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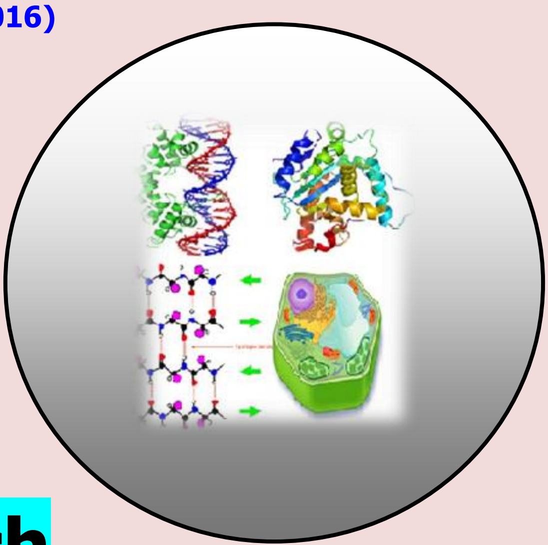

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RESEARCH PAPER

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Role of Nanoparticles in Plants under Changing Circumstances

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ABSTRACT

Nanotechnology is a promising field of science with the far ranging applications in cancer therapy, targeted drug delivery, biomedicines, waste water treatment, cosmetic industries, electronics and biosensors. Plants are exposed to varied levels of environmental stress such as salinity, drought, heavy metals, low and high temperature. Due to the presence of various toxic gases in atmosphere, biological yield of plants is reduced; therefore number of methods is applied to uphold the crop productivity. This review addresses certain important aspects of nanoparticles (NPs) which will be helpful in improving the productivity of the crops. There are several types of NPs which occurs in nature, such as TiO_2, ZnO, Ag, Au, etc. In this review we try to summarize the biosynthesis, types and characterization of nanoparticles as well as its role in improving the productivity of the crop under normal and stress conditions.
Keywords: Nanoparticles and Heavy metals.

Abbreviations

NPs Nanoparticles
ZnO Zinc oxide
Au Gold
Ag Silver
TiO_2 Titanium Dioxide

INTRODUCTION

A particle which is too small and behaves as an entire unit is called nanoparticles (NPs). The size ranges from 1 to 100 nm. They are distributed in all the three mediums, such as solid, liquid and gas (Buzea et al., 2007). Certain NPs properties proved to be detrimental on human health and environmental conditions (Maynard et al., 2006). However, in a very short time the use of NPs has commercially increased as compared to past years. Some reports suggest that NPs are harmful to plants but at the same time some aspects are favoured for NPs. In1974, one of the Japanese Professors Norio Taniguchi used the term Nanotechnology for the first time. Paul Ehrlich termed NPs as “Magic Bullets” (Kreuter, 2007). In recent time, nanotechnology is playing a revolutionary role in agriculture (Stern and Neil, 2008). Nanoparticles have been categorised into dimensionality, uniformity, composition and morphology (Fig.1). Nanotechnology is an emerging field of research with great scope in future. NPs can be extracted from natural sources as well as artificial sources (Nowack and Bucheli, 2007). There are number of natural processes that form NPs, such as photochemical reactions, volcanic eruptions, forest fire, simple erosion, through plants and animals (Buzea et al., 2007). NPs are used in different fields, such as electronics, biomedical, pharmaceutical, cosmetic, energy, environment, etc. (Nowack and Bucheli, 2007).

BIOSYNTHESIS OF NANOPARTICLES

There are number of methods used in the formation of NPs. NPs constructed through radiation, chemical precipitation, photochemical approaches, electrochemical, and Langmuir–Blodgett method but these methods are often tremendously luxurious and non eco-friendly due to the use of poisonous, explosive, and perilous chemicals (Awwad et al., 2013). Green synthesis of NPs makes it environmental friendly, less toxic and safe. Green synthesis of NPs can be done by various methods such as

(1) Polysaccharide method
(2) Tollens method
(3) Irradiation method
(4) Biological method
(5) Polyoxometalates method

Biosynthesis of NPs through plant is widely accepted technology for the formation of metallic NPs. Comparable to microbes which have been used as a “bio-factory” in the synthesis of metallic NPs, plants are considered as natural “chemical” factories for NPs synthesis that are economically cheap. It is important to note that the mechanism of NPs synthesis in plants is associated with phytoremediation concept (Haverkamp et al., 2007). There are number of factors which affect the synthesis of NPs. These factors include temperature, pressure, time, pH, preparation coast, particle shape and size, pore size, environment etc. (Jayanta and Kwang, 2014).

Temperature

Temperature is one of the most important factors which affect the synthesis of NPs. All three NPs synthesizing methods (physical, chemical and green synthesis) require temperature as an important component. The physical methods require uppermost temperature (>350°C) while chemical methods require a temperature of less than 350°C. Green synthesis requires temperatures of less than 100°C. Temperature determines the nature of the newly formed NPs (Rai et al., 2006).

Pressure

Pressure is functional for the reaction medium which alters the morphology of the newly synthesized NPs (Abhilash, 2012). Reduction rate of ions by biological agents has been found to be quicker at surrounding atmosphere (Tran et al., 2013).

Time

NPs which are synthesized by green synthesis methods are influenced by time, in which the reaction medium is incubated (Darroudi et al., 2011). Likewise, description of synthesized NPs changed with time and it greatly influenced by the synthesis process, disclosure to light, as well as storage circumstances (Mudunkotuwa et al., 2012).

pH

pH is also an important factor which had a significant impact on the formation of NPs by green synthesis methods. Various scientists demonstrated that pH of the medium influences the size and texture of the manufactured NPs (Armendariz et al., 2004).

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Therefore, size of the NPs can be guarded by changing the pH of the solution. Size and shape of synthesized Ag-NPs are affected by pH (Soni and Prakash, 2011).

Preparation cost

NPs synthesis is highly cost effective. Both physical and chemical methods are very costly as compared to the biological method of NPs synthesis. Therefore, biological method is suggested to be used for its synthesis.

Particle shape and size

Size of the particle is one of the most important aspects for its effectiveness. The active nature and morphology of the manufactured NPs highly affect their chemical properties.

Pore size

NPs superiority and use are greatly influenced by the porosity of newly formed NPs. Mutilation of biomolecules by NPs has been achieved to boost their use in the delivery of drug and biomedical field (Ruckenstein and Kong, 1999).

Environment

Surrounding environment plays a vital role for determining the nature of newly formed NPs. There are some common examples to describe the effect of environment on the quality of the synthesized NPs. The crystalline character of the zinc sulphide NPs distorted immediately when its environment was changed from wet to parched condition. Likewise, the chemical character of cerium nitrate NPs changed with the existence of peroxide in the solution in which they are suspended.

TYPES OF NANOPARTICLES

A number of nanoparticles which are used in agriculture are mentioned in Fig. 2 and described below.

Zinc oxide nanoparticles

There are several evidences which indicate the positive role of zinc oxide nanoparticles (ZnO-NPs) in plants. Different scientist evaluate the role of NPs in different plant species, such as pea, (Prasad et al., 2012), soybean, (Sedghi et al., 2013), wheat, (Ramesh et al., 2014), onion, etc. (Raskar and Laware, 2014). It is deduced from the above studies that lower concentration of ZnO-NPs enhanced the growth while higher concentration cause toxicity.

Carbon nanotubes

Among different types of NPs, carbon nano tubes are included as important component of nature because of their mechanical, electrical, thermal and chemical properties. The knowledge about the role of carbon nanotubes in plants is not available however, single walled carbon nanotubes are used as a vector for DNA delivery (Srinivasan and Saraswathi, 2010).

Gold nanoparticles

A few studies have been reported the impact of Au-NPs within plants such as positive and negative both. It causes toxicity in plants and has been reported to boost seed germination and metabolic activity by increasing seed coat permeability (Gopinath et al., 2014).

Silver nanoparticles

NPs either have positive or negative effects on plants depending on their concentrations. Silver nanoparticle (Ag-NPs) in *Bacopa monnieri* induces the synthesis of proteins and carbohydrates but retard the amount of total phenolic contents (Krishnaraj et al., 2010).

Titanium Dioxide nanoparticles

Mostly the effect of TiO_2-NPs were reported on bacteria, algae, plankton, fish, mice or rats but only few with higher plants. TiO_2-NPs is reported to enhance the rate of seed germination and promote the radicle and plumule growth in *Capsicum annum L.* (Mahmoodzadeh et al., 2013).

CHARACTERIZATIONS OF NANOPARTICLES

Various techniques, such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), high performance liquid chromatography (HPLC) are used for characterization of NPs (Fig.3). Along with these techniques, some other methods are also used such as separation, microscopy, and spectroscopy (Fabrega et al., 2011).

Characterization based on separation technique

These techniques are used to establish the size (Soto-Alvaredo et al., 2013) and shape of NPs (Surugau and Urban, 2009). In this technique, the particles are characterized on the basis of the time difference in their settlement and porosity of the filter (Hassellow et al., 2008). HPLC is the most important techniques which promote the separation of minor particles (Soto-Alvaredo et al., 2013).

Characterization based on microscopy techniques

Microscopy is one of the most important techniques used in the process of NPs separation. It is generally used to quantify the size, shape, and aggregation of NPs (Lopez-Lorente et al., 2011). One of the most important advantages of this technique is that there is no comparison between standard and samples. In these techniques, the most diverse method used is TEM (Hagendorfer et al., 2012).

Characterization based on the spectrometric techniques

UV-visible spectrometry is used in the characterization process of NPs, which gives information about the particle size and the aggregation (Rajasekharreddy et al., 2010). XRD (X-ray diffraction) techniques are also most widely used to examine the crystalline nature of NPs (Hassellow et al., 2008).

NANOPARTICLES AND BIOLOGICAL SYSTEM

Nanoparticles act together with biological systems in the following ways

(i) Chemical effects as metal ions in solution upon dissolution
(ii) Mechanical effects owing to hard spheres and defined interfaces
(iii) Catalytic effects on surfaces
(iv) Surface effects owing to binding of proteins to the surface, either by non-covalent or covalent mechanisms or oxidative effects
(v) Changes in the chemical environment (pH)

Chemical effects

There are number of toxic metals, such as Cu, Cd, Hg, and Ni that binds to cell components along with proteins (sulfhydryl, carboxyl or imidazole groups) and alter their activities. This interest with cellular processes often causes redox disproportion and oxidative stress in metal-exposed plants (Sharma and Dietz, 2009).

Mechanical effects

The special mechanical effect of nanoparticles allow for novel applications in many fields, e.g., surface engineering, biology and nonmanufacturing (Guo et al., 2014). Particle size is more important in mechanical effects as compared to particle chemistry. Blocking of water transport in presence of higher amount of NPs in soil is one of the examples (Asli and Neumann, 2009).

Catalytic effects

Several metals, such as silver, platinum, palladium, gold, iron and cobalt are involved in oxidation and reduction process. Metal nanoparticles are frequently used as a heterogeneous catalyst for hydrogenation, hydroformylation, carbonylation, etc. (Tauster, 1987). Researchers mainly focus on metal particles i.e. copper, gold, palladium due to their promising catalytic activity (Jana and Pal, 1999). They have large surface to volume ratio and consequently exhibit increased surface activity that enables them to act as good catalysts. Metal ions at cell-compatible low concentrations are usually bound to constitutive or inducible chelators, including phytochelatins, organic acids, metallothionein and ferritin (Hall, 2002) that are compartmentalized by transport processes (Hall and Williams, 2003).

UPTAKE AND TRANSLOCATION OF NANOPARTICLES IN PLANTS

NPs are adsorbed to plant surfaces and taken up during growth. NP entered into the plants through various ways. Uptake frequency will depend on the NPs size and surface properties. The outermost surfaces of leaves, fruits and epidermal cells are mainly enclosed by cuticle.

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Incredibly, small and lipophilic NPs can be integrated into apolar fluid areas of the cuticle, which contains apolar and polar pathways for uptake. When the NPs are come in contact with plants, makes way in to the cell wall and cell membrane of root epidermis accompanied by an intricate sequence of events to enter into xylem and shift to the stele symplastically for further translocation in leaves. However, in order to cross the intact cell membrane, NPs go by way of pores on the cell membrane which indicates that uptake of NPs is size dependent (Rico et al., 2011). Mostly, large NPs can enter through cuticle-free areas, such as hydathodes, the stigma of flowers and stomates (Rico et al., 2011).

NPs must pass through the cell wall before entering the protoplast of intact plant cell. Solute exclusion techniques give information on preventive pore sizes in cell walls. The highest pore size of plant cell walls is usually in the range of a few nanometers. For example 3.5–3.8 nm in root hairs and 4.5–5.2 nm in palisade parenchyma cells (Carpita et al., 1979). Barring pore sizes divalent ions and boric acid (Fleischer et al., 1999), which considers that only NPs less than 5 nm in diameter will be capable to traverse the cell wall of undamaged cells effectively.

NANOPARTICLES AND PLANT DEVELOPMENT

Role of nanoparticles in plant growth

Plants growing under natural ecological situation are constantly exposed to a combination of biotic and abiotic stresses. As far as abiotic stresses are concerned, drought, salinity, water logging, heat, cold, metal, UV radiation, etc., are some recurrent stresses which plants face at one or the other stages of their life process. NPs play an essential role in plant growth and development. Various types of NPs are present in environment, such as ZnO, CuO, TiO_2, Ag, Au, etc. One of them is TiO_2 which show positive effect on plant growth (Yang et al. 2007). When the TiO_2-NPs applied to spinach plant through seeds or spraying, then growth of plants dramatically enhanced (Zheng et al., 2005). ZnO-NPs increase the rate of germination in peanut plants (Prasad et al., 2012). Increased germination rate is the effect of penetration of NPs in the seed coupled with improved seed water uptake (Khodakovskaya et al., 2009). In 2009, Khodakovskaya et al. reported that, when NPs enter in to the tomato seeds, the rate of germination increase several times due to the uptake of water through seeds.

Roles of nanoparticles in photosynthesis

Photosynthesis plays a pivotal role in plant cellular mechanisms. During the process of photosynthesis, chemical energy synthesizes from radiant energy but the plants used only some of them for growth. There are various types of enzymes which are involved in the process of photosynthesis but the Rubisco is the most abundant in plants. Giraldo et al. (2014), suggest that when the single wall carbon nanotube are inserted in to the plastids or chloroplast, the rate of photosynthesis elevated up to three times. Exogenous application of TiO_2-NPs enhances the rate of transpiration, photosynthesis and water conductance in plants (Qi et al., 2013). TiO_2-NPs improve plant growth by enhancing nitrogen metabolism and photosynthesis (Yang et al., 2006). Metal NPs increases the production of chemical energy which produced in photosynthesis. Rate of transpiration slow down when plant cell expose to the Ag-NPs. TiO_2 play a significant role in plant physiological activities. Spray of 0.25% of NPs to the leaf of the plant enhances the oxygen evolution, rubisco activities, photosynthesis, carbon reaction, etc (Ma et al., 2008).

Nanoparticles in environment

The role of nanoparticles in ecological ecosystem is limited (Klaine et al., 2008). There are two types of NPs, one is primary and the other is secondary which is released from the source. There are specific volatile conditions under which secondary NPs are released in to the atmosphere, such as temperature, residence time, dilution rate, dilution ratio, etc. (Morawska et al., 2008). The water body where all the waste material is accumulated possess a high risk of NPs presence. However, at present no reliable data is available on the presence of NPs in such water bodies (Nowack and Bucheli, 2007).

Still, it has been observed by scientists that, some toxic effect is caused by NPs on organisms which live in water bodies (Zhu et al., 2007). The size, surface charges and chemical reactivity of NPs show some biological changes in aqueous environment (Auffan et al., 2009).
Soil is the perfect locality for NPs where various phenomenons occur in soil. NPs accumulate with in the soil, such as sewage treatment, aerial deposition, waste handling, etc. In terrestrial ecosystem, NPs are present in different forms which play a significant role in biogeochemical cycles. These forms are clay, iron oxide, organic matter and other materials. These NPs may cause changes in the soil behaviour because of interference of NPs in the environments (Klaine et al., 2008). Different types of NPs are available in the environment therefore; their impact on the terrestrial ecosystem is different (Klaine et al., 2008).

Phytoremediation with nanoparticles

Plants account for the foremost fraction of biomass on the earth that plays an imperative role in the ecological system. Conventional methodologies used in the subtraction of excess toxic heavy metals from soil and water are expensive. However, the use of plants (phytoremediation) is a cost-effective alternative to clean up heavy metal contamination. Phytoremediation is a process in which the contaminated soil and water body is cleaned with the help of biologically active organisms (Souza et al., 2013). In recent years, NPs are used as a beneficial source for plants. NPs, being effective absorbent for metal ions and also useful in phytoremediation technique of metal removal from contaminated sites (Singh and Lee, 2016). Response of plants to NPs varies depending on the plant species and methods of NPs applications.

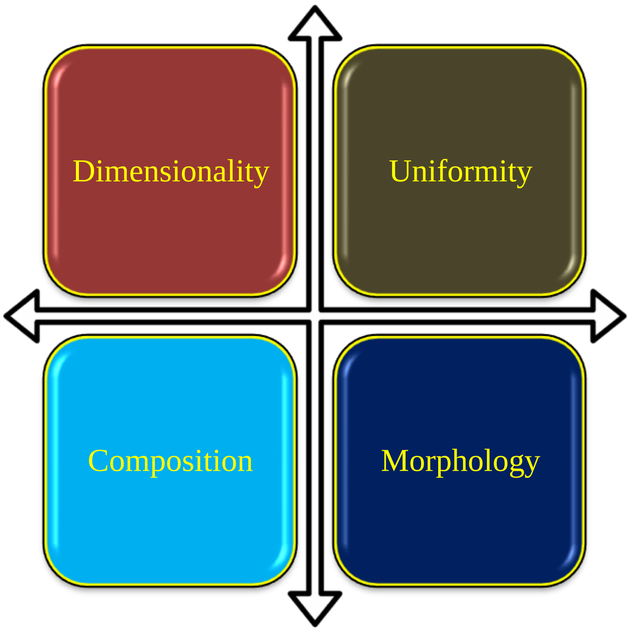

Fig. 1 Categorization of nanoparticles.

Toxicity of nanoparticles in plants

In plants, NPs cause beneficial as well as harmful effects. NPs elevated some parameters of plants, such as height shoot and root length, etc. Along with these effects, NPs also causes various toxic effects in plants. These toxic effects reduce the length of plants and transpiration rate. Mushtaq et al. (2011) demonstrated that Fe_3O_4, TiO_2 and carbon NPs play a adverse role in functioning of plants life cycle, such as seed germination, root elongation, etc. ZnO-NPs at 1000 mg/L may cause the destruction of all enzymatically active process in the cell and finally leads to the death of the cell (Lin and Xing, 2008). The effect of NPs are varies depending on their size. The response is more in smaller particles as compared to larger one.

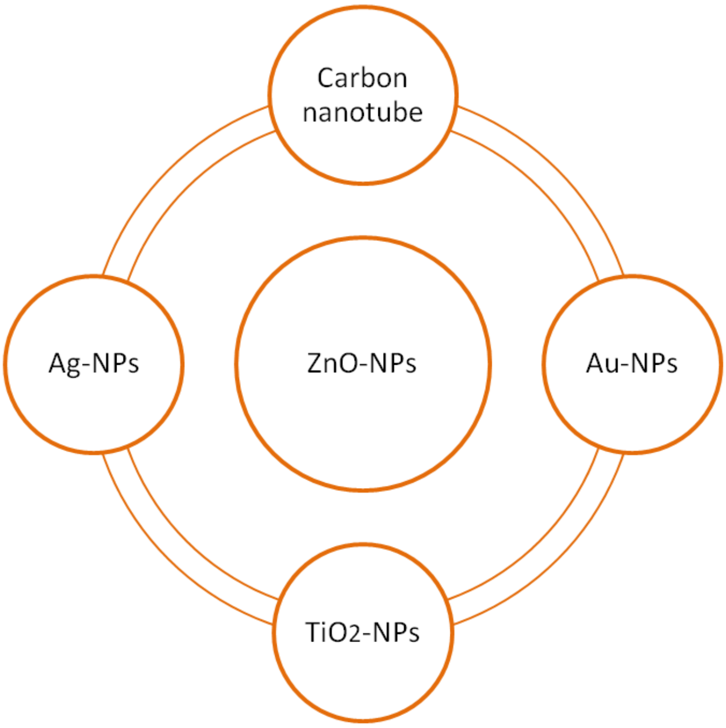

Fig. 2 Types of nanoparticles

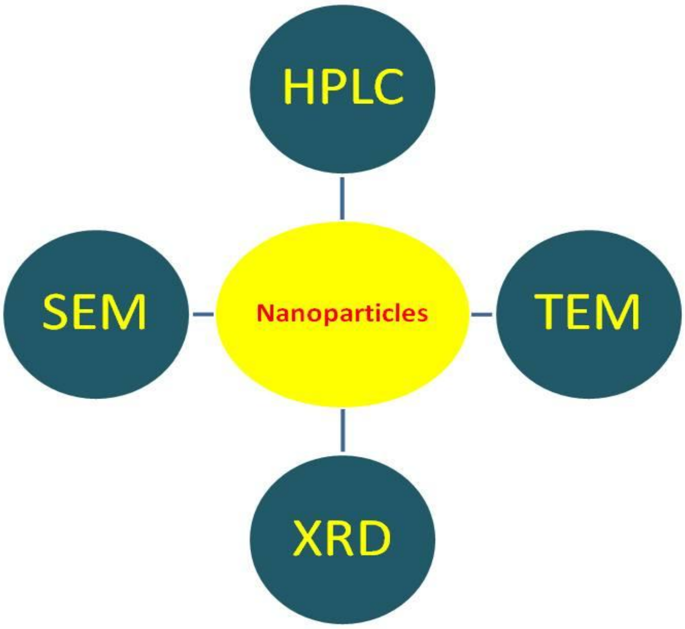

Fig. 3 Techniques used for characterization of nanoparticles

These responses were further confirmed by the proteomic and genomic studies. In plants, toxicity of NPs may be induced by two methods one is chemical toxicity, which is based on chemical composition. Second is stress or stimuli which are caused by ions released by the NPs. Aluminium coated SiO_2-NPs were less toxic for *Pseudokirchneriella subcapitata* as compared to non coated NPs (Hoecke et al., 2011). Atha et al. (2012) suggest that copper oxide NPs break DNA in some plant species.

Applications of nanoparticles

In the present scenario nanoparticles are used in agriculture, surface coating, polymers, plants, pharmaceuticals, cosmetics, food and beverage, etc., (Fig. 4) for their betterment.

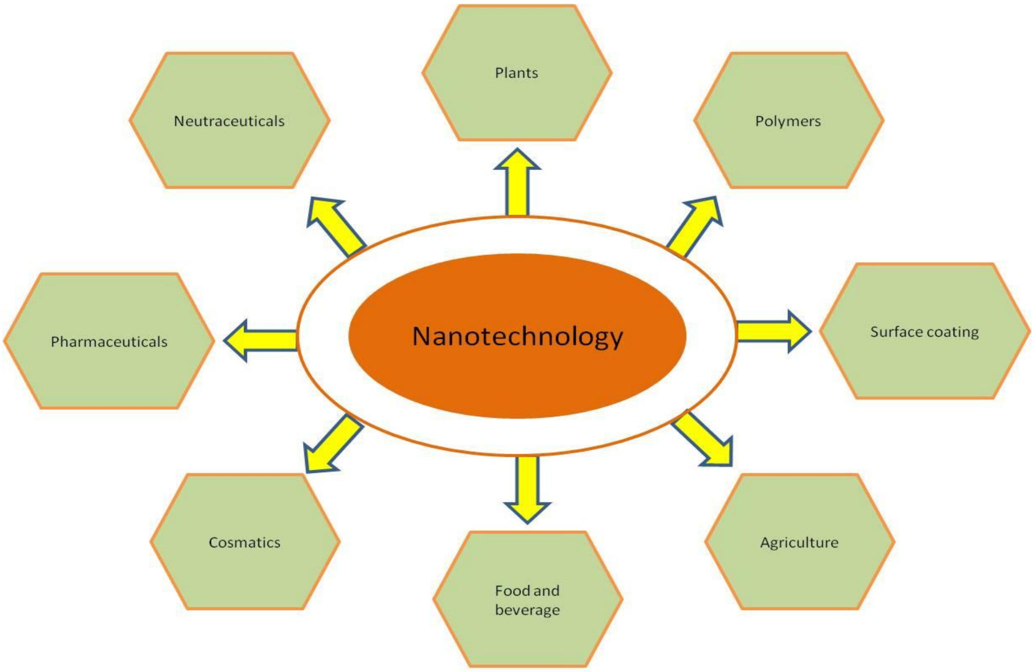

Fig. 4 Application of nanotechnology

CONCLUSION

Nanotechnology is one of the important branch of science and nanoparticles also have a role for the growth of the plant. A number of nanoparticles have been characterized by various techniques and all these particles play a significant role in the growth and development of the plant. Some of the nanoparticles play a positive role, while others have a negative impact. This may be due to the various factors such as size, type, methods of preparation as well as mode of application of nanoparticles. Therefore, it can be concluded that nanoparticles can act as a regulator of plant growth and development and may be cost effective in increasing the productivity of the crop in changing environment in near future.

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