Chapter 1
Nanoagriculture and Water Quality Management

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Abstract Nanomaterials have rapidly gained importance in many fields of science and technology due to their unique properties. Nanomaterials are used in the agri-food sector notably for preservation and packaging, for agriculture and for water quality management. Future applications will improve shelf life, food quality, safety, and fortification. Nanosensors will be used to analyse contaminated food and water. Here we review the application of nanotechnology in agriculture and subdisciplines. The major points are the following. We explain the classification and synthesis of nanomaterials used for agriculture and water management. Then we present major applications such as nanoscale carriers, fabricated xylem vessels, nanolignocellulosic materials, clay nanotubes, photocatalysis, bioremediation of resistant pesticides, disinfectants, agricultural wastewater treatment, nanobarcode technology, quantum dots for staining bacteria, and nano-biosensors. Applications to water quality management include nanolignodynamic metallic particles, photocatalysis, desalination, removal of heavy metals, and wireless nanosensors.

Keywords Nanotechnology • Nanomaterials • Agriculture • Water quality management • Environment

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S. Ranjan et al. (eds.), *Nanoscience in Food and Agriculture 1*,
Sustainable Agriculture Reviews 20, DOI 10.1007/978-3-319-39303-2_1

1.1 Introduction

The term ‘nano’ is coined from the Greek word for dwarf. A nanometre (nm) is 1-billionth of a metre, or approximately 100,000th of the width of a human hair. Nanotechnology has many applications in biotechnology and its allied field e.g. tissue engineering, drug delivery, biomedical engineering, food science and technology among others (Danie et al. 2013; Ranjan et al. 2014; Dasgupta et al. 2014). The applied nanotechnology has been shown in Fig. 1.1 using solar system model. A wide range of applications of nanotechnology is also emerged into the “agri-food sector” which includes the nanosensors, tracking devices, targeted delivery of required components, food safety, new product developments, precision processing, smart packaging and others, shown in Fig. 1.2 (Huang et al. 2010; McClements et al. 2009; Ranjan et al. 2014; Dasgupta et al. 2014). Nanotechnology can also improve the water solubility, thermal stability and bioavailability of the functional compounds of food (McClements et al. 2007, 2009; Miguel et al. 2014). Figures 1.3 and 1.4 represent the major applications of nanotechnology in food processing and packaging, the same has already been discussed in many review articles earlier, by Ranjan et al. (2014) and Dasgupta et al. (2014).

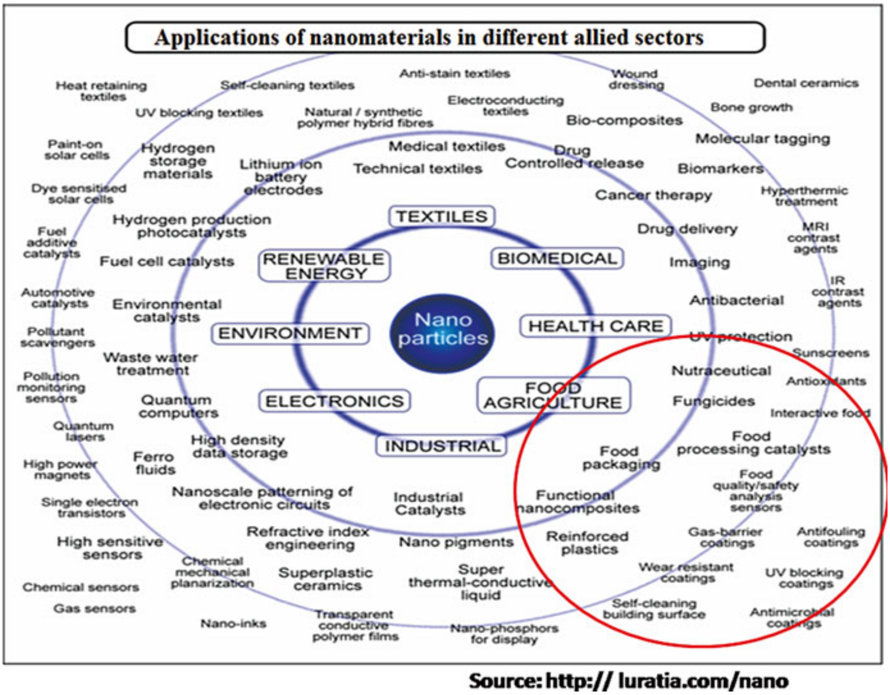

Fig. 1.1 Solar system model showing applications of nanotechnology in different allied sectors including industrial, electronics, environment, renewable energy, textiles, biomedical, healthcare, foods, agriculture and agro-foods. The *red-circled* part has been covered in this chapter (Courtesy: www.lurasia.com/nano and www.xpertarena.com)

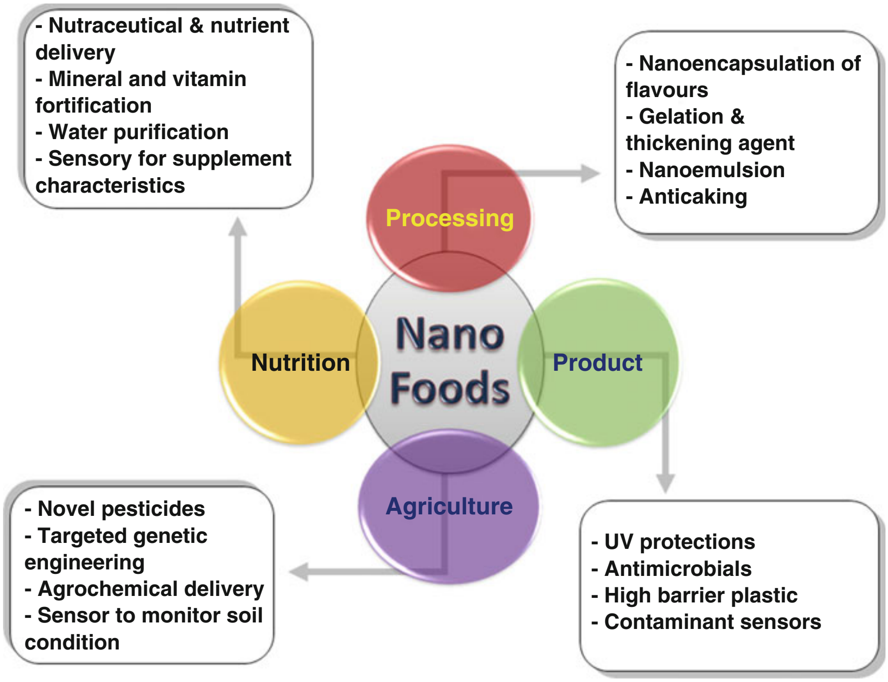

Fig. 1.2 A mind-map showing the linkage of nano-foods with agriculture, nutritional, process development and product development. Pictorial representation for some of the major applications of nanotechnology in different sectors of food and agriculture (Courtesy: Ranjan et al. 2014)

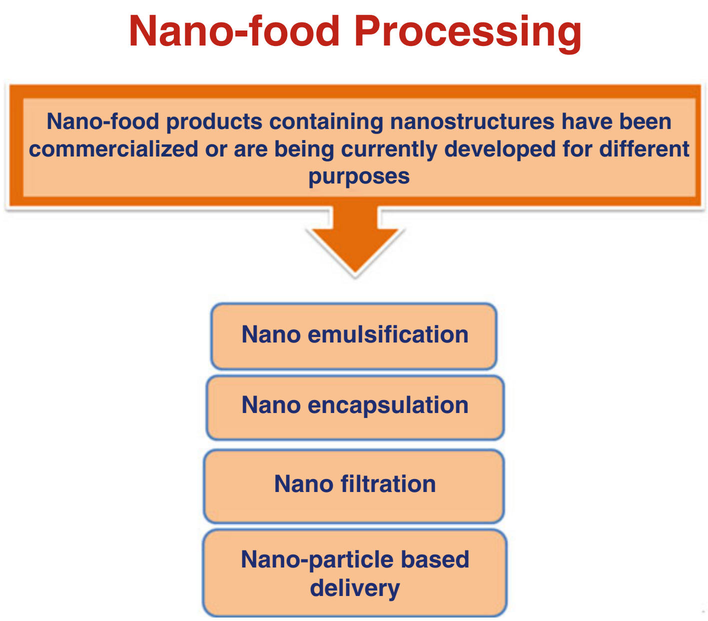

Fig. 1.3 Major types of nano-structures or processes which are being used to develop nano-foods to be launched in market

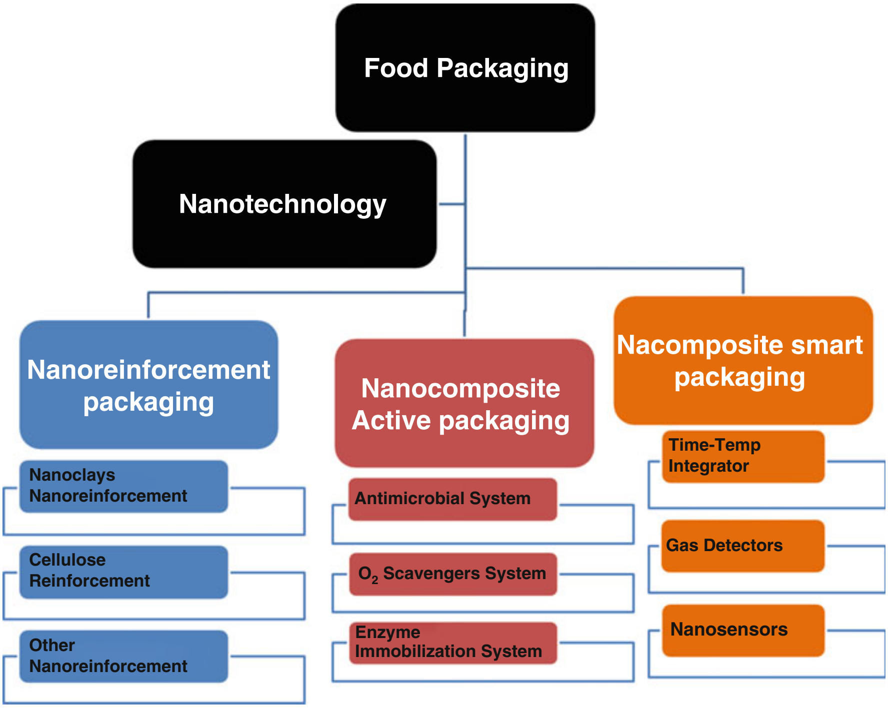

Fig. 1.4 Pictorial representation to sumamrize the different types and sub-types of nano-food-packaging being used along with their different applications (Courtesy: Ranjan et al. 2014)

Agricultural products influence most aspects of life, including everyday materials, such as fuels, textiles, furniture, feedstock for bio-based products including food and feed. Technology advancement is needed to achieve the future global needs from agriculture. Nanoscience and nanotechnology has shown great potential in improving food safety, quality, product traceability, nutrient delivery, enhancing packaging performance, and improving agricultural and food processing. In the present review an attempt has been made to summarize the classification and the synthesis method for the nanomaterials used in agricultural practices and water quality management. Also, the application of nanomaterials in the agriculture such as nanoscale carriers, fabricated xylem vessels, nanolignocellulosic materials, clay nanotubes, photo-catalysis, bioremediation of resistant pesticides, disinfectants, agricultural wastewater treatment, nanobarcode technology, quantum dots for staining bacteria, different types of nano-biosensors along with the current research trends, future directions, opportunities and research gaps in this field has been discussed in detail. The goal of this article is to provide the perspectives of researchers working with nanotechnology to address agricultural and water quality management problems.

1.2 Classification of Nanomaterials

Nanomaterials can be classified as (i) nanoparticles (ii) nanoclays and (iii) nano-emulsions, which can be synthesized by a number of methods and have many applications in agri-food sector.

1.2.1 Nanoparticles

Nanoparticles can be categorized into different types based on their ability to carry different reactions with different ingredients and environmental conditions. Depending on the chemical characteristics, Nanoparticles can also be divided into two broad categories- organic and inorganic.

Organic Nanoparticle-sometimes referred to as nanocapsules, when used to enhance the bioavailability of nutrient and their delivery. However, seen from a general level, they can be defined as nano-vesicular systems that exhibit a typical core-shell structure in which the drug is confined to a reservoir or within a cavity surrounded by a polymer membrane or coating (Anton et al. 2008). There are six classical methods for the preparation of nanocapsules: nanoprecipitation, emulsion-diffusion, double emulsification, emulsion-coacervation, polymer-coating and layer by-layer (Mora-Huertas et al. 2010) as mentioned in Table 1.1. Recently a new class of water-soluble red fluorescent organic nanoparticles have been prepared for an application in cell imaging which further can be used in the development of nano-sensors (Xiqi et al. 2014). Also, a fluorescent organic nanoparticle has been developed by Zhang et al. (2014) with dye removal (remediation) from soil as well as and water. This facilely incorporated polymeric nanoparticle showed high water dispersibility, uniform size, strong red fluorescence and excellent biocompatibility, which makes them promising in water purification, nano-sensor development for water as well as agricultural products (Zhang et al. 2014).

1.2.1.1 Inorganic Nanoparticles

Inorganic ingredients manufactured at the nanoscale with variations of compounds and approved for use in food, e.g. titanium dioxide, a food colorant, can be used as a UV protection barrier in food packaging when used as a nanoparticle. New storage containers/utensils (food contact materials) based on embedded inorganic nanoparticle have been designed for preservation of prepared agricultural products. Grain storage bins are being produced with silver nanoparticle embedded in the plastic for killing bacteria from any food that was previously stored in the bins and minimizing health risks (Food Safety Authority of Ireland 2008). A cellulose-based bactericidal nanocomposites containing silver nanoparticle have been developed, which

Table 1.1 Upstream and downstream procedures for the preparation of nanocapsules (Mora-Huertas et al. 2010)

<table>
<tr><th>S. No.</th><th>Upstream process for nanocapsule formation</th><th>Downstream process for nanocapsule concentration, purification and stabilization</th></tr>
<tr><td>1</td><td>Nanoprecipitation Method
➢ Organic phase is slowly injected (dropwise and moderate stirring) to the aqueous phase</td><td rowspan="6">Solvent Elimination
➢ Moderate magnetic agitation
➢ Evaporation by vacuum
➢ Tangential ultrafiltration

Purification
➢ Water washing
➢ Diafiltration
➢ Filtration through 0.45μm
➢ Gel filtration

Recuperation
➢ Ultrasonication

Stabilization
➢ Spray drying
➢ Lyophilization/freeze drying</td></tr>
<tr><td>2</td><td>Emulsification-diffusion Method
➢ Organic and aqueous phase are emulsified (high shear mixture)
➢ Diffused (moderate stirring) to dilution phase</td></tr>
<tr><td>3</td><td>Emulsification-coacervation Method
➢ Organic and aqueous phase are emulsified (mechanical stirring or sonication)
➢ Coacervation (moderate stirring) in the presence of crosslinking agents or dehydratant agent</td></tr>
<tr><td>4</td><td>Double emulsification Method (Water-Oil-Water)
➢ Organic phase and first Aqueous phase are emulsified in water-oil system (sonication)
➢ Second aqueous phase and previous solution are emulsified in oil water system (high shear mixture)</td></tr>
<tr><td>5</td><td>Polymer coating Method (Water-Oil-Water)
➢ Organic and aqueous phase are emulsified in water-oil system (sonication)
➢ Second phase i.e. coating agent and previous solution are emulsified in oil water system (sonication or high shear mixture)</td></tr>
<tr><td>6</td><td>Layer by layer
➢ Template will be encapsulated with several layers of mixture of anionic/cationic polymers and coat charged polymer</td></tr>
</table>

exhibited an improved bactericidal and nanocomposite properties. Further it has been concluded that these properties may have the future applications in active packaging of food and agricultural products (Márcia et al. 2012). Also, silver nanoparticle incorporated into carboxymethylcellulose films have been studied for its antimicrobial studies for food and agricultural products packaging and found suitable for the same (Siqueira et al. 2014). The detailed view on packaging of agricultural and food product is provided by Ranjan et al. (2014) and Dasgupta et al. (2014).

Similar to organic, inorganic nanoparticles are also having several methods of production e.g. gas and liquid phase synthesis method, which are further classified into different methods. Gas phase synthesis methods have mainly three types for synthesis (a) flamed spray synthesis (b) laser induced gas evaporation method synthesis (c) plasma based synthesis. However, liquid phase inorganic nanoparticles synthesis methods may further categorized into (a) co-precipitation method and (b) sol-gel approach (Food Safety Authority of Ireland 2008). The properties of nanoparticles have shown to be dependent on the size and other surface properties, which ultimately depend on the synthesis procedure. Hence, it is necessary to understand the synthesis procedures of nanoparticles for their specific application. The detailed overview of inorganic nanoparticles synthesis has been given in the book of Jesus et al. (2012), which has been summarized below for better understanding.

1.2.1.2 Flame Spray Synthesis

Three large scale commodities have been around for half a century which are pigmentary titania (white pigment), aerosol-made silica and carbon black (tire soot) are made by flame processes at several megatons per year (Layman 1995; Ulrich 1984). Production of these materials started in the 1940s. In principle, it would appear attractive to extend this apparently useful flame processes to other materials (Stark et al. 2002). Flame-made oxides have been explored for applications as sensors which further can be used in agricultural field (Athanassiou et al. 2006). As a result, a number of products have become available in the form of nanoparticles, such as nano-gypsum (Osterwalder et al. 2007), nano-salt (Grass and Stark 2005) and nano-tricalcium phosphate (Maciejewski et al. 2008). Further adaptations within the flame spray synthesis technology gives access to the production of metal nanoparticles (Athanassiou et al. 2006; Grass and Stark 2006). This is achieved by a modification of the flame reactor operating under reducing (oxygen starved) conditions (Grass and Stark 2006). Very recently, one further step was taken and the controlled deposition of carbon on the metal surface of nanoparticle also became accessible (Athanassiou et al. 2006, 2007). For example, the suitability of carbon coated copper nanoparticles in water based dispersions or inks of such have been shown to offer a simple production method to highly sensitive humidity sensor coatings (Luechinger et al. 2007). In summary, flame spray synthesis allows the scalable fabrication of most accurate mixed oxide compositions, salt, metal and carbon-coated metal or silica-coated metal oxide nanoparticle (Teleki et al. 2008) based on metal loaded liquid precursors.

1.2.1.3 Laser Induced Gas Evaporation Method

Instead of combustion of a liquid precursor giving access to oxidic nanoparticles, Kato (1976) produce a range of different ultrafine refractory oxides (SiO_2, MgO, Al_2O_3, Fe_3O_4, Mg_2SiO_4, $CaTiO_3$ and $MgAl_2O_4$) by the use of a CO_2 laser. The laser was used to vaporize starting material in form of powder or sintered or fused blocks. The vaporized material condensed in an environment of inactive gases and resulted in nanoparticles of around 10 nm particle diameter at a production rate of 10 mg/min (0.6 g/h). Ullmann et al. (2002) studied the systematic influence of the operating parameters on laser ablation for the aerosol generation and concluded that laser ablation is a convenient method for laboratory scale nanoparticles generation.

1.2.1.4 Plasma Based Nanoparticles Production

A similar method to laser induced gas evaporation are plasma reactors. In this case plasma delivers the energy necessary to evaporate the starting materials of various types including gases, liquids and solids. At temperatures of around 10,000 °C the plasma generates reactive ions and radicals. During the pull-out from the plasma region the temperature of the gas drops and nanoparticles are formed (Young and Pfender 1985). Plasma based methods have been used to synthesize nanoparticles in form of metal oxides (Suzuki et al. 2001), metals (Jiang and Yatsui 1998) or metal nitrides (Kinemuchi et al. 2003).

1.2.1.5 Co-precipitation Method

In a first step of a typical co-precipitation reaction, the conditions are adjusted to maximize the simultaneous generation of sparingly soluble particles. The key properties of the final product (above all particle size and morphology) are subsequently determined in secondary processes such as aggregation or Ostwald ripening. In the final step, the as-formed particles are usually thermally decomposed to oxides. An advantage of the co-precipitation method is that particle sizes can be well controlled for the fabrication of monodisperse inorganic nanoparticles possible. A major disadvantage though is the involvement of vast amounts of solvents and surfactants (Cushing et al. 2004).

1.2.1.6 Sol-Gel Method for Inorganic Nanoparticles Synthesis

Another inorganic nanoparticles synthesis method based on liquid precursors is the processing of materials by the *sol-gel* method. This process dates back to the mid 1800s where scientists found that they were able to synthesize ceramic or glassy material from a viscous gel. Typically, metal alkoxides or metal chlorides are used as starting materials forming the solvated metal precursor (the *sol*). This precursor undergoes hydrolysis and polycondensation reactions to form a gelated colloid (the *gel*). The reactions of this oxide- or alcohol-bridged network continue until the gel transforms into a solid mass under expulsion of the solvent from the pores. Subsequently, the monolith is calcined at temperatures up to 800 °C. In the firing step when the temperature rises above 800 °C densification and decomposition of the gel occurs under collapse of the gel network. The sol-gel process is ideally suited for the fabrication of synthetic zeolites, where a porous "open" structure is desired for the accommodation of a wide variety of cations (Hench and West 1990).

1.2.2 Nanoclays

They are naturally occurring aluminium silicate, primarily composed of fine-grained minerals having sheet-like geometry. The sheet-structured hydrous silicates are generally referred to as phyllosilicates. They are inexpensive and eco-friendly materials and have been found for multifarious application. These clay minerals have been widely studied in practical applications such as in geology, agriculture, construction, engineering, process industries, and environmental applications. They provide an attractive alternative for the decontamination of soils, underground waters, sediments and industrial effluents i.e. in the field of water purification and recently nanoclays have been found to have application in sensor development (Garrido-Ramirez et al. 2010; Grasielli et al. 2012). The most studied nanoclayis montmorillonite (MMT), whose chemical general formula is $Mx(Al_4\text{-}xMgx)\ Si_8O_{20}(OH)_4$. montmorillonite is a representative of 2:1 layered *phyllosilicates*, whose platelets have two layers of tetrahedral silica sheets filled with a central octahedral alumina sheet (Weiss et al. 2006). This kind of clay has a moderate negative surface charge that is important to define the interlayer spacing (Xin-Juan et al. 2015). The imbalance of the surface negative charges is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces (Tan et al. 2008). Montmorillonite is excellent reinforcing filler, due to its high surface area and large aspect ratio, which ranges from 50 to 1000 (Uyama et al. 2003). The improved barrier properties of polymer-clay nanocomposites seem to be due to an increased tortuosity of the diffusive path for permeants, forcing them to travel a longer path to diffuse through the film. The increase in path length is a function of the aspect ratio of the clay and the volume fraction of the filler in the composite. This theory was developed by (Nielsen 1967) and was further corroborated by other authors (Mirzadeh and Kokabi 2007; Adame and Beall 2009). Clays have also been reported to improve the mechanical strength of biopolymers (Cyras et al. 2008), although they may decrease polymerelongation (Petersson and Oksman 2006).

Recently many applications have been found using montmorillonite and/or incorporating/modifying montmorillonite using several techniques. Gholam et al. (2013) have been found the increased adsorption rate and more nanocomposite strength when modified montmorillonite based nanoclay – further the application of which was found for water purification by removal of crystal violet dye. Hydrogel nanocomposites were synthesized from grafting of acrylamide onto hydroxypropyl methylcellulose using methylenebisacrylamide cross linker and sodium montmorillonite (Na-MMT) nanoclay. The investigation of the dye adsorption capacity and rate of nanocomposite hydrogels as a function of Na-MMT content revealed that the both adsorption capacity and rate is enhanced as the nanoclay content is increased in nanocomposite composition (Gholam et al. 2013). Soy protein hydrogels with intercalated montmorillonite nanoclay bound with transglutaminase cross-linking shows enhanced elastic properties. This intercalated soy proteins with montmorillonite can be used to manufacture biodegradable nanocomposite materials with improved functional performances further application of which is food and agricultural products packaging (Jin and Zhong 2013). A nanofilm have been developed by novel dispersion method using gum exudates from Brea tree and nanoclayparticles (montmorillonite) and characterized – the main properties of this biofilm are improved water barrier capacity, reduced film permeability and reduced permselectivity for gases. These properties of this (montmorillonite nanoclay based biofilm) gives ample scope for its application for packaging as well as preservation of agricultural products (Aníbal et al. 2014). Montmorillonite nanoclay has been found application in biosensor development as well. Grasielli et al. (2012) have developed a novel atemoya biosensor for glyphosate determination which was based on the inhibitor effect of the pesticide on enzymatic activity. The peroxidase enzyme was immobilised on nanoclay based on montmorillonite modified (Grasielli et al. 2012). Other than montmorillonite a novel polyvinylidene fluoride (PVDF)/NC hollow fibre membranes were fabricated by non-solvent induced phase separation (NIPS) to study the improvement of membrane physical endurance. PVDF membranes containing commercial nanoparticles are therefore promising for improved abrasion resistance in water treatment applications (Yan et al. 2014).

1.2.3 Nanoemulsions

Nanoemulsion consists of a lipid phase dispersed in an aqueous continuous phase, with each oil droplet being surrounded by a thin interfacial layer consisting of emulsifier molecules (Acosta 2009; McClements et al. 2007; Nicolas et al. 2014). Usually, nanoemulsions are highly stable to gravitational separation because the relatively small particle size means that Brownian motion effects dominate gravitational forces. They also have good stability against droplet aggregation because the range of attractive forces acting between the droplets decreases with decreasing particle size, while the range of steric repulsion is less dependent on particle size (Tadros et al. 2004; Siti et al. 2013).

Other than increasing bioavailability (Hira et al. 2014) and antioxidant (Dasgupta et al. 2015) the bactericidal (Vijayalakshmi et al. 2013), antimicrobial (Karthikeyan et al. 2012; Dasgupta et al. 2015), antihelminthc (Karthikeyan et al. 2011), insecticidal (Megha et al. 2014) properties of nanoemulsion gave it importance to be used in agriculture – mainly to increase the shelf life of agricultural products and water quality management (Ranjan et al. 2014; Dasgupta et al. 2014). Chaw et al. (2013) have formulated a nanoemulsion with the insecticidal and pesticidal activity. The green nanoemulsion – laden glyphosate isopropylamine – formulated were able to suppress creeping foxglove (*A. gangetica*), slender button weed (*D. ocimifolia*) and buffalo grass (*P. conjugatum*). This initial discovery could be the platform for developing better penetration of agrochemical formulations in the future (Chaw et al. 2013). Similarly they have again used the same nanoemulsion with slight modification as a herbicide and have concluded that it is having controlling ability for *Eleusine indica* (Chaw et al. 2012). Recently many authors have given hypothesis that the microbial products can be used as natural emulsifier to have safer nanoemulsion to be used in the field of agro-food products (Shivendu et al. 2014;

Vanaja et al. 2014). Also many have hypothesized that the plant extracts or natural products could be more efficient for its activity when the same can be used in the form of nanoemulsions (Nandita et al. 2014, 2015b, c). To understand the activity of nanoemulsion, it is mandatory to understand the synthesis procedures. Also, to get better bioactivity, the understanding of the bioactive components retention with nanoemulsion should also be understood.

1.2.3.1 Production of Nanoemulsion

Nanoemulsion can be produced using a variety of methods, which are classified as either high-energy or low energy approaches (Acosta 2009; Leong et al. 2009; Tadros et al. 2004; Koroleva and Evgenii 2012; Silva et al. 2012).

High-energy approaches revolve around the use of mechanical force to generate intense disruptive forces that breakup the oil and water phases thereby forming oil droplets. For example, high-pressure valve homogenisers, micro-fluidizers, and sonication methods (Leong et al. 2009; Wooster et al. 2008). The production of nanoemulsions via this method is primarily governed by composition i.e. mainly surfactants, functional compounds and secondarily by the quantity of energy applied. Hence these emulsions depict a tendency towards preserving their formation against formulation modification like addition of monomer, surfactant, co-surfactant etc. (Anton et al. 2008). High energy approach for production of nanoemulsionis further classified into high pressure homogenization, Ultrasound approach (Quintanilla-Carvajal et al. 2010) and high speed devices approach (Anton et al. 2008).

1.2.3.2 High-Pressure Homogenization

The mixture is exposed to very high pressures and is pumped through a restrictive valve. The very high shear stress causes the formation of very fine emulsion droplets (Quintanilla-Carvajal et al. 2010). Further the impact of homogenization on design and structure of nanoemulsion have been described by Finke et al. (2014). Nanoemulsions with antimicrobial/microbial inactivation property have been developed by high-pressure homogenization method. This formulation can be further applied for increasing shelf life of agricultural products and also can be used in water quality management by decreasing microbial load of the water (Francesco et al. 2013).

1.2.3.3 Ultrasound

When two immiscible liquids are submitted to high-frequency sound waves in the presence of a surfactant, emulsion droplets are formed by cavitation. This causes intense shock waves in the surrounding liquid and the formation of liquid jets at high speed is responsible for the formation of emulsion droplets. However, this technology has not yet been efficiently used for industrial-scale applications (Maa and Hsu 1999; Quintanilla-Carvajal et al. 2010; Sanguansri and Augustin 2006). The scaled up process fornanoemulsion formulation at industrial level by ultrasound method have been described by using continuous-flow production method – which can be further applied for formulating nanoemulsion for agricultural applications (Alexey and Simon 2014). Shams and Ahi (2013) have developed 5A zeolite nanocrystals using kaolin via nanoemulsion by ultrasonic technique with a increased sorption properties which can further be used in water quality management for remediating the sludge (Shams and Ahi 2013).

1.2.3.4 High-Speed Devices

Rotor/stator devices (such as Ultra-Turrax) when compared with the other high energy approaches do not provide a good dispersion in terms of droplet sizes. With the energy provided mostly being dissipated as generating heat. Stable nanoemulsions are difficult to obtain (Anton et al. 2008; Walstra 1993). Francesco et al. (2012) have increased the antimicrobial delivery system of nanoemulsion when designed by high-speed devices (Ultra-Turrax) and proper emulsifier. Same method can be used to develop nanoemulsions with improved activities which can be applied in the field of agriculture and water quality management.

Low energy approaches rest upon the impromptu formation of oil droplets within mixed oil-water-emulsifier systems as and when solution conditions are altered, e.g., phase inversion and solvent demixing methods (Anton et al. 2008; Yin et al. 2009). Nanoemulsions are obtained in response to phase transitions during emulsification at constant temperature and altered composition (Usón et al. 2004) or vice versa (Morales et al. 2003). Low energy approaches are further classified into membrane emulsification (Sanguansri and Augustin 2006), spontaneous emulsification (Anton et al. 2008), solvent displacement (Yin et al. 2009), emulsion inversion point (Sadtler et al. 2010) and phase inversion point (Sadurní et al. 2005).

1.2.3.5 Membrane Emulsification

It is a low-energy process that requires less surfactant (when compared with high energy methods) and produces emulsions with a narrow size distribution range. This method involves formation of a dispersed phase (droplets) through a membrane into a continuous phase. Nevertheless, this method has as limitation the ‘low flux’ of the dispersed phase through the membrane, this being an issue during scale-up (Sanguansri and Augustin 2006). Membrane emulsification mainly used to increase the bioavailability of the nutrients e.g. vitamine E (Abdallah et al. 2012; Dasgupta et al. 2015). Many nanoemulsions have been formulated (by membrane emulsification) to increase the shelf life of post harvested products (Ghosh et al. 2014). Some nanoemulsions have been formulated by this method with improved bioactivity (Joseph and Heike 2014) and also which acts as a carrier to deliver some bioactive compound and/or compounds (Keun et al. 2012). In the same way some nanoemulsion should be discovered/identified which can be used as a carrier either in plant tissues or at soil/water/plant interface; also some nanoemulsion conjugated with the compounds needed for plant growth and can increase the bioavailability of it should be researched.

1.2.3.6 Spontaneous Emulsification

This mechanism occurs when an organic phase and an aqueous phase are mixed, with the organic phase being a homogeneous solution of oil, lipophilic surfactant and water-miscible solvent, and the aqueous phase consisting of water and hydrophilic surfactant (Bouchemal et al. 2004). Spontaneous emulsification is produced by different mechanisms (e.g. diffusion of solutes between two phases, interfacial turbulence, surface tension gradient, dispersion mechanism, condensation mechanism) which seem to be affected by the systems' compositions and their physicochemical characteristics like the physical properties of the oily phase and nature of the surfactants (Bouchemal et al. 2004). This process itself increases entropy and thus decreases the Gibbs free energy of the system (Anton et al. 2008).

1.2.3.7 Solvent Displacement

This method consists of mixing a water-miscible organic solvent containing lipophilic functional compounds in an aqueous phase containing an emulsifier. The rapid diffusion of the organic solvent in the aqueous phase promotes the formation of nanoemulsions enabling their preparation in one step at low-energy input with high yield of encapsulation. Finally, the organic solvent is removed from the nanodispersion under reduced pressure. Nevertheless the use of this technique is limited to water-miscible solvents (Yin et al. 2009). The non soluble compounds can be made available by using this method of nanoemulsion fabrication (Regina et al. 2007; Kyle et al. 2014; Gabriel and David 2015) – thus solvent displacement method can be used in those agricultural soils in which some of the compounds are unavailable because of its poor solubility.

1.2.3.8 Emulsion Inversion and Phase Inversion Point

It involves variation of system composition at a constant temperature. The structures are formed through a progressive dilution with water or oil in order to create kinetically stable nanoemulsions (Anton et al. 2008; Sadtler et al. 2010). Phase inversion point method uses the specific ability of surfactants (non-ionic) to alter their affinities to water and oil in function of temperature at a fixed composition. It consists in suddenly breaking-up the micro-emulsions maintained at the phase inversion point by a rapid cooling (Izquierdo et al. 2004; Sadurní et al. 2005) or by a dilution in water or oil (Anton et al. 2008). Nanoemulsions immediately formed are kinetically stable and can be considered as irreversible. This process is relatively simple, prevents the encapsulated drug being degraded during processing, consumes low amounts of energy and allows an easy industrial scale-up (Anton et al. 2008). Emulsion inversion and phase inversion methods are used to control the droplet size and stability of nanoemulsion (Felix et al. 2012). For nanoemulsion research for agricultural applications these two methods should also be analyzed.

1.3 Nanotechnology and Research Trends in Agriculture

Currently, the major challenges faced by world agriculture include changing climate, urbanization, sustainable use of natural resources and environmental issues like runoff and accumulation of pesticides and fertilizers. These problems are further intensified by an alarming increase in food demand that will be needed to feed an estimated population of six to nine billion by 2050 (Chen and Yada 2011). This above-mentioned scenario of a rapidly developing and complex agricultural system exists and greater challenges will be posed to the developing countries as, in the developing countries, agriculture is the backbone of the national economy.

Nanotechnology, this vast field of the twenty-first century, is making a very significant impact on the world's economy, industry and people's lives (Gruere et al. 2011; Scott and Chen 2003). Applications of nanotechnology in materials science and biomass conversion technologies applied in agriculture are the basis of providing food, feed, fibre, fire and fuels. Through advancement in nanotechnology, a number of state-of-the-art techniques are available for the improvement of precision farming practices that will allow precise control at nanometer scale (Fig. 1.5). Nanotechnology can also be an alternative source of fertilizer. In an experiment, it was observed that SiO_2 Nanoparticles enhanced germination in tomato (*Lycopersicum esculentum*) seeds (Manzer and Mohamed 2014).

1.3.1 Nanoscale Carriers

Nanoscale carriers can be utilized for the efficient delivery of fertilizers, pesticides, herbicides, plant growth regulators etc. The mechanisms involved in the efficient delivery, better storage and controlled release include: encapsulation and entrapment, polymers and dendrimers, surface ionic and weak bond attachments among others. These mechanisms help improve stability against degradation in the environment and ultimately reduce the mass/amount to be applied, which reduces chemical runoff and alleviates environmental problems. These carriers can be designed in such a way that they can anchor the plant roots to the surrounding soil structure and organic matter. This can only be possible through the molecular and conformational mechanisms between the delivery nanoscale structure and targeted structures and

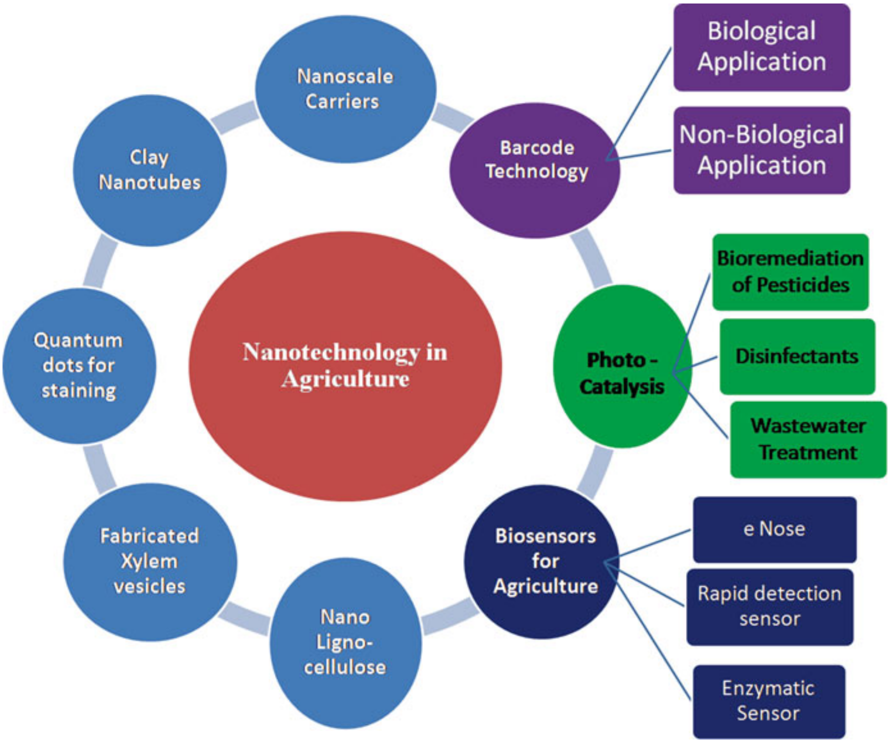

Fig. 1.5 Schematic representation for the application of nanotechnology in modern agriculture (Courtesy: Dasgupta et al. 2014)

matter in soil (Johnston 2010). These advances will help in increasing the bioavailability of active ingredients, thereby reducing the amount of inputs to be used and also the waste produced. Cai et al. (2014) developed nanoclays which can be added to traditional fertilizer to improve the retention capacity of nitrogen. Thus, nitrogen loss is reduced and sufficient nutrition is provided to crops. Many nanoemulsions have also been formulated to increase the bioavailability of herbicide and pesticide (Chaw et al. 2012, 2013; Megha et al. 2014).

1.3.2 Fabricated Xylem Vessels

Recent advancement in nanofabrication and characterization tools has enabled the study of physico-chemical and biological interactions of plant cell bodies and various disease-causing organisms. These tools are useful in understanding the mechanisms of pathogenesis and ultimately improved the strategies for the treatment of these diseases (Cursino et al. 2009; Chen and Yada 2011). To study xylem-inhabiting bacteria, changes in bacterial populations were monitored through destructive sampling techniques at different distances from inoculation sites but this does not provide information about colonization, film development, and subsequent movement and re-colonization at new areas because the same sample site cannot be followed temporarily. It has only been through the discovery of micro-fabricated xylem vessels with nano-sized features that we are able to study the above mechanisms which otherwise was not possible through traditional methods (Zaini et al. 2009; Allah 2012). A probe is used which can be inserted into the xylem vessel at the root base which can monitor xylem pressure, the radial electrical gradients in the root and activity of particular ions (Wegner 2012). A detailed description of nanotechnology in fabricated xylem vessels have been described by Bandyopadhyay et al. (2013) and fabricated xylem system in the form of nanoliter/picoliter scale fluidic systems have been summarized (Morgan et al. 2013). Biomimicking of micro/nano-fabricated xylem vessels system by using microbes e.g. researchers have looked at the attachment behaviour of *Xylella fastidiosa* (Leonardo et al. 2007) and *Escherichia coli* (Bunpot et al. 2011) in microfluidic flow chambers mimicking plant xylem. Biomimicking of capillary action has been developed by using micro/nanofabrication – which may have future application in fabricated xylem vessel development (Qian et al. 2014; Bharat 2011). To control the photoluminescent emission Carlos et al. (2013) have used ZnO and Al_2O_3 nanoparticles in *Calamus rotang* plant *in natura* xylem samples.

1.3.3 Nanolignocellulosic Materials

Recently, nanosized lignocellulosic materials have been obtained from crops and trees which had opened a new market for innovative and value-added nano-sized materials and products, e.g. nano-sized cellulosic crystals have been used as lightweight reinforcement in polymeric matrix (Laborie 2009). These can be applied in food and other packaging, construction, and transportation vehicle body structures. Cellulosic nano-whisker production technology from wheat straw has been developed by Michigan Biotechnology Incorporate (MBI) International, and is expected to make biocomposites that could substitute for fibre glass and plastics in many applications, including automotive parts. North Dakota State University (NDSU) is currently engaged in a project for the commercialization of this technology (Leistritz et al. 2007). With the applications of food and other packaging, construction, and transportation vehicle body structures production of nanolignocellulosic materials is the best way for agricultural waste management – since we can derive nanolignocellulosic materials from lignin and cellulose based agricultural waste (Brinchia et al. 2013; Ming-xiong et al. 2014).

1.3.4 Clay Nanotubes

Clay nanotubes (Halloysite) have been developed as carriers of pesticides for low cost, extended release and better contact with plants, and they will reduce the amount of pesticides by 70–80 %, hence reducing the cost of pesticide and also the impact on water streams (Murphy 2008). The sorptive and electrical behaviour of nanocomposites (polylactide and carbon nanotubes/smectite-clay nanocomposites) was studied and found that polylactide nanocomposites are endowed with increased sorption and outstandingly enhanced conductivity (up to six or even nine orders of magnitude) with respect to the pristine polymer (Conductivity = $1 * 10^{-10}$ S/m) (Saveria et al. 2011). This increased sorptive and increased conductivity properties of nanocomposites may have the future application as selective purification of water and also this property can be applicable in plant-soil-water interface to increase the ion transport and sorption of nutrients. Hsu and Jheng (2009) have synthesized and characterized carbon nanotubes on clay minerals with the application of biosensor for glucose and hydrogen peroxide detection (Hsu and Jheng 2009) – which may has major applications in pre as well as post harvested agricultural products and their quality control. Suprakas (2013) has highlighted the tensile strength of clay/carbon nanotubes which may further be used in agricultural fields to provide strength to the crops and protect them from strong wind.

1.3.5 Photocatalysis

One of the processes using nanoparticles is photocatalysis. It involves the reaction of catalyst with chemical compounds in the presence of light. The mechanism of this reaction is that when nanoparticles of specific compounds are subjected to UV light, the electrons in the outermost shell (valence electrons) are excited resulting in the formation of electron hole pairs, i.e. negative electrons and positive holes (Zhaoxia et al. 2011). These are excellent oxidizing agents and include metal oxides like TiO_2 (Bhatkande et al. 2001; Khataee et al. 2013), Silver (Zhaoxia et al. 2011), gold (Vongani et al. 2011) ZnO (Li and Haneda 2003; Mohammad et al. 2011), SnO_2 (Ko et al. 2009), platinum (Zhi and Wenfeng 2014), Ag-α-Fe_2O_3 nanocomposites (Shaofeng et al. 2014), lanthanum ferrite Nanoparticles (Abazari et al. 2014), etc., as well as sulfides like ZnS (Feigl et al. 2010) and CdS (Xingyuan et al. 2014). As the size of particles decrease, surface atoms are increased, which results in tremendous increase in chemical reactivity and other physico-chemical properties related to some specific conditions such as photocatalysis, photoluminescence, etc. So this process can be used for the decomposition of many toxic compounds such as pesticides, which take a long time to degrade under normal conditions (Malato et al. 2002), e.g. pathogens. Ankita and Vidya (2014) have remediated reactive blue 220 dye with solar light induced photocatalytic degradation by using Ag core–TiO_2 shell (Ag@TiO_2) nanoparticles. They found higher rate of photocatalysis under solar light as compared to UV light and also Ag@TiO_2 is a better photocatalyst than Degussa-P25, TiO_2NP and Ag doped TiO_2 nanoparticle. It can be noted that Degussa-P25 is a existing product with these properties manufactured by Evonik Degussa India Pvt. Ltd. Their basic research may turn up with a development of WQM instruments and/or other agricultural engineering devices (Ankita and Vidya 2014). Using nano-titania Pigeot-Rémy et al. (2011) have used TiO_2 nanoparticle for photocatalysis and disinfection of water and also to decrease target bacterial load and a rectangular photoreactor has been designed and optimized (Fathinia and Khataee 2013). Recent research trend is shifting towards finding doped-nanoparticles with better efficiency for photocatalysis (Saraschandra et al. 2015; Tahir and Amin 2015; Sankar and Vijayanand 2015; Khataee et al. 2015).

1.3.6 Nanobioremediation

Nanoparticles can be used for the bioremediation of resistant or slowly degradable compounds like pesticides. These harmful compounds tend to join the positive holes, are degraded and converted into non-toxic compounds. Otherwise these harmful compounds enter the food chain and result in serious problems for the body, hence nanoparticles can be used for environmental safety (Lhomme et al. 2008). The main applications of nanotechnology in bioremediation (nanobioremediation) are as uranium remediation, hydrocarbon remediation, groundwater and wastewater remediation, solid waste remediation, heavy metal remediation. Some main nanomaterials involved in nanobioremediation are as: nanoiron and its derivatives, nano-sized dendrimers, carbon nanotubes, single enzyme nanoparticles, engineered nanoparticles etc. (Rizwan et al. 2014; Avinash et al. 2014). Engineered polymeric nanoparticles have been used in bioremediation of hydrophobic contaminants (Tungittiplakorn et al. 2005) and soil remediation (Tungittiplakorn et al. 2004). Biogenic uranite nanoparticles have been used for uranium bioremediation (Bargar et al. 2008). Biologically synthesized nanomaterials from organisms *Gundelia tournefortii*, *Centaurea virgata*,*Reseda lutea*, *Scariola orientalis*, *Eleagnum angustifolia*, *Bacillus* sp. and*Noaea Mucronata* accumulated heavy metals – mainly Cu, Zn, Pb, and Ni (Arvind et al. 2011; Avinash et al. 2014; Rizwan et al. 2014).

1.3.7 Disinfectants

The electron hole pair, especially the negative electrons resulting from the excitation of nanoparticles, can also be used as a disinfectant of bacteria, as when bacteria make contact with nanoparticles, the excited electrons are injected into their bodies, which results in the bacterial removal from the object concerned, as in fruit packaging and food engineering (Melemeni et al. 2009). Comparatively nanoparticles are better disinfectants than chemical disinfectants e.g. sodium hypochlorite (NaClO) and phenol (C_6H_5OH) etc. (Karthik et al. 2011).Wei et al. (2012) have concluded that the porous Ca-Si based nanospheres may be developed into a new intra-canal disinfectant-carrier for infected canal treatment. Nano-disinfectant in the form of biofilm has shown improved antimicrobial activity for *salmonella* and *staphylococcus* Sp. (Carla et al. 2012; Hans et al. 2012; Kumar and Ting 2013; Nithila et al. 2014).

1.3.8 Wastewater Treatment

In modern environmental science, the removal of wastewater is an emerging issue due to its effects on living organisms (Babula et al. 2008; Mulligan et al. 2001). Many strategies have been applied for wastewater treatment including nanotechnology. Photocatalysis can be used for purification, decontamination and deodorization of air. It has been found that semiconductor sensitized photosynthetic and photocatalytic processes can be used for the removal of organics, destruction of cancer cells, bacteria and viruses. Application of photocatalytic degradation has gained popularity in the area of wastewater treatment (Melemeni et al. 2009). The detailed mechanism of action (Fig. 1.6) for bactericidal/antimicrobial activity of nanomaterials has been described (Fahim et al. 2014). There will be differences

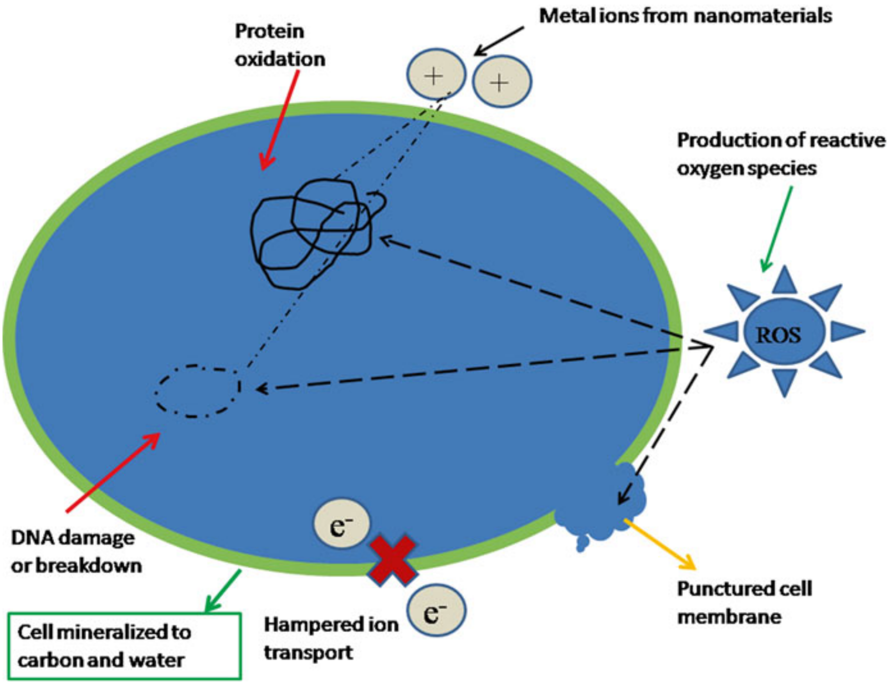

Fig. 1.6 Mechanism of bacteria cell damage by the induction of reactive oxygen species

between the mechanism of action for bactericidal activity of metal and metal oxide Nanoparticles (Solmaz et al. 2014). Understanding the differences in inactivation mechanisms helps to identify rate-limiting steps involved in the inactivation process as well as to develop more effective disinfection strategies. Detailed discussion on wastewater treatment is given in later section of this article.

1.3.9 Nanobarcode Technology

In our daily life, identification tags have been applied in wholesale agriculture and livestock products. Due to their small size, nanoparticles have been applied in many fields ranging from advanced biotechnology to agricultural encoding. Nanobarcodes (>1 million) have been applied in multiplexed bioassays and general encoding because of their possibility of formation of a large number of combinations that make them attractive for this purpose. The UV lamp and optical microscope are used for the identification of micrometer-sized glass barcodes which are formed by doping with rare earth containing a specific type of pattern of different fluorescent materials. The particles to be utilized in nanobarcodes should be easily encodeable, machine-readable, durable, sub-micronsized taggant particles. For the manufacture of these nanobarcode particles, the process is semi-automated and highly scalable, involving the electroplating of inert metals (gold, silver) into templates defining particle diameter, and then the resulting striped nanorods from the templates are released. These nanobarcodes have the biological as well as non-biological applications (Mathew et al. 2009). Cost effective nanobarcode technology development is a major challenge for the researchers – this can be concluded based on the fact that total of 18 documents found on Scopus indexed article database (SIAD). Out of 18 articles notes (1 in number), conference paper (6 in number) review article (2 in number) and only 9 research articles were available in last 10 years by the keyword of “nanobarcode” (SIAD 2014). Similarly, only 32 articles are present in SciFinder® database with the same keyword. After refining it with year wise none of the article were found for 2014; only one article in duplicate were found of Han et al. (2013) which have been discussed earlier; similarly, only three articles have been found for the year 2012 but none of them have described the application of nanobarcode in agricultural field (SciFinder 2014). This shows that development of nanobarcode technology for agricultural application is one of the thrust areas.

1.3.9.1 Biological Applications of Nanobarcodes

Nanobarcodes have been used as ID tags for multiplexed analysis of gene expression and intracellular histopathology. Improvement in the plant resistance against various environmental stresses such as drought, salinity, diseases and others have only been possible through advancement in the field of biotechnology at the nanoscale. In the near future, more effective identification and utilization of plant gene trait resources is expected to introduce rapid and cost effective capability through advances in nanotechnology-based gene sequencing (Branton et al. 2008). Nanobarcodes can also be used for cost- effective detection of pathogens from food products (Han et al. 2013).

1.3.9.2 Non-Biological Applications of Nanobarcodes

Nanobarcodes serve as uniquely identifiable nanoscale tags and have been applied for non-biological applications such as for authentication or tracking in agricultural food and husbandry products. This nanobarcode technology will enable us to develop new auto-ID technologies for the tagging of items previously not practical to tag with conventional barcodes (Branton et al. 2008).

1.3.9.3 Quantum Dots for Staining Bacteria

There are numerous bacteria which are responsible for many diseases in humans like tetanus, typhoid fever, diphtheria, syphilis, cholera, food-borne illness, leprosy and tuberculosis caused by different species. As a remedial process, we need to detect bacteria and for this, dye staining method is used. To stain bacteria, the most commonly used biolabels are organic dyes, but these are expensive and their fluorescence degrades with time. So the need of the hour is to find durable and economical alternatives. Fluorescent labelling by quantum dots with bio-recognition molecules has been discovered through the recent developments in the field of luminescent nanocrystals. Quantum dots are better than conventional organic fluorophores (dyes) due to their more efficient luminescence compared to the organic dyes, narrow emission spectra, excellent photostability, symmetry and tunability according to the particle sizes and material composition. By a single excitation light source, they can be excited to all colors of the Quantum dots due to their broad absorption spectra (Warad et al. 2004). Bio-labeled bacillus bacteria with Nanoparticles consisting of ZnS and Mn^{2+} capped with bio compatible ‘chitosan’ gave an orange glow when viewed under a fluorescence microscope. For the detection of *E. coli* O157:H7, Quantum dots were used as a fluorescence marker coupled with immune magnetic separation (Su and Li 2004). For this purpose, magnetic beads were coated with anti-*E. Coli* O157 antibodies to selectively attach target bacteria, and biotin-conjugated anti – *E. coli* antibodies to form sandwich immune complexes. Quantum dots were labelled with the immune complexes via biotin streptavidin conjugation after magnetic separation.

1.3.10 Biosensors

A variety of characteristic volatile compounds are produced by microorganisms that are useful as well as harmful to human beings, e.g. fermentation makes use of yeasts while alcohol is produced as a by-product when bacteria eat sugar. The most common causal organisms of food rotting are bacteria. Foul odour is a clear indication of food degradation which may be detected by visual and nasal sensation, but sometimes it may be impractical and a further cause for poisoning. Therefore, it is more sensible to use an instrument like rapid detection biosensors for the detection of these odours (Compagnone et al. 1995). The future application of nano-biosensors recently developed by Xiqi et al. (2014) and Zhang et al. (2014). Nanobiosensors are hot area of interest in the fields other than food and agriculture but recently many sensors have been developed after considering its importance. A detailed review on this has been done by Teresa (2013). ZigBee™ is a wireless mesh networking standard with low-cost and utilizes low-power. It has given the concept of 'Smart Fields' and 'SoilNet'. It consists of one or more sensors for environmental data (temperature, humidity, etc.), a signal conditioning block, a microprocessor/microcontroller with an external memory chip and a radio module for wireless communication between the sensor nodes and/or a base station. It can be used for the identification and monitoring of pests, drought or increased moisture levels in order to counterbalance their adverse effects on crop production (Kalra et al. 2010). Through this wireless sensor technology with nanoscale sensitivity, we can control plant viruses and level of soil nutrients, as the plant surfaces can be changed at nanoscale with specific proteins. This technology is important in realizing the vision of smart fields in particular. Wireless network sensor technology can also be used for monitoring the optimal conditions for mobile plants biotechnology.

1.3.10.1 Rapid Detection Biosensors

These instruments are able to reduce the time required for lengthy microbial testing and immunoassays. Applications of these instruments include detection of contaminants in different bodies such as water supplies, raw food materials and food products (Compagnone et al. 1995). Recently, nano biosensors are developed for rapid detection of IgG and metabolites (Labroo and Cui 2014; Türkoğlu et al. 2013).

1.3.10.2 Enzymatic Biosensors

Enzymes can act as a sensing element as these are very specific in attachment to certain biomolecules. According to Patel (2002), enzymatic biosensors on the basis of immobilization surface are classified into four groups (i) controlled-pore glass beads with optical transducer element, (ii) polyurethane foam with photo-thermal transducer element, (iii) ion-selective membrane with either potentiometric or amperometric transducer element and (iv) screen-printed electrode with amperometric transducer element. Considering microbial contamination a device (Electrogenerated chemiluminescence immunosensor) has been found by using Fe3O4@Au to detect *Bacillus thuringiensis* (Jianping et al. 2013). By keeping food and agricultural safety into consideration a biosensor using chemiluminescence and electro-chemiluminescence immunoassay have been found to detect botulinum neurotoxin serotypes A and B (Cheng and Stanker 2013). While considering aquaculture – to measure volatile amines levels in fishan optical fiber-based micro-analyzer was designed – this has future aspect as to develop such nano-biosensor instead of micro (Silva et al. 2010).

1.3.11 Electronic Nose

It is a device based on the operation of the human nose and is used to identify different types of odours; it uses a pattern of response across an array of gas sensors. It can identify the odorant, estimate the concentration of the odorant and find characteristic properties of the odour in the same way as might be perceived by the human nose. It mainly consists of gas sensors which are composed of nanoparticles e.g. ZnO nanowires (Hossain et al. 2005; Sugunan et al. 2005). ZnO nanorods are used to develop electronic nose which can detect impurities from vapour mixture (Ko et al. 2013). Their resistance changes with the passage of a certain gas and generates a change in electrical signal that forms the fingerprint pattern for gas detection. This pattern is used to determine the type, quality and quantity of the odour being detected. There is also an improved surface area which helps in better absorption of the gas.

1.3.12 Gold Nanoparticles

Gold nanoparticles, commercially used as rapid testing arrays for pregnancy tests and biomolecule detectors, are based on the fact that the colour of these colloids depends on the particle size, shape, refractive index of the surrounding media and separation between the nanoparticles. A quantifiable shift in the surface plasmon response (SPR) absorption peak results due to a small change in any of these parameters. We can make these nanoparticles attach to specific molecules by carefully choosing the capping agent for stabilizing gold nanoparticles. These specific molecules get adsorbed on the surface of these nanoparticles and change the effective refractive index of the immediate surroundings of the nanoparticles (Nath and Chilkoti 2004; Yuanyuang et al. 2010). A few nanoparticles will be adsorbed if the detecting molecules (bio-macromolecules) are larger than the gold nanoparticles and result in the formation of lumps after agglomeration. Ultimately, colour of gold nanoparticles is changed due to shift in SPR that result from the reduction of particle spacing. These properties provide a great opportunity to use gold nanoparticles for biosensor development. In the field of pharmaceutical science and other biomedical fields many Gold-nanoparticles-based biosensors have been already developed for detection of enzyme activity – the same should be researched in the field of food, agriculture and water quality management (Eliza and Dusica 2013).

1.4 Nanotechnology and Research Trends in Water Quality Management

Currently, provision of clean and abundant fresh water is one of the most important challenges faced by the world for human use and industrial applications such as agriculture (Vörösmarty et al. 2010; Allah 2012). According to a survey, more than one billion people in the world are deprived of clean water and the situation is getting worse. In the near future, it has been estimated that average water supply per person will drop by a factor of one third, which will result in the avoidable premature death of millions of people. Meanwhile non contaminated water is also not available for proper agricultural practices (Cross et al. 2009). A large amount of fresh water is required in agriculture, but in turn, it contributes to groundwater pollution through the use of pesticides, fertilizers and other agricultural chemicals. To combat this problem, novel, sustainable and cost effective technologies will be required for the treatment of this large amount of waste water produced. During the treatment of wastewater, critical issues like water quality and quantity, treatment and reuse, safety due to chemical and biological hazards, monitoring and sensors should be considered (Schoumans et al. 2014; Thorburn et al. 2013). Research and development in nanotechnology has enabled us to find novel and economically feasible solutions for remediation and purification of this wastewater. Accessible water resources are mostly contaminated with water-borne pathogenic microorganisms like cryptosporidium, coliform bacteria, virus, etc., various salts and metals (Cu, Pb, As), runoff agricultural chemicals, tens of thousands of compounds considered as pharmaceuticals and personal care products (PPCP), and endocrine disrupting compounds (EDC) and radioactive contaminants, either naturally occurring or as the result of oil and gas production as well as mining activities due to natural leaching and anthropogenic activities (Speed et al. 1987; Jasra et al. 1999). Nano-scale zero-valent iron can be used for the treatment of distillery wastewater (Homhoul et al. 2011). For improving water quality, nanotechnology has provided novel solutions (Fig. 1.7).

1.4.1 Nano-oligodynamic Metallic Particles

Physico-chemical microbial disinfection systems like chlorine dioxide, ozone and ultraviolet are being commonly used in developed countries, but most of the developing countries are lacking these systems due to the requirement of large infrastructure which make them costly. The need of the hour is to search and develop alternative cost-effective technologies. Nanotechnology based oligodynamic metallic particles have the ability to serve this function. Among these nanomaterials, silver is the most promising one as it is both bactericidal and viricidal due to the production of reactive oxygen species that cleaves DNA and can be utilized for a wide range of applications. Other properties include low toxicity, ease of use, its charge

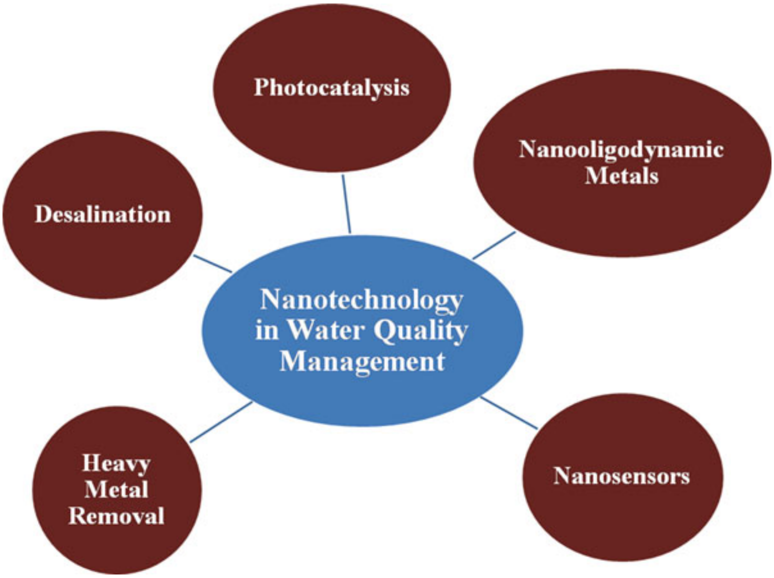

Fig. 1.7 Diagrammatic representation of nanotechnological aspects in water quality management which includes heavy metal removal, desalination, photocatalysis, nnao-oligodynamic metals and nano-sensors

capacity, high surface-to-volume ratios, crystallographic structure and adaptability to various substrates (Nangmenyi and Economy 2009; Chen and Yada 2011; Faunce et al. 2014; Jain et al. 2016). Recently researches have been done to vary the size of silver and gold nanoparticles with simple approaches i.e. changing the concentration of reactants. The improved activity of antimicrobial and anticancerous activity was observed for them (Nandita et al. 2015a; Maddineni et al. 2015; Shivendu et al. 2016; Janardan et al. 2016). It also can be noted that, recently trends are changing toward in silico and computational approach towards toxicity evaluation of inorganic nanoparticles (Ranjan et al. 2015, 2016).

1.4.2 Photocatalysis

Visible light photocatalysis of transition metal oxides, another nanoscale technological development, produces nanoparticles, nanoporous fibers and nanoporous foams that can be used for microbial disinfection (Li et al. 2009) and for the removal of organic contaminants like personal care products (PPCP) and endocrine disrupting compounds (EDC). Moreover, tubular nanostructures, embedded into microbial cell wall, can disrupt its cell structure resulting in the leakage of intracellular compounds, and ultimately cell death. A detailed research trends in the field of photocatalysis has been discussed above in detail. As discussed above – the recent research trends for photocatalysis using nanomaterials has been shifted from single nanoparticles to hybrid nanocomposite e.g. Ag/$AgVO_3$ one-dimensional hybrid nanoribbons with enhanced performance of plasmonic visible-light photocatalysis (Zhao et al. 2015); fabrication of plasmonic Pt nanoparticles on Ga-doped ZnO nanopagodas array with enhanced photocatalytic activity (Hsien-Ming et al. 2015); PbS quantum dots in ZnO@PbS/graphene oxide has been synthesized for enhanced photocatalytic activity (Xi-Feng et al. 2015); Zirconium and silver co-doped TiO_2 nanoparticles for degradation of methyl orange and methylene blue (Saraschandra et al. 2015).

1.4.3 Desalination

Due to limited resources of fresh water, it is likely that in the near future, desalination of sea water will become a major source of fresh water. Conventional desalination technologies like reverse osmosis (RO) membranes are being used but these are costly due to the large amount of energy required. Nanotechnology has played a very important role in developing a number of low-energy alternatives, among which three are most promising. (i) protein-polymer biomimetic membranes, (ii) aligned-carbon nanotube membranes and (iii) thin film nanocomposite membranes (Hoek and Ghosh 2009; Victor et al. 2014). These technologies have shown up to 1000 times better desalination efficiencies than RO, as these have high water permeability due to the presence of carbon nanotube membranes in their structure. Some of these membranes are involved in the integration of other processes like disinfection, deodorizing, de-fouling and self-cleaning. In another approach, zeolite nanomembrane can be used for seawater desalination (Liu and Chen 2013). Some of these technologies may be introduced in the market place in the near future but scale-up fabrication, practical desalination effectiveness and long-term stability are the most critical challenges to be considered before their successful commercialization (Yan et al. 2003). Desalination using nanotechnology with the aspects of carbon nanotubes (Rasel et al. 2014), reverse osmosis (Peng et al. 2011), forward osmosis for seawater and wastewater (Linares et al. 2014) have been reviewed earlier. Recently many devices with improved efficiency and performance have been developed- self-sustained webs of polyvinylidene fluoride electrospun nano-fibers (Essalhi and Khayet 2014); PVA/PVDF hollow fiber composite membrane modified with TiO_2 nanoparticles (Xipeng et al. 2014); novel integrated system coupled with nanofluid-based solar collector (Kabeel and Emad 2014); zinc oxide micro/nanostructures grafted on activated carbon cloth electrodes (Myint et al. 2014); tubular MFI zeolite membranes (Martin et al. 2012); titanium oxide nanotubes/polyethersulfone blend membrane (Abdallah et al. 2014); Graphene wrapped MnO2-nanostructures (Ahmed et al. 2014a); thin film nanocomposite membranes (Arun et al. 2014); Graphene/SnO2 nanocomposite (El-Deen et al. 2014; Ahmed et al. 2014b); carbon nanotubes (Goh et al. 2013).

1.4.4 Removal of Heavy Metals

Ligand based nanocoating can be utilized for effective removal of heavy metals as these have high absorption tendency. It becomes cost effective as it can be regenerated in situ by treatment with bifunctional self-assembling ligand of the previously used nanocoating media. Farmen (2009) used crystal clear technology for water purification in which multiple layers of metal can be bonded to the same substrate using crystal clear technologies (Farmen 2009). According to, another strategy for the removal of heavy metals is the use of dendrimer enhanced filtration and it can bind cations and anions according to acidity (Diallo 2009). Nowadays nanomaterials have been widely used to remove heavy metals from water/wastewater due to their large surface area and high reactivity. Metal oxide nanoparticles, including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, provide high surface area and specific affinity for heavy metal adsorption from aqueous systems. To date, it has become a hot topic to develop new technologies to synthesize metal oxide nanoparticles, to evaluate their removal of heavy metals under varying experimental conditions, to reveal the underlying mechanism responsible for metal removal based on modern analytical techniques (XAS, ATR-FT-IR, NMR, etc.) or mathematical models, and to develop metal oxide-based nanomaterials of better applicability for practical use i.e. granular oxides or composite materials (Ming et al. 2012). Additionally, humic acid and fulvic acid exist ubiquitously in aquatic environments and have a variety of functional groups which allow them to complex with metal ions and interact with nanomaterials. These interactions can not only alter the environmental behaviour of nanomaterials, but also influence the removal and transportation of heavy metals by nanomaterials. Thus, the interactions and the underlying mechanisms involved warrant specific investigations. Wang-Wang et al. (2014) have given a detailed review on the effects of humic acid and fulvic acid on the removal of heavy metals from aqueous solutions by various nanomaterials, mainly including carbon-based nanomaterials, iron-based nanomaterials and photocatalytic nanomaterials. Mainly they have discussed the mechanisms involved in the interactions and evaluated the potential environmental implications of humic acid and fulvic acid to nanomaterials and heavy metals.

1.4.5 Wireless Nanosensors

Crop growth and field conditions like moisture level, soil fertility, temperature, crop nutrient status, insects, plant diseases, weeds, etc. can be monitored through advancement in nanotechnology. This real-time monitoring is done by employing networks of wireless nanosensors across cultivated fields, providing essential data for agronomic intelligence processes like optimal time of planting and harvesting the crops. It is also helpful for monitoring the time and level of water, fertilizers, pesticides, herbicides and other treatments. These processes are needed to be administered given specific plant physiology, pathology and environmental conditions and ultimately reduce the resource inputs and maximize yield (Scott and Chen 2003). Scientists and engineers are working to develop the strategies which can increase the water use efficiency in agricultural productions, e.g. drip irrigation. This has moved precision agriculture to a much higher level of control in water usage, ultimately towards the conservation of water. More precise water delivery systems are likely to be developed in the near future. These factors critical for their development include water storage, in situ water holding capacity, water distribution near roots, water absorption efficiency of plants, encapsulated water released on demand, and interaction with field intelligence through distributed nano-sensor systems (Cross et al. 2009). Sensing and detection of various contaminants in water at nanoscale under laboratory and field conditions has remained a hot issue over the last decade. In the near future, state-of-the-art nanotechnology-based techniques will help in developing many new technologies that will have better detection and sensing ability (Chen and Yada 2011). Similar to nanobarcode development – wireless nanosensor development for WQM is one of the vital fields of the research. Sensor networks are a key technological and economic driver for global industries in the near future, with applications in health care, environmental monitoring, infrastructure monitoring, national security, and more. Developing technologies for self-powered nanosensors is vitally important. Zhong (2012) has given a brief summary about recent progress in the area, describing nanogenerators that are capable of providing sustainable self-sufficient micro/nanopower sources for future sensor networks. Negligible research work has been done in the field of wireless nanosensor development (SIAD 2014; SciFinder 2014) out of which mostly are conceptual notes and/or book chapters and reviews. Mannoor et al. (2013) have done an outstanding work after developing wireless raphene-based nanosensor for detection of bacteria. In particular, they have demonstrated integration onto a tooth for remote monitoring of respiration and bacteria detection in saliva. Since they have developed a wireless nanosensor to detect bacterial load in saliva which is an aqueous phase – by keeping this concept in mind one can think about developing such device for bacterial load detection.

It can be noted that other than food and agriculture, nanotechnology has grown interest in many fields. Figure 1.1 represents the allied fields and Fig. 1.8 represents the patents (Edgar et al. 2011). The beneficial properties – increased surface area, apparent solubility, good retention time, direct uptake of nanomaterials, and enhanced nutritional quality – open the ample scope for the nanotechnology with different applications and have best future to cover the market has been summarized in Fig. 1.9. On contrary, one should not ignore the toxicological aspect of nanomaterials on humans, animals and its impact on ecosystem, the same has been discussed in other chapters of this book (Fig. 1.10).

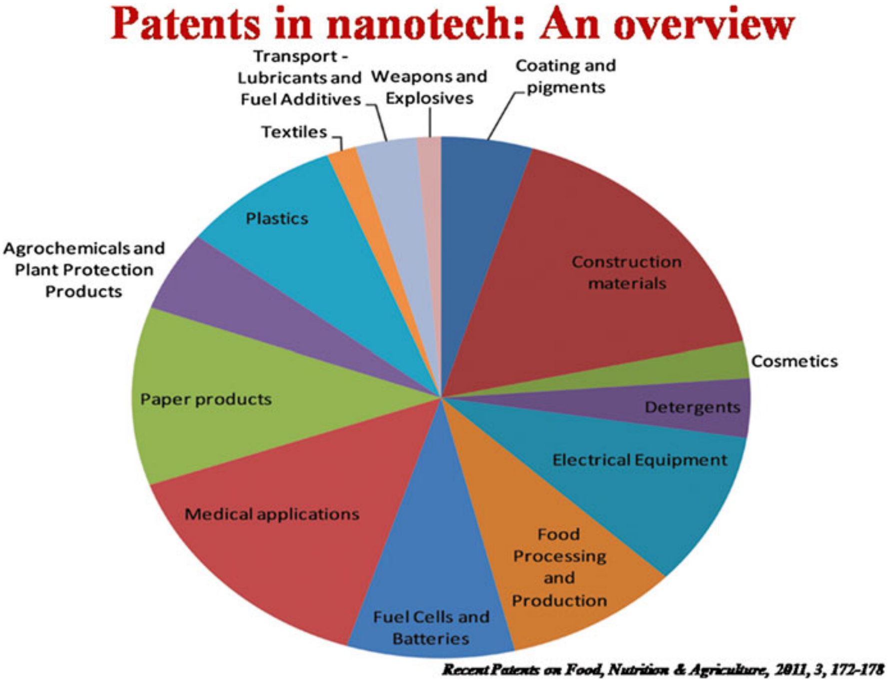

Fig. 1.8 A diagrammatic representation of patents in different applied nanotechnology sector in previous decade. It represents the sharp increase in use of nantechnology in different sectors including agriculture and foods (Courtesy: Edger et al. 2011)

1.5 Conclusion

Nanotechnology has not only improved the quality of modern agricultural practices by making them technical, susceptible, safer and improved quality in agricultural products nutritious but have also helped a lot in generating new agricultural products, better packaging and storage techniques and improved the quality of the its allied field such as water quality management. Conversion of materials to its nano form helps in enhancement of their physiochemical properties and applications e.g. silver nanoparticles shows antibacterial property and they are being incorporated into bandages for their beneficiary effect in ailing wound; however the bulk particles are less effective. Titanium dioxide, used as an intense white pigment is opaque in nature. However, nanoparticles of titanium dioxide are transparent and due to its physical nature, they are being used in transparent sunscreens, food packaging or plastic food containers.

Application of nanotechnology has enhanced the delivery of fertilizers, pesticides, herbicides and plant growth regulators with the help of nanoscale carriers; also its application in agricultural sector as fabricated xylem vessel, clay nanotubes,

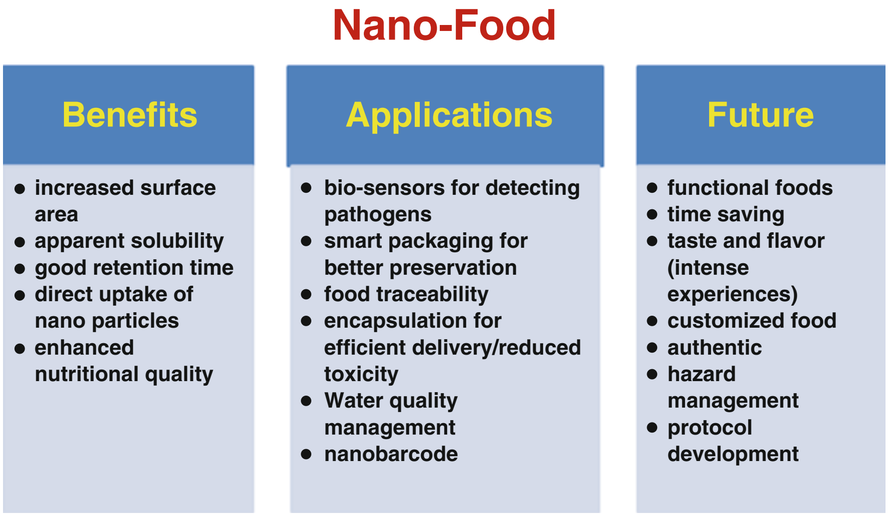

Fig. 1.9 The beneficial properties – increased surface area, apparent solubility, good retention time, direct uptake of nanomaterials, and enhanced nutritional quality – open the ample scope for the nanotechnology with different applications and have best future to cover the market

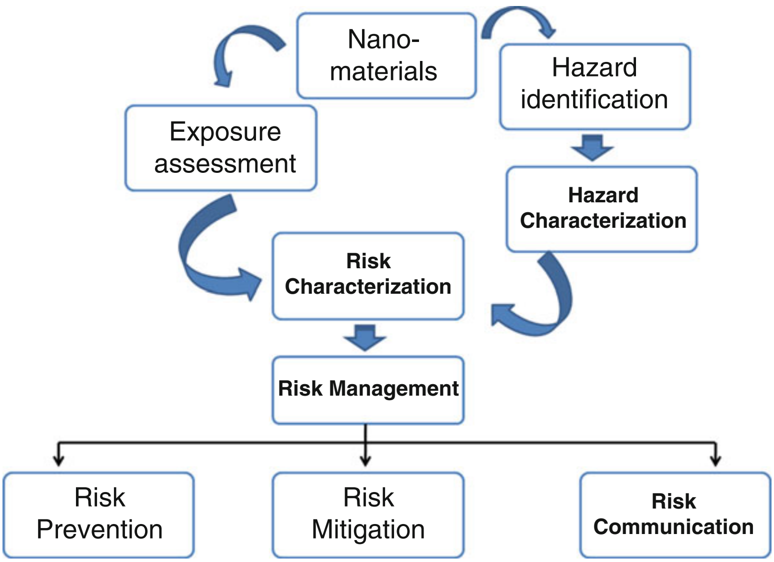

Fig. 1.10 The toxicological aspect of nanomaterials on humans, animals, environment and whole ecosystem. Diagrammatic representation of overview of nano-toxicological analysis

photocatalysis, wastewater treatment, nanobarcode technique, different types of biosensors, Quantum dots for bacterial staining etc. In addition, nanomaterials are further researched to keep the product fresher with increased shelf life. Nanoscience and nanotechnologies have vast applications in water quality managementas heavy metal removal, nano-bioremediation through nanolignodynamic metals, desalination, disinfecting process and the sensors to check the quality. Nevertheless, many of their applications are currently at a beginning stage and most of them require a high quality of research and development for their safe application. The safety of nanoparticles in agri-food industry also offers challenge to government and industry both. The food processing industry must ensure the consumer confidence and acceptance of nanofoods safety. When it comes to the application of nanotechnology in industrial scale, it is important to evaluate the release of nanoparticles into the environment and to estimate the subsequent levels of exposure to these materials. As the nanoparticles can easily penetrate into the human organ and organelles, exposure time, exposure concentrations, sites of penetration, immune response and accumulation and retention of nanoparticles in body and their subsequent effects should be assessed carefully.

Even though the research regarding the application of nanotechnology is growing every day, still insufficient scientific examination of naturally occurring nanosystems is available. The compulsory testing of nano-modified agricultural products and/or treated water should be performed before they allowed to be introduced into the market. Standardized test procedures are required to study the impact of nanoparticles on living cells for evaluation of the risk assessment on human exposure to nanoparticles. Toxicology of nanoparticles is poorly understood because of the lack of validated test methods and the inconsistency in the reported data. The inconsistency in the published data is due to the improper characterization of nanoparticles and the interferences induced by the nanoparticles in the available test system. Hence, the regulatory bodies and the policy makers should provide the guidance document for the validated protocols, safe uses and the disposal of the nanoparticles. The understanding of the safe application of nanoscience and nanotechnology in agri-food and water quality management will help in the sustainable growth of "nanoagri-technology".

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