative packaging materials.

Table 2. Methods for synthesis of copper nanoparticles

Reducing agent	Conditions, observations	Properties of formed Cu nanoparticles	Advantage	Disadvantage	References
L-Ascorbic Acid (Vitamin C)	At 90 ^{0}C for 17 h	Average diameter of the prepared nanoparticles in solution was about 50–60 nm	The use of ascorbic acid makes the process a non-toxic, cost effective and environmental friendly green method.	Reaction time and temperature is very high.	(Umer *et al.*, 2014)
Sodium borohydride	At 25^{0}C for 12 h, Stable metallic copper nanoparticles coated with the surfactant bis(ethylhexyl)hydrogen phosphate prepared using solvent-extraction reduction method.	Spherical shape with a diameter 50–60 nm	Surfactant bis(ethylhexyl)hydrogen phosphate avoids oxidation of the copper nanoparticles in non-polar solvents.	Use of organic solvent.	(Song *et al.*, 2004)
Hydrazine hydrate	At ambient condition, for 7 to 8 h in the presence of gelatin as a stabilizer.	The average size of the Cu nanoparticle was found to be in the range of 60–80 nm.	The reaction was carried out at ambient temperature without maintaining inert condition.	Chances of getting oxidation.	(Chatterjee *et al.*, 2012)
Sodium hypophosphite	At 90 ^{0}C for 2-3 min. Using Polyvinylpyrrolidone surfactant in ethylene glycol	The average particle size was30 and 65 nm.	Oxidation of Cu avoided using Polyvinylpyrrolidone surfactant.	Conversion was only 68 to 73%	(Lee Y. *et al.*, 2008)
Magnolia kobus leaf extract	At 25–95 ^{0}C with reflux.	The average particle size ranged from 37 to 110nm.	Naturally occurring plant extract as a reducing agent.	Required large quantity of extract.	(Lee *et al.*, 2013)
Potassium borohydride	Reaction carried out at 30^{0}C.	The average particles size of Cu powders with spherical shape with diameter of 100 nm.	High conversion of copper salt.	Required alkaline environment	(Zhang et al 2010)
Glucose and sodium hypophosphite	At pH of 3 and temperature of 60 ^{0}Cin the presence of oleic acid as a stabilizer.	Spherical nanoparticles ranging between 20 and 40nm.	Oleic acid was used to avoid oxidization and agglomeration.	Reaction carried out at high acidic pH.	(Wen *et al.*, 2011)

This is mainly due to their unique properties such as electric, optical, catalytic, thermal stability, and particularly antimicrobial properties (Marambio-Jones and Hoek, 2010). In particular, the benefits of silver materials have been recognized in many applications, including packaging, due to the strong antimicrobial activity of silver against a broad spectrum of bacteria, viruses, and fungi (Abdel-Aziz *et al.*, 2014). Silver nanoparticles based on silver salts or metallic silver may be readily incorporated into thermoplastic packaging polymeric materials such as polyethylene, propylene, polystyrene and nylon (Zhou *et al.*, 2011a). Silver nanoparticles have been incorporated into biopolymer films such as chitosan and starch, and they had strong antimicrobial activity against both Gram-positive and Gram-negative bacteria. Such nanocomposite films with profound antimicrobial function have suggested the potential application in food packaging for the extension of shelf life and enhancement of the safety of packaged food (George *et al.*, 2014a). Various methods for the synthesis of silver nanoparticles have been shown in the Table 3. From the literature survey in Table 3, it can be concluded that a green synthetic approach for preparing antimicrobial silver nanoparticles have been suggested by using different plan extract, fish scale extract, egg white and bacteria. These extracts act as both reducing and stabilizing agents and also as a template for carrying silver nanoparticles with excellent antibacterial activity. It has also been reported that biologically synthesized silver nanoparticles had greater bactericidal activity than did chemically synthesized silver nanoparticles.

Table 3. Methods for synthesis of silver nanoparticle

Reducing agent	Conditions	Observation	Advantage	Disadvantage	References
Various plant extract such as citrus limon (lemon) extract, ocimum sanctum leaves extract, Garcinia mangostana fruit extract, extract of Syzygium aromaticum, Arbutus unedo leaf extract, Mimusops elengi, Linn., Alternanthera dentata leaf, Ficusbenghalensis leaf extract, Artocarpushetero phyllus Lam. seed extract, tea leaf extract, Terminalia chebula fruit extract	Different concentrations of silver salt solution directly interact with this extract for different time periods at various temperatures.	Spherical shape silver nanoparticles ranging from 50 to 20nm.	The naturally occurring reducing agent makes the process a nontoxic, cost effective and environmental friendly green method.	Since, composition of these extract are unknown; therefore mechanism of action cannot be predicted. Purity of silver nanoparticles is problem	(Edison and Sethuraman, 2012; Prathna *et al.*, 2011; Rajakannu *et al.*, 2015; Ramteke *et al.*, 2012; Subba Rao *et al.*, 2013; Sun *et al.*, 2014)
Lobeorohita fish scales extract	Aqueous solution of silver nitrate reduced using different conc. of fish scale extract (10, 20, 30 and 40%) at 70^{0}C for 10 min. followed by slow cooling of the solutions to room temperature.	Average size of spherical silver nanoparticles ranging from 16-18 nm.	The extract of the fish scales which is considered as a waste material can be successively utilized.	Percentage conversion of the reaction is relatively low.	(Singh *et al.*, 2014)
Egg white	Aqueous solution of silver nitrate treated with egg white at room temperature for 72 hours.	Ag spherical shape nanoparticles with an average size of 20 nm.	This synthesis method is very simple, cost effective and environmentally friendly, and the nanoparticles biocompatible through *in vitro* cell arrays.	Percentage conversion of the reaction is relatively low.	(Lu *et al.*, 2012)
Pseudomonas aeruginosa culture supernatant	The reduction of silver ions occurred when silver nitrate solution was treated with the *Pseudomonas aeruginosa* culture supernatant at room temperature.	Silver nanoparticles formed were spherical in shape with an average particle size of 13 nm, crystalline in nature.	Reaction carried out at room temperature.	Needs to prepare the *Pseudomonas aeruginosa* strain BS-161R culture supernatant, which is tedious.	(Kumar and Mamidyala, 2011)
Sodium alginate	A simple, green, microwave-assisted method of synthesizing silver nanoparticles was developed using sodium alginate as stabilizer and reducer.	Well-distributed spherical silver nanoparticles of size 10 nm.	Microwave irradiation can accelerate the formation rate of particles.	Scale of process is difficult	(Zhao *et al.*, 2014)

But, percentage conversion of silver salt into silver nanoparticles by biological process is low. This table also shows that stable nanoparticles synthesized using plant extracts may have advantages such as nontoxic, cost effective and environmental friendly compared with chemically synthesized nanoparticles (Lee *et al.*, 2013).

Application of Silver nanoparticles in nanocomposites

Silver has an application in antimicrobial food packaging. Jagminas *et al.*, 2015 used nano-silver in alumina films and checked its antimicrobial activity against different fungi and bacteria. They indicated that the nano-Ag-in-alumina films containing ≥19 µg cm − 2 of silver possessed antimicrobial properties. They also suggested the possible application of these films in fabrication of transparent food packaging alumina films with a low refractive index due to low silver content. Zhou *et al.*, 2011b reported that the silver nanoparticles incorporated in low density polyethylene (LDPE) helped to maintain the freshness of apple slices. Nanostructured PE/Ag2O bag also delayed apple browning and decreased the weight loss of apple slices during storage. In addition, it prevented apple slices from microbial spoilage. Similar nanocomposite was prepared by Azlin-Hasim *et al.*, 2015 to get modified atmosphere packaging on the shelf life of chicken breast fillets.

George *et al.*, 2014b improved tensile strength and water resistance properties of the

Hydroxypropyl methyl cellulose (HPMC) by adding a unique combination of two nanomaterials i.e. silver and bacterial nanocellulose (BCNC) into the hybrid HPMC nanocomposites (eco-friendly food packaging). They explained that water resistance property was due to strong interaction of silver nanoparticle with the hydroxyl groups of both HPMC and BCNC, making it unavailable for other molecules like water to interact. BCNC improved the tensile strength and modulus of HPMC, but it made the film more brittle. The addition of AgNPs along with BCNC, helped to regain some of the lost elongation properties without affecting other properties.

TiO_2 nanoparticles

Synthesis of TiO_2 nanoparticles

Titanium dioxide (TiO_2) has been used as color additive in the food industry. TiO_2 nanoparticles have high stability and relatively low-cost production (Anwar, 2010). It also shows potential activity against all kind of microbes. Its use as catalytic agent and UV protecting agent results in industrial applications such as pigments (Pigment White 6), fillers, catalyst supports and photocatalysts (Kim *et al.*, 2012; Xing *et al.*, 2012). The amorphous form of TiO_2 is not photocatalytically active. The crystalline structures of TiO_2 are classified as anatase (stable at sizes less than 11 nm), brookite (stable at sizes between 11-35 nm) and rutile (stable at sizes greater than 35 nm).

The anatase and rutile are commonly observed phases. Anatase has higher surface area and hence high photocatalytic activity.

The rutile is thermodynamically more stable than anatase and brookite. Rutile can be obtained when heating is concomitant with coarsening the anatase and brookite (Gupta and Tripathi, 2011). In reality, the preparation method defines the crystal structure of TiO_2 nanoparticles. Several methods for the synthesis of TiO_2 have been depicted in Table 4.

Thus, it can be concluded from the Table 4 that a number of methods including the most common methods sol-gel (Sugimoto *et al.*, 2003; Vijayalakshmi R. and Rajendran V., 2012), ultrasound assisted sol–gel technique (Prasad *et al.*, 2010a) and microorganisms like *Lactobacillus* sp. and *Sacharomyces Cerevisae* (Jha *et al.*, 2009) have been used to prepare TiO_2 nanomaterials.

But, the ultrasonic-assisted sol–gel method is suitable for TiO_2 synthesis as it saves almost 70 % energy for calcination and also controls many important parameters such as the particle size, surface area, pore volume, pore size, anatase and rutile phase ratio and crystallinity. In the case of the ultrasonic-assisted synthesis of TiO_2, such operating variables as the ultrasonic power density, reactor size, stirring effect, and mode of application for the ultrasonic waves may have a strong influence on the properties of mesoporous TiO_2 photocatalysts apart from the chemical influence on their morphology.

Table 4. Methods for synthesis of TiO_2 nanoparticles.

Method of preparation	Description	Observation	Advantage	Disadvantage	Ref.
Hydrothermal Method	Titanium isopropoxide reacted at 240 ^{0}C for 4 h in acidic ethanol/water environment.	Particle sizes obtained in the range of 7-25 nm	Mainly obtained anatase phase	Required very high temperature	(Chae *et al.*, 2003T; Kobayashi *et al.*, 2007; Peng *et al.*, 2005)
Sol-gel method	Titanium tetra isopropoxide hydrolyzed in a mixture of ethanol	Spherical particle, diameter ranges from 10-50 nm	Mainly obtain anatase phase	Need of costly organic solvents	(Sugimoto *et al.*, 2003; Vijayalakshmi R. and Rajendran V., 2012)

Method of preparation	Description	Observation	Advantage	Disadvantage	Ref.
	and water.				
Ionic Liquid-Assisted Synthesis	Titanium tetrachloride hydrolyzed using 1-ethyl-3-methyl-imidazolium bromide ionic liquid in hydrochloric acid at 100 ^{0}C for 24 h.	Diameters of the anatase nanoparticles are in the range of 4-6 nm and the well-defined rutile nanorods are about 3-6 nm in diameter and 20-60 nm in length.	Simple process; performed under atmospheric	Ionic liquid is expensive.	(Zheng *et al.*, 2009)
Low temperature	Bis-(cyclooctatetraene) titanium reacts with dimethyl sulfoxide in organic solution at temp.as low as room temperature to produce TiO_2.	The spherical nanoparticles with wider size distribution ranging from 3 to25 nm in diameter.	Reaction carried out in absence of any supporting ligands.	Temperature needs to be maintained.	(Tang *et al.*, 2005)
Ultrasound assisted sol-gel technique	Titanium dioxide was successfully synthesized by utilizing sol–gel technique modified by incorporation of ultrasound as a reaction aid.	A 100% rutile polymorph of nanostructured TiO_2.	Complete phase transformation of the TiO_2 was achieved. A substantial (almost 70%) savings of the energy for calcination.	Scale-up of a process is an issue.	(Prasad *et al.*, 2010a, 2010b; Shirsath *et al.*, 2013)
Synthesis of TiO2 by biological methods	20 ml of 0.025(M) TiO·(OH)2 solution was added to the culture (*Lactobacillus* sp or Yeast) solution and it was heated on steam bath up to 60 ◦C for 10–20 min	The particles are found almost spherical in shape having a size of the order of 8–35 nm.	Biosynthetic method is truly a green cost-effective approach. Mechanism is also known.	Purity of the product is an issue.	(Jha *et al.*, 2009)

Application of TiO_2nanoparticles in nanocomposites

Important properties of the inorganic solid TiO_2 nanomaterials are their photocatalytic activity and antimicrobial activity. In principle, TiO_2 nanoparticles in food packaging absorb short-wavelength and protect food content from the oxidizing effects of UV irradiation. TiO_2-based food packaging shows antimicrobial activity in the presence of UV illumination but not in the dark as this activity of TiO_2 nanoparticles is photocatalyzed. In presence of ultraviolet radiation, TiO_2 acts as O_2 scavenger to avoid browning of fruits, rancidity of vegetable oils and aerobic microorganisms in food packaging.

Photoactive titanium dioxide can also oxidize ethylene to H_2O and CO_2 (Llorens *et al.*, 2012b). As a result, it extend the shelf life of ready to use fruit and vegetables by interacting with ripening gas (ethylene) and hence slowing down the maturation rate of climacteric fruits (Bodaghi *et al.*, 2013). It's a very important point for import-export of food. Recently, TIO_2 based nanocomposites have been prepared by a few researches. Bodaghi *et al.*, 2015 have reported that adding small amounts (3 wt%) of TiO_2 nanoparticles and chlosite 20A (5 wt%) to low density polyethylene (LDPE), significantly improved gas barrier properties (water vapor, oxygen and carbon dioxide). The photocatalytic effect of the nanocomposite film was carried out by antimicrobial evaluation against *Pseudomonas* spp. and *Rhodotorula mucilaginosa* and by ethylene removal test using 8 W ultraviolet (UV) lamps with a constant relative intensity of 1 mW cm^{-2}.

TiO_2 nanoparticle-coated low density polyethylene (LDPE) films exhibited potential for antimicrobial applications in food packaging (Othman *et al.*, 2014). They revealed that the antimicrobial activity of the films exposed to both fluorescent and UV light increased with an increase in the TiO_2 nanoparticle concentration. The UV light was found to be more effective in expediting the antimicrobial activity of TiO_2 compared to fluorescent light due to the suitable bandgap energy of UV light and the higher hydroxyl radical concentration on the surface of the coated LDPE films.

Naik and Kowshik, 2014 proposed AgCl-TiO_2 nanoparticle (ATNP) as an efficient nanoparticle to control food spoilage due to quorum sensing. ATNPs incorporated in food packaging materials could play an important role in food preservation and ensure safety of food by prolonging their shelf life.

ZnO nanoparticles

Synthesis of ZnO nanoparticles

Zinc oxide (ZnO) has strong antimicrobial activity on a board spectrum of microorganisms . As a result if this, it has many applications in daily life such as in drug delivery, food packaging, cosmetics, medical devices and pigments. It also attenuate (absorb and/or scatter) the UV radiation or UV-blocking (Lombi *et al*., 2012; Raghupathi *et al*., 2011).The sizes and morphology of the nanostructure of zinc oxide affects physical and chemical properties. The methods of preparation also have effects on the shapes of ZnO nanostructures like spherical nanoparticles, nanorods, nanowires, needles, and flower-like structures (Kołodziejczak-Radzimska and Jesionowski, 2014), which have been discussed in Table 5.

Thus, it can be concluded from the literature in Table 5 that methods have been developed to synthesize zinc oxide nanocrystals including sol–gel process (Farhadi-Khouzani *et al*., 2012), biological (Nagarajan and Arumugam Kuppusamy, 2013), hydrothermal (Chen *et al*., 1999; Yu and Yu, 2008), microwave irradiation (Kajbafvala *et al*., 2012), solvothermal process (Zak *et al*., 2011), sonochemical (Banerjee *et al*., 2012; Bhatte *et al*., 2012; Khorsand Zak *et al*., 2013; Vaezi and Sadrnezhaad, 2007). All these methods indicate that the crystallinity and morphology of ZnO nanoparticle depends upon the source species, pH, temperature, time and solvent used in the reaction. The ultrasound assisted (US) process is capable of synthesizing thermally stable ZnO at lower reaction times and at higher yields as compared to the Non-Ultrasound assisted (NUS) conventional process. The US process is an energy saving process. For large scale synthesis of ZnO, hydrodynamic cavitation can be used (Pinjari *et al*., 2014). A simple, rapid biological procedure appears to be a potentially exciting tool for large-scale synthesis of zinc oxide nanoparticles with tunable optical properties directed by particle size using varying concentration of suitable leaf broth extracted solution (Sangeetha *et al*., 2011; Thamima and Karuppuchamy, 2015).

Application of ZnO nanoparticles in nanocomposites

ZnO is used as reinforcing material in polymeric nanocomposites. Increasing content of ZnO nanoparticles in the polypropylene based nanocomposites reduced the extent of photo-oxidation and increased the storage modulus (E') along with the strain at break (εb). It also increased the glass transition temperature (Tg) of PVC based nanocomposite (Elashmawi *et al*., 2010). It also caused the increase in thermal stability and decrease in tensile strength of chitosan/poly vinyl alcohol films (Vicentini *et al*., 2010).

Effects of ZnO nanoparticles as filler in a gelatin matrix as food packaging have been investigated (Umamaheswari *et al*., 2015). Nano-ZnO improved mechanical properties (tensile yield, strain at break) and the decomposition temperature of gelatin. This improvement in nanobiocomposite properties attributed to the strong interaction between nano-ZnO filler and the gelatin matrix contributed.

Akbar and Anal, 2014 dispersed ZnO nanoparticles in a calcium alginate film for the packaging of poultry meat. Antimicrobial activity of ZnO loaded calcium alginate film was found to be more efficient against two prominent foodborne pathogens, *Salmonella typhimurium* and *Staphylococcus aureus*. Antimicrobial activity of the film was due to the production of reactive oxygen species such as hydroxyl radicals, super oxides, and hydrogen peroxide in the presence of moisture by ZnO nanoparticles, which react with the cell surface of bacteria and cause damage to cell contents such as protein, lipids and DNA.

Sanuja *et al.*, 2015 improved the mechanical and barrier property of biopolymer i.e. chitosan by adding ZnO nanoparticles and neem oil into the nanocomposite. Enhancement in mechanical properties (tensile strength, elongation) was due to strong interaction between ZnO and functional groups of chitosan. Chitosan/0.5%ZnO/neem oil film showed low affinity towards water due to the effect of more hydrophobic and many bioactive components present in the neem oil which restricts the uptaking of water.

Zirconium Phosphate (ZrP)

Synthesis of Zirconium Phosphate (ZrP)

Layered low-dimensional 1D structure of zirconium phosphates and their derivatives for their own nature are easily accessible and able to be functionalized for many applications. Zirconium bis (monohydrogen orthophosphate) monohydrate has many notable features like thermal and chemical stability along with the catalytic activity for selective heavy metals removal from waters. It also have good intercalation properties in polymers to form food packaging (Tai *et al.*, 2010).

Table 5. Methods for synthesis of zinc oxide nanoparticles

Method	Description	Observation	Advantage	Disadvantage	References
Combustion method	Industrial pure zinc was melted and then ignited by the flame of acetylene and oxygen gas mixture.	Zinc oxide was largely tetrapod of 20–30 nm in diameter and 200–300 nm long.	High purity in the product.	Need of very high temperature.	(Chen *et al.*, 2007)
Combustion method	Metallic zinc and glycine powders were used as the fuels, where as zinc nitrate acted as the oxidant.	different types of morphologies (that is, agglomerated particles, rod-like structures, and tetrapod whiskers) in air ambience.	Product having low impurity content and high specific surface area.	Need of very high temperature.	(Lin *et al.*, 2007)
Self-propagating high-temperature synthesis	Powders of Zn and NH_4NO_3 were mixed ignited by heating.	Zinc oxide mainly composed a long, thin tetrapod whisker with a leg-length of ~2-6 nm and a width of <100 nm.	High production Efficiency.	Process performed in the furnace open to air, it may cause the problem of safety and difficulty in collecting product.	(Hwang *et al.*, 2009)
Polymeric complex sol–gel method	Zinc nitrate, citric acid (CA) and ethylene glycol (EG) were used as the source of Zn^{+2}, the chelating agent and the solvent agent, respectively.	The ZnO nano structures in rod-like, spherical or flower-like morphologies have been fabricated by a simple polymeric approach with EG:CA mole ratio.	Morphology of the zinc oxide can be change by changing EG:CA ratio.	Yield of reaction is comparatively low.	(Farhadi-Khouzani *et al.*, 2012)
Reduction of zinc salt by *Aloe vera* leaf extract (Biological methods)	Highly stable and spherical zinc oxide nanoparticles are produced by reduction of zinc nitrate by using *Aloe vera* leaf extract	The zinc oxide nanoparticles prepared were poly dispersed and the average size ranged from 25 to 40 nm.	Greater than 95% conversion to nanoparticles has been achieved with *aloe* leaf broth concentration greater than 25%.	Mechanism of action of reaction is not clear.	(Sangeetha *et al.*, 2011)
Reduction of zinc salt by seaweed leaf extract (biological method)	5 ml ofS. *Myriocystum*seaweed leaf extract was added 95 ml of aqueous solution of 1 mM zinc nitrate. the flask containing the solution was heated on a water bath at 80°C for 5–10 min. The pH was adjusted between 5 and 10 and placed on magnetic stirrer for 1 h.	ZnO was rapidly biosynthesized at pH 8 and the size of nanoparticles was 36. zinc oxide nanoparticles were of different shapes viz., spherical, triangle, radial, hexagonal, rod, and rectangle size 76-186 nm.	The findings also revealed that brown seaweeds have the natural potential for the synthesis of nanoparticles	Purity of the product is an issue.	(Nagarajan and Arumugam Kuppusamy, 2013)
Hydrothermal	Hydrothermal treatment of	Various types of	High purity without	Yield of the	(Chen *et al.*,

Method	Description	Observation	Advantage	Disadvantage	References
Process	zinc acetate in pure water, KOH or ammonia aqueous solution	morphologies have been observed depends on solvents and their concentrations.	heat treatment at high temperature.	reaction is less.	1999; Yu and Yu, 2008)
Mechanochemical method	Initially, anhydrous ZnCl$_2$, anhydrous Na2CO$_3$and NaCl milled and then heated at 400 to 800 ^{0}C in an air atm. for 2 h to produce nanocrystalline ZnO.	The crystal size of the ZnO nanoparticle was in the range of 18 m to 36 nm.	Highly pure product produces.	High cost method.	(Ao *et al.*, 2006)
Direct precipitation method	Zinc salts and various oxidizing agents (ammonium carbonate, lithium hydroxide etc.) aqueous solutions used as reactant.	ZnO nanoparticles having pseudo-spherical shape with an average particle size of 7-9 nm.	Uniform nanoparticle with narrow particle size distribution.	Purity of the product is an issue.	(Chen *et al.*, 2008; Hong *et al.*, 2006; Meulenkamp, 1998)
Sol-gel technique	Zinc acetate and oxalic acid dihydrate as the starting materials in a ethanol at 45 ^{0}C and then calcinated at 400-600 ^{0}C for 2 hr.	Spherical nanoparticle of size ranges from 20-40 nm.	Simple process.	Calcination is required.	(Ba-Abbad *et al.*, 2013)
Microwave irradiation methods	Synthesis was performed using zinc acetate dehydrate, ammonium hydroxide and deionized water, carried out at pH of 8.0, solution heated by a domestic microwave oven for 3 min.	The average crystallite size of the flower-like and spherical nanostructures about 55 nm and 28 nm, respectively.	This method is simple, fast and cost effective.	Scale of process is difficult.	(Kajbafvala *et al.*, 2012)
Laser ablation method	Zinc oxide nanoparticles synthesized by pulsed laser ablation of a zinc metal target at room temperature indifferent liquid environment (water, isopropanol and acetone)	In water and isopropanol solvent yields spherical nanoparticles of 14-20 nm while in acetone two types of particles, one spherical with sizes around 100 nm and another platelet-like structure of 1 ・min diameter and 40 nm in width.	The technique offers an alternative for preparing the nanoparticles of active metal.	Yield is very less and scale-up is very difficult.	(Thareja and Shukla, 2007)
Solvothermal method	Zinc acetate, ethanol, and triethanolamine (as a polymer agent to terminate the growth) were used as starting materials, reaction carried out at 150^{0}C for 18 hours.	A hexagonal (wurtzite) structure, with a crystalline size of 30-35 nm, and particle size of 40-50 nm	No need perform calcination.	Yield is less, time consuming process.	(Zak *et al.*, 2011)
Sonochemical method	Zinc salt, sodium hydroxide and ammonia solution used as precursors. Sonication carried out at 60-70 ^{0}C for 15, 30, and 60 min.	Zinc oxide prepared at ultrasonication time of 15, 30, and 60 min possess hexagonal structure with crystallite size of 30, 40, and 35 nm, respectively	This is one of the facile and environmental benign protocol for synthesis of nano-size zinc oxide.	Scale of process is difficult.	(Banerjee *et al.*, 2012; Bhatte *et al.*, 2012; Khorsand Zak *et al.*, 2013; Vaezi and Sadrnezhaad, 2007)

Table 6. Methods for synthesis of zirconium phosphate nanoparticle

Method of preparation	Description	Observation	Advantage	Disadvantage	References
Reflux Method	Zirconyl chloride and phosphoric acid reflux at 100 ^{0}C for 24h	Obtained crystalline plate shape of size 60 to 200 nm. 86 to 96% yield	Nano-scale material	Broad particle size distribution	(Sun *et al.*, 2007)
Hydrothermal	Zirconyl chloride and	Obtained highly	High yield (90 to	Narrow size	(Sun *et al.*, 2007)

Method of preparation	Description	Observation	Advantage	Disadvantage	References
Method	phosphoric acid heated at 200 ^{0}C for 5h	crystalline plate shape of size 300 nm.	97%)	distribution	
Hydrogen Fluoride (HF) Method	Mixture of zirconyl chloride, phosphoric acid and HF reflux at 100 ^{0}C for 24h	Obtained highly crystalline plate shape of size 1 to 4 • m. 41 to 87% yield	High aspect ratio	Wide particle size distribution.	(Sun *et al.*, 2007)
Microwave assisted	The microwave assisted synthesis was carried out at 60, 80 and 90 ^{0}C power (300–800 W).	Spherical morphology with particle size varying in the range of 100–500 nm	Water was used as a solvent.	Reaction completed in 6h, which is much higher.	(Sinhamahapatra *et al.*, 2011)
Surfactant assisted	Reaction carried out between zirconium n-propoxide and orthophosphoric acid in presence of cetyltrimethylammoniumbromide at room temperature.	Mesoporous solid with higher surface area, pore diameter, and surface acidity.	No need to preformed calcination for getting surface Acidic Properties.	Reaction completed in 3 days.	(Jiménez-Jiménez *et al.*, 1998)

Synthetic ZrP exhibits similar structural characteristics to natural montmorillonite (MMT) clay. Compared with natural MMT clay, the main drawbacks of MMT clay are its wide particle size distribution and difficulty in achieving full exfoliation in polymer matrices and ZrP has several additional advantages, including much higher purity and surface energy and ion exchange capacity, more controllable surface functionality and easier processing of intercalation/exfoliation due to the fact that ZrP has different elements within its structure (Boo *et al.*, 2007). But these layered phosphates are unable to swell inwater, unlike smectite clays and it is therefore necessary to press them well with alkylamines, alcohols, or amino acids before intercalating large cations. Synthetic zirconium phosphate layer structures have been prepared via several different approaches reported in Table 6.

Thus, literature in Table 6 indicates that ZrP with a wide variation in aspect ratios has been prepared by controlling the concentration of reactants, temperature, pressure, and using a complexing agent. The size distribution of synthetic ZrP nanoplatelets can be more tightly controlled by varying reactant concentration, temperature, and reaction time. It also indicates that microwave irradiation (MWI) assisted synthesis of ZrP is an easy, convenient, economical and rapid synthetic procedure as the required MWI time (6 h) is much lower than that reported for conventional heating methods(5 days) (Jiménez-Jiménez *et al.*, 1998).

Application of Zirconium Phosphate (ZrP) in nanocomposites

ZrPs are dispersed in a polymer matrix in order to modify its characteristics or to enhance its use. More recently, nanocomposites based on polymers have been obtained by dispersing α-ZrP in polyvinyl alcohol (Liu and Yang, 2009; Yang *et al.*, 2009a), starch (Wu *et al.*, 2009a), chitosan (Wu *et al.*, 2010) and cellulose based paper composite (Li *et al.*, 2015).

However, application of α-ZrP nanoparticles in natural biopolymers for food packaging purpose is very limited. Structure and properties of starch or cellulose based paper and ZrP based films have been investigated by (Wu *et al.*, 2009a) and (Li *et al.*, 2015) respectively . They emphasized that enhancement in tensile strength, water resistance of starch was due to strong hydrogen bond between polar starch or cellulose and ZrP nanoparticles. But, incorporation of ZrP into the starch or cellulose based nanocomposites decreased its thermal stability due to increase in acidity of α-ZrP with temperature increasing, which in turn induces the decomposition of the glycoside bonds.

(Liu and Yang, 2009; Yang *et al.*, 2009a) succeeded to synthesize oxidized PVA/α-zirconium phosphate nanocomposites for obtaining special mechanical and barrier properties. However, degradation temperature of the resulted nanocomposites was increased due to hydrogen bonding between α-ZrP and PVA, which restricted the movement of molecular chains of PVA.

Also, Wu *et al.,* 2010 prepared chitosan/α-ZrP nanocomposite films and observed that addition of α-ZrP increased the water resistance and improved the strain at break, tensile strength, thermal stability of the chitosan based nanocomposite films.

Nano-silica

Synthesis of Nano-silica

Nano-silicon dioxide is a kind of amorphous powder with a molecular structure that is a tridimensional network.Nano-SiO_2 deviates from a stable silicon–oxygen structure for lack of oxygen in its surface. Its molecular formula is SiO_2-x, in which x ranges from 0.4 to 0.8. Because of its small size, large specific surface area, high surface energy, as well as a lot of unsaturated chemical bonds and hydroxyl groups on the surface, nano-SiO_2 is easy to disperse into the macromolecular chains (Rahman and Padavettan, 2012a). Silicon dioxide (E551), is a permitted food additive which is preferably insoluble. SiO_2 used in food contact surfaces and food packaging. Nano-silica increases the toughness of food packaging (Mihindukulasuriya and Lim, 2014).

Table 7. Methods for synthesis of silica nanoparticles

Method of Synthesis	Description	Observation	Advantage	Disadvantage	References
Wet Chemical Synthesis	Wet chemical synthesis of SiO_2nano particles using tetraethyl orthosilicate, ethanol, water and ammonium hydroxide with different surfactants (cetyltrimethylammonium bromide, sodium dodecyl sulphate and poly vinyl pyrrolidone.	The amorphous silica nanoparticles form. Size is less in presence of sodium dodecyl sulphate than other surfactants.	Getting very low particle size	Reaction time is very high.	(Stanley and Nesaraj, 2014)
Sol-gel method	The process involves hydrolysis and condensation of metalalkoxides ($Si(OR)_4$) such as etraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$) or inorganic salts such as sodium silicate (Na_2SiO_3) in the presence of mineral acid (e.g., HCl) or base (e.g., NH_3) as catalyst.	Forms spherical nanoparticles ranging from 7 to 200 nm depends on the reaction conditions i.e. concentration of reagents, temperature, pH, drying method, mixing of reagents etc.	Produce monodispersed particles with narrow-size distribution using mild conditions	Partial hydrolysis of orthosilicate takes place when it is mixed with water and ethanol.	(Hassan *et al.*, 2013; Le *et al.*, 2013; Rahman and Padavettan, 2012b; Singh *et al.*, 2014)
Acid treatment.	The waste ash from biomass combustion Was successfully converted into silica nanoparticles.	Amorphous, mono dispersed silica nanoparticles with 10 nm size.	Waste can be utilized as a source of silica.	Silica contain in the ash is very low.	(Abraham *et al.*, 2014)
Precipitation method	Precipitation of commercially available silica gel using sodium hydroxide and sulphuric acid.	Spherical silica nanoparticles with 50 nm size.	High reaction yield.	High Reaction time.	(Jal *et al.*, 2004)

The coating is also applied using a continuous process as a thin amorphous film of 50 nm or less to prevent cracking of the barrier if the product is flexed. The flexibility of the coatings may be increased by the addition of other additives during production. Various methods for synthesis of nano-silica have been described in table 7.

Table 7 indicates that the source compounds for SiO_2 used in the production of the nano-scale SiO_2 includes organo silicates, silanes, chlorosilanes and tetraethylorthosilane and waste ash from biomass. Sol-gel is suitable method for synthesis of nano-silica as it provides nanoparticles with narrow size distribution as compared to wet chemical synthesis method. Reaction time for the both wet chemical synthesis and precipitation method is high as compared to sol-gel method(Hassan *et al*., 2013; Le *et al*., 2013; Rahman and Padavettan, 2012b; Singh *et al*., 2014). Acid treatment is a good option to recover nano-silica from waste ash of biomass. But, the silica content in the ash is very low (Abraham *et al*., 2014).

Application of Nano-silica in nanocomposites

Tensile strength and water vapor resistance of the starch/poly(vinyl alcohol) (PVA) films was improved due to incorporation of nano-sized silicon dioxide particles into the starch/PVA blend (Tang *et al*., 2008). Intermolecular hydrogen bond formed between nano-silicon dioxide and starch or n-SiO_2 and PVA was responsible for the miscibility between film components and hence improvement in tensile strength and water vapor barrier property.

The nano-SiO_2 content significantly impacted on the oxygen barrier coating of pullulan biopolymer to be applied on poly(ethylene terephthalate) (PET), especially for food packaging applications. They revealed that the mixing the two Phases (Pullulan organic phase/ nano-silica inorganic phase = 3) yielded a three-dimensional hybrid network formed by self-assembly and mediated by the occurrence of new hydrogen bond interactions at the intermolecular level. Therefore, the deposition of the hybrid coatings decreased the oxygen transmission rate (OTR) of the plastic substrate (PET) (Farris *et al*., 2012).

Shi *et al*., 2013 prepared a novel chitosan/nano-silica hybrid film for preservation of longan fruits (*Dimocarpus longan Lour. cv Shijia*). Their study revealed that the excellent semi-permeable film of chitosan/nano-silica markedly extended shelf life, reduced browning index and retarded weight. This was due to excellent bone bioactivity and high stiffness of the silica xerogel. The retardation of color development in the longan fruits treated with chitosan/nano-silica coating could be attributed to the slow rate of respiration and reduced ethylene production, leading to a modified internal atmosphere of the fruit. In similar way, (Yu *et al*., 2012) also prepared chitosan (1%)/nano-silica (0.04%) hybrid coating on jujube.

Starch nanocrystal

Synthesis of starch nanocrystal

Starch is a semicrystalline biopolymer and when native starch granules are submitted to an extended-time hydrolysis at temperatures below the gelatinization temperature, the amorphous regions are hydrolyzed allowing separation of crystalline lamellae, which are more resistant to hydrolysis. The starch crystalline particles (crystallites) show platelet morphology with thickness of 6–8 nm, length of 20–40 nm and width of 15–30 nm.

Table 7. Methods for synthesis of silica nanoparticles

Method of Synthesis	Description	Observation	Advantage	Disadvantage	References
Wet Chemical Synthesis	Wet chemical synthesis of SiO_2 nanoparticles using tetraethyl orthosilicate, ethanol, water and ammonium hydroxide with different surfactants	The amorphous silica nanoparticles form. Size is less in presence of sodium dodecyl sulphate than other surfactants.	Getting very low particle size	Reaction time is very high.	(Stanley and Nesaraj, 2014)

Method of Synthesis	Description	Observation	Advantage	Disadvantage	References
	(cetyltrimethylammonium bromide, sodium dodecyl sulphate and poly vinyl pyrrolidone.				
Sol-gel method	The process involves hydrolysis and condensation of metalalkoxides ($Si(OR)_4$) such as tetraethyllorthosilicate (TEOS, $Si(OC_2H_5)_4$) or inorganic salts such as sodium silicate (Na_2SiO_3) in the presence of mineral acid (e.g., HCl) or base (e.g., NH_3) as catalyst.	Forms spherical nanoparticles ranging from 7 to 200 nm depends on the reaction conditions i.e. concentration of reagents, temperature, pH, drying method, mixing of reagents etc.	Produce monodispersed particles with narrow-size distribution using mild conditions	Partial hydrolysis of orthosilicate takes place when it is mixed with water and ethanol.	(Hassan *et al.*, 2013; Le *et al.*, 2013; Rahman and Padavettan, 2012b; Singh *et al.*, 2014)
Acid treatment.	The waste ash from biomass combustion Was successfully converted into silica nanoparticles.	Amorphous, mono dispersed silica nanoparticles with 10 nm size.	Waste can be utilized as a source of silica.	Silica contain in the ash is very low.	(Abraham *et al.*, 2014)
Precipitation method	Precipitation of commercially available silica gel using sodium hydroxide and sulphuric acid.	Spherical silica nanoparticles with 50 nm size.	High reaction yield.	High Reaction time.	(Jal *et al.*, 2004)

Table 8. Methods for synthesis of starch nanocrystal

Method of preparation	Description	Observation	Advantage	Disadvantage	References
Cast light method	Potato starch was dispersed (5% wt/wt) either in 2.2 or 3.7 M hydrochloric acid and incubated at 35 ^{0}C for up to 50 days while shaken at 120 rpm.	The preferential hydrolysis of amorphous regions of starch by acid at ambient temperature resulted in nano-meter range particles with crystalline nature.	The preferential hydrolysis of amorphous regions of starch by acid at ambient temperature resulted in nano-meter range particles with crystalline nature.	Time consuming process.	(Jivan *et al.*, 2013)
Ultrasonic method	Waxy maize starch was dispersed in an aqueous sulfuric acid solution, and hydrolyzed by stirring for up to 7 days at 40 ^{0}C with ultrasonic treatments at different vibration amplitudes and durations. The amount of starch nanoparticles in the hydrolyzates isolated after 7 days.	Starch nanoparticles produces in round shape with average diameter of 70 nm	Ultrasonication played an important role in dissociating the nanoparticle aggregates that may thereby effectively increasing the yield of starch nanoparticles.	Ultrasonication reduces the crystallinity of starch.	(Kim *et al.*, 2013)
Acid hydrolysis based on enzymatic method	Starch nanocrystals are crystalline platelets resulting from the acid hydrolysis of starch. An enzymatic pretreatment of starch to reduce the acid hydrolysis duration.	With a 2 h pretreatment of waxy maize starch, the extent of acid hydrolysis currently reached in 24 and120 h (5days) were reached in only 6 and	An enzymatic pretreatment can reduce hydrolysis time.	Enzymes are costlier.	(LeCorre *et al.*, 2012)

Method of preparation	Description	Observation	Advantage	Disadvantage	References
		45 h, respectively.			
Nano-precipitation Method	Synthesis of starch nanoparticles with controllable particle sizes from natives ago starch using the nano-precipitation method. The NaOH/urea (NU) (0.8:1 wt%) solution mixture used as a solvent system for the dissolution of native sago starch.	Starch nanoparticles of particle size range between 300 nm and 400 nm.	The synthesis method used is simple, fast and easy to perform.	Separation and purification is very difficult.	(Chin *et al.*, 2011)
High power ultrasonication method	High power ultrasound treatment of the waxy maize starch suspension in water and at low temperature for 75 min.	The formation of starch nanoparticles between 30 and 100 nm in size.	The advantage of being quite rapid, presenting a higher yield and not requiring any chemical treatment.	Ultrasonication reduces the crystallinity of starch.	(Bel Haaj *et al.*, 2013)

However, individual starch crystallites could hardly be obtained since the starch platelets flocculate and form aggregates. Nevertheless, since at least one of the dimensions of aggregates is at the nanometer scale, the term ‘nanoparticle’ is applicable for starch crystalline particles derived by acid etching of granular starch (Kristo and Biliaderis, 2007b). Apart from acid etching, there are several methods for the synthesis of starch nanoparticles, which are shown in the Table 8.

Only a limited number of articles concerning starch nanocrystal production have been published during the past decade. They are gathered in table 8. Most of them relate to acid hydrolysis along with the ultrasonic or enzymatic pretreatment to reduce hydrolysis duration. No work on a purely enzymatic hydrolysis method for producing starch nanocrystals has been reported (Le Corre *et al.*, 2010).

The most innovative approach for starch nanocrystal is the use of high power ultrasonication method. Because, it being quite rapid, presenting a higher yield and not requiring any chemical treatment and giving starch nanoparticles between 30 and 100 nm in size (Bel Haaj *et al.*, 2013; Kim *et al.*, 2013).

Application of starch nanocrystal in nanocomposites

Starch nanocrystals as reinforcing phase have been introduced into natural polymer matrix as well as synthetic polymer matrix. Rajisha *et al.*, 2014 used potato starch nanocrystal as a nanofiller for natural rubber. The tensile strength and modulus of the natural rubber composites were found to improve tremendously with increasing nanocrystal content. Addition of starch nanocrystals induced a decrease in permeability to both water vapor and oxygen of natural rubber-based nanocomposites. This dramatic increase observed was attributed to the formation of the starch nanocrystal three-dimensional network through hydrogen linkages between starch nanoparticle clusters and also to favorable interactions between the matrix and filler. This network immobilizes the polymer chains leading to an increase in the modulus and other mechanical properties. Condés *et al.*, 2015 studied the effect of addition of maize starch nanocystal in to amaranth protein film. Addition of maize nanocrystal improved water vapor permeability (WVP), water uptake (WU), surface hydrophobicity and mechanical behavior of amaranth protein film. Disulfide bonds for waxy maize nanocrystals and by hydrogen bonds for normal maize nanocrystals induced these reinforcing effects for amaranth protein films.

González and Alvarez Igarzabal, 2015 prepared starch nanocrystal reinforced soy protein films to sequester cholesterol when brought into contact with cholesterol rich food, such as milk. This was attributed to the improved hydrophobicity (more affinity for cholesterol) due to immobilization of the protein films by three-dimensional network through hydrogen linkages starch nanocrystals.

Zou *et al.*, 2011 reported that the addition of starch nanocrystals improved tensile strength and

Young's modulus of waterborne polyurethane (WPU) based film. The Tg values shifted to higher temperatures with increasing starch nanocrystals content up to 8 %, which was attributed to a restricted mobility of waterborne polyurethane chains due to the formation of strong interactions between starch nanocrystals as well as between filler and matrix. However, with increasing of the starch nanocrystal content more than 8%, the nanocrystals probably self-aggregated as large domains which in turn decreased the starch nanocrystal surface for interacting with the waterborne polyurethane. This self-aggregation resulted in decrease in the Tg values and tensile strength.

Chitosan nanoparticles

Synthesis of chitosan nanoparticles

Chitin, poly (-(1-4)-N-acetyl-d-glucosamine), is the most abundant polysaccharide in the world. It is synthesized by an enormous number of living organisms. It is extracted from crab and shrimp shells as a byproduct of the seafood industry (Kumar *et al.*, 2010). The most important derivative of chitin is chitosan which obtained by (partial) deacetylation of chitin in the solid state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of chitin deacetylase.

Table 9. Methods for synthesis of chitosan nanoparticles

Method of preparation	Description	Observation	Advantage	Disadvantage	References
Top down method	A top down preparation method of chitosan nanoparticles and chitosan nanofibers employing direct ultrasonication of deacetylated chitin nanofibers. Pure chitin isolated from crab shells was treated chemically and mechanically to obtain chitin nanofibers.	The diameter and the length of the chitosan nanofibers were found to be less than 100 nm and 3 µm respectively. Chitosan nanoparticle with diameter less than 300 nm.	Natural source of chitin.	Deacetylation of chitin needs to be carried out using a concentrated alkaline solution at high temperature.	(Wijesena *et al.*, 2015; Younes and Rinaudo, 2015)
Emulsion Cross-linking	The reactive functional amine group of chitosan to cross-link with aldehyde groups of the cross-linking agent such as glutaraldehyde, to stabilize the polysaccharide droplets. Then nanoparticles are washed and dried.	Spherical nano and microspheres.	Size of the particles can be controlled by controlling the size of aqueous droplets of emulsion.	Involves tedious procedures as well as use of harsh cross-linking agents. Removal of the un-reacted crosslinking agent may be difficult in this process.	(Akbuğa and Durmaz, 1994)
Emulsion-Droplet Coalescence	Chitosan is insoluble in alkaline pH medium, but precipitates/coacervates when it comes in contact with alkaline solution. Particles are produced by blowing chitosan solution into an alkali solution like sodium hydroxide, NaOH-methanol or ethanediamine using a compressed airnozzle to form coacervate droplets.	Varying compressed air pressure or spray-nozzle diameter controlled the size of the particles.	Particles produced by this method have better acid stability than observed by other methods.	Difficult to get nanoparticles.	(Nishimura *et al.*, 1986)
Ionotropic Gelation	Chitosan is dissolved in an aqueous acidic solution such as acetic, malic, tartaric, or citric acid in order to obtain cations of chitosan. Then, the solution is added to tripolyphosphate solution	Spherical nano and microspheres.	Efficiency of the method was dependent upon the deacetylation of chitosan, since it involves the gelation of protonated amino	Microparticles formed have poor mechanical strength.	(Shu and Zhu, 2000)

Method of preparation	Description	Observation	Advantage	Disadvantage	References
	drop-wise under constant stirring. Due to the complexation between oppositely charged species, chitosan undergoes ionic gelation and precipitates to form spherical particles.		groups of chitosan.		
Reverse Micelles	In this technique, the surfactant was dissolved in an organic solvent to prepare reverse micelles. The micellar droplets are displaced randomly and subjected to Brownian motion. They exchange their water content and reform into two distinct micelles. Then, the aqueous phase containing the chitosan nanoparticles form in the core of the reverse micelles.	Forms the chitosan nanoparticles.	Extremely fine particles (1-10 nm) with a narrow size distribution.	Undergo continuous coalescence followed by re-separation.	(Mitra *et al.*, 2001)

Because of the semicrystalline morphology of chitin, chitosan obtained by solid-state reaction has a heterogeneous distribution of acetyl groups along the chains. Chitin and chitosan are biocompatible, biodegradable and non-toxic polymers (Zhai *et al.*, 2004). Methods used for the synthesis are summarized in Table 9. Table 9 indicates that different methods have been used to prepare chitosan nanoparticles. Selection of any of the methods depends upon factors such as particle size requirement, thermal and chemical stability of the active agent, stability of the final product and residual toxicity associated with the final product. The emulsion cross-linking method has a few drawbacks since it involves tedious procedures as well as the use of harsh cross-linking agents, which might possibly induce chemical reactions with the active agent. Also, complete removal of the un-reacted cross-linking agent may be difficult in this process (Akbuğa and Durmaz, 1994). It is difficult to obtain nanoparticles by emulsion droplet coalescence (Nishimura *et al.*, 1986). Chitin nanoparticles obtained by ionic gelation have poor mechanical strength thus, limiting their usage in drug delivery (Shu and Zhu, 2000). Reverse micelles method is a good method for synthesis for the preparation of ultrafine polymeric (chitosan) nanoparticles were narrow size distribution is possible (Mitra *et al.*, 2001).

Application of chitosan nanoparticles in nanocomposites

Chitosan whiskers were used as reinforcing phase in both synthetic polymer matrices and natural polymeric matrices. (Wang *et al.*, 2015) added chitosan whiskers (CS) to polylactic acid (PLA). They reported that when CS/PLA ratio was at 1:1 (w/w) and above, a notable enhancement was observed in the tensile strength with the increase of PLA content, while the elongation at break was decreased slightly at the same time. However, a significant decrease in tensile strength and elongation at break were present when the CS/PLA ratio was below 1:1. Notable enhancement was due to intermolecular hydrogen bonds between CS and PLLA molecules.

Lago *et al.*, 2014 showed the improvement in antimicrobial property of polyamide films with 5-10 % chitosan loading and polyethelene terephthalate with a coating of 0.6% chitosan. Abdollahi *et al.*, 2012 developed active food packaging film from chitosan and Rosemary essential oil (REO). The effects of REO concentration (0.5, 1.0 and 1.5% v / v) on film properties were studied by measuring the physical, mechanical and optical properties of the REO-loaded films. The solubility and water gain of the chitosan film decreased about 25% and 85%, respectively, by REO incorporation, up to 1.5% v/v. this was attributed to the interaction between hydrophilic groups of chitosan and REO. Films containing REO showed more antibacterial activity.

CONCLUSIONS

This review illustrated the synthesis of nanoparticles used in the improvement of polymer based composites for food packaging purposes. Over the past decades, the tremendous effort put into nanomaterials has resulted in a rich database for their synthesis, properties and applications. The continuing breakthroughs in the synthesis of nanomaterials have brought new properties and new applications with improved performance of food packaging. Properties of nanomaterials such as size, as well as shape and structure-dependent optical, electronic, thermal properties depend upon the method of synthesis. A biological method using bacteria and plant extracts appears to be a potentially exciting tool for large-scale synthesis of nanoparticles. But, the purity and percentage conversion are the main issue with biological methods. Ultrasound (cavitation) based methods are more suitable for the synthesis of nanoparticles as it has shown its potential in reducing the size of millimeter or micrometer-sized particles to nanoparticles. Nowadays, Hydrodynamic cavitation has been used for large scale synthesis of nanoparticles. All these nanomaterials have continued to be highly active in food packaging applications and they also demonstrate new applications including electrochromics, sensing and photocatalytic and photovoltaic, hydrogen storage and wastewater treatment. Thus, these nanomaterials are playing and will continue to play an important role in the protections of food from the environment.

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Conflicts of Interest

The authors declare no conflict of interest.