

Plant-nanoparticle interaction: An approach to improve agricultural practices and plant productivity

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Abstract: Nanoparticles (NPs) due to their unique physiochemical properties are being used in the field of biotechnology and agriculture industry. Plenty of studies have been conducted to explore mechanism by which NPs influence on plant growth and development. Application of biosynthesized NPs in agricultural field leads us for sustainable development. Nanomaterials (NMs) are carriers of Agrochemicals. They facilitate site targeted delivery of various nutrients needed for better growth and high productivity of plants. Another application of NPs in agriculture includes application of nanobiosensors in the crop protection and nanodevices for genetic manipulation of plant. However, some reports reflect the negative impact of NPs on the environment. The researchers are working on NMs to minimize the negative impacts on the environment. This review summarizes application of NMs in agriculture which may play a crucial role to increase agriculture production in the future to feed a growing population.

Keywords: agriculture; agrochemicals; nanobiosensors; crop protection; nanodevices

I. INTRODUCTION

Nanotechnology, a new emerging and interesting field of science is currently applied in many areas. It has great application in the field of biotechnology and agriculture. Nanoparticles (NPs) are commonly accepted as materials with at least two dimensions between 1-100 nm [1]. NPs fall in a transitional zone between individual molecules and the corresponding bulk materials and therefore hold unique properties which are peculiar from their molecular and bulk counterparts [2]. Unique properties of NPs include very large specific surface area, high surface energy, and quantum confinement [3]. The characteristic feature of NPs may result in different environmental fate and behaviors than their bulk counterparts.

Agriculture is the backbone of most developing countries. The explosive growth of world population demanding higher agricultural productivity to feed the increasing population. It is necessary to use the modern technologies which can help agriculture to boost the yield. Nanotechnology and nanobiotechnology are the emerging fields which have tremendous potentials to renovate agriculture and allied fields. Nanotechnology in the field of agriculture focuses currently on target farming that involves the use of NPs with unique properties to boost crop and livestock productivity [4, 5]. Nanotechnology has the potential to increase food quality, global food production, plant protection, detection of plant and animal diseases, monitoring of plant growth and reduce waste for “sustainable amplification” [6-12]. The applications of nanotechnology in agriculture also include fertilizers to increase plant growth and yield, sensors for monitoring soil quality and pesticides for pest and disease management. The aim of the use of nanomaterials (NMs) in the field of agriculture is to improve the efficiency and sustainability of agricultural practices by putting less input and generating less waste than conventional products and approaches. The fertilizers are vital for plant growth and development, most of the applied fertilizers remain unavailable to plants due to several factors such as leaching and degradation by hydrolysis, insolubility and decomposition, in addition, application of conventional fertilizers at a high rate and for a long period in the agriculture field have caused major environmental issues worldwide. Heavy use of nitrogen (N) and phosphorus (P) fertilizers has become the major anthropogenic factors resulting in world-wide eutrophication problems in freshwater bodies and coastal ecosystems [13, 14]. Thus, imperative research needs to develop to minimize nutrient losses in fertilization and to increase the crop yield through the exploitation of new applications with the help of NMs and nanotechnology. In the perspective of sustainable agriculture, the application of modern nanotechnology in agriculture is considered as one of the important approaches to enhance crop production considerably and feed the world's fast growing population [15]. Nanofertilizers or nano-encapsulated nutrients have properties effectively to release nutrients and chemical fertilizers on demand that regulate plant growth and enhance target activity [16, 17]. Nanoscale science and nanotechnology have the potential to transform the agriculture and food systems [18]. Nanotechnology has immense potentials in agricultural uprising, high reactivity, better bioavailability, bioactivity and the surface effects of NPs [19].

The engineered nanoparticles (ENPs) are able to enter into plants cells and leaves, and can also transport DNA and chemicals into plant cells [20, 21]. This area of research provides a platform for biotechnology to target specific gene manipulation and expression in the specific cells of the plants. Various researches are going on the target drug delivery for disease diagnosis applicable for both flora and fauna. Research in the field of nanotechnology is required to discover the novel applications to target specific delivery of chemicals, proteins, nucleotides for genetic transformation of crops [21, 22].

There are various methods for the synthesis of NPs, but now a days researchers giving attention towards the green synthesis of NPs where mostly plant extract is used to synthesize NPs. Green synthesis of NPs from its corresponding metal ions is environmental friendly, free from chemical contamination, less expensive and safe for biological application [23, 24].

In the field of agriculture, the use of NMs is comparatively new and needs further exploration. This article summarizes the developments and application of novel NMs in agriculture field, green synthesis of NPs, uptake, translocation, and accumulation of NPs in the plants, NPs as growth promoters, nanopesticides and nanoherbicides, nanofertilizers, NPs in disease suppression, role of NPs in photosynthesis and nanobiosensors. Moreover, the emphasis is given to the recent developments in plant science regarding nanobiotechnology that focuses on agricultural practices, plant growth and yield.

II. GREEN SYNTHESIS OF NANOPARTICLES

Synthesis of NPs may be achieved mainly by physical, chemical and biological methods. Biological methods follow “Bottom Up” approaches in which the NPs are built from small entities by reduction and oxidation processes and thus the NPs are obtained with lesser defects (Table 1). The synthesis of NPs highlighting biological methods is schematically represented in Fig. 1. The biological entities possess capping and stabilizing agents in the synthesis process. Bio-reduction of NMs takes place either in-vitro or in-vivo. Enzymes, proteins, sugars, and phytochemicals like flavonoids, phenolics, terpenoids, cofactors, etc. mainly act as reducing and stabilizing agents during synthesis.

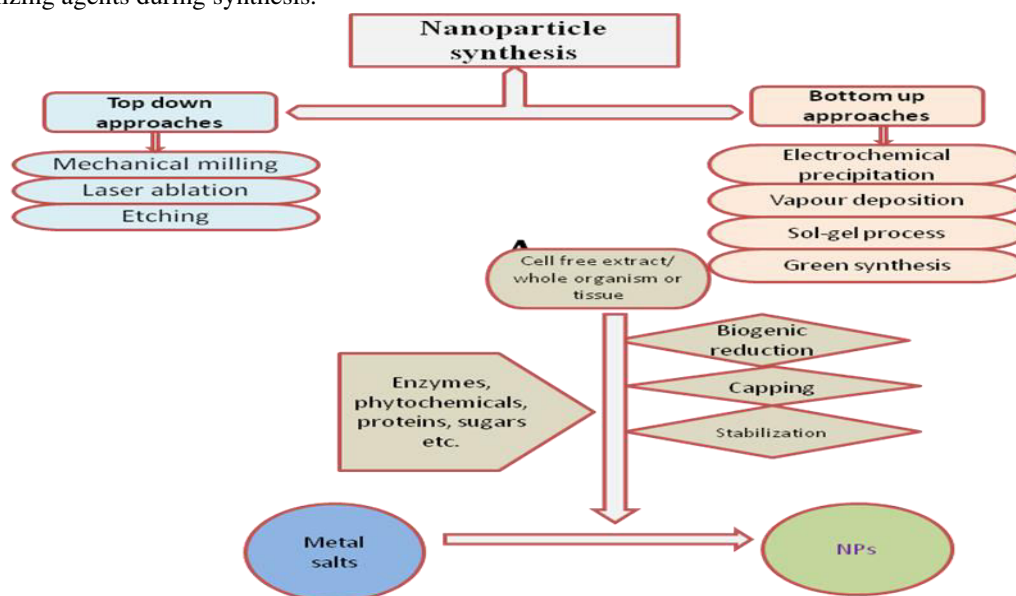


Fig. 1 Schematic representation of synthesis of nanoparticles highlighting biological/green method

Synthesis of TiO_2 NPs (36-38 nm, spherical) using a leaf extract of *Eclipta prostrata* was carried out at room temperature from titanium hydroxide $\text{TiO}(\text{OH})_2$ solution [25]. The reduction was credited to the carboxyl group (COOH) stretching and amine (N-H) stretching present in the extract. Cu ions reduced by *Malva sylvestris* resulting in the biosynthesis of CuO NPs (5-10 nm, spherical) and they were found to be active against both gram positive and gram negative bacteria [26]. CuO NPs (20 nm, spherical) synthesized by *Phyllanthus amarus* leaf extract when exposed to copper sulfate (Cu_2SO_4) solution, condition involved 7h vigorous stirring at 130 °C [27]. The produced NPs exhibited greater antibacterial activity against *Bacillus subtilis* in comparison to rifampicin. CeO_2 NPs (5 nm, spherical) with antibacterial properties were successfully synthesized using *Gloriosa superba* leaf extract [28]. The samples exhibited blue green emission at 486nm due to the presence of oxygen vacancy and oxygen interstitial defects. The authors further observed that the toxicological behavior of NPs was due to small size, with uneven ridges and oxygen defects. A simple one step, eco-friendly, bio-organic agarose polymer based synthesis of CeO_2 NPs (10 nm) has been reported [29]. It was observed that the NPs

above 200 °C exhibited high homogeneity with the cubic fluorite structure. The produced NPs exhibited no significant cytotoxic effect on the L929 cell line at different concentrations, thus have viable applications in different fields of medicine. Spherical Fe NPs were synthesized via a facile one- step green method using *Eucalyptus* leaf extracts applied in a swine waste water treatment [30]. The authors reported 71.7% of total nitrogen, 30.4% of total phosphorus, 84.5% of chemical oxygen demand (COD) were removed respectively by producing NPs, thus play a great role in remediation of wastewater. In another experiment, leaves extract of both green tea and eucalyptus produced Fe NPs (20-80 nm, spherical) [31]. Fe NPs reactivity towards nitrate was investigated and compared to the traditional chemically prepared Fe₃O₄ NPs and found that the biologically produced NPs showed significant in situ remediation of waste water especially in nitrate contaminated sites. Philip [32] reported the extracellular synthesis of Ag, Au and Au-Ag NPs (20-150 nm, triangular, spherical, and hexagonal) in water using the extract of *Volvariella volvacea*, an edible mushroom. Gopinath *et al.*, [24] reported an eco-friendly approach for the synthesis of ruthenium NPs (36nm) using leaf extract of *Gloriosa superba*.

Table 1. Nanoparticles synthesized via plant parts and its applications.

NPs	Plants	Precursor	Findings	Reference
CuO	<i>Cassia alata</i>	CuSO ₄	Wide application in medicine.	147
Pd/ Fe ₃ O ₄	<i>Euphorbia condylocarpa</i>	PdCl ₂ & FeCl ₃ ·6H ₂ O	Magnetically recyclable catalyst	148
CeO ₂	<i>Gloriosa superba</i>	CeCl ₃	NPs have toxicological behavior	28
ZnO	<i>Camellia sinensis</i>	Zn(O ₂ CCH ₃) ₂ (H ₂ O) ₂	Effective against microbes	149
CuO	<i>Gum karaya</i>	CuCl ₂ ·2H ₂ O	Antimicrobial activity against <i>E. coli</i>	150
CuO	<i>Malva sylvestris</i>	CuCl ₂ ·2H ₂ O	Effective against both gram +ve & -ve bacteria	26
CuO	<i>Phyllanthus amarus</i>	CuSO ₄	Effective than rifampicin against <i>B. subtilis</i>	27
TiO ₂	<i>Oryza sativa</i>	TiO ₂ (OH) ₂	Synthesized TiO ₂ NPs highly potential photocatalyst	151
Pd	<i>Catharanthus roseus</i>	Pd(OAc) ₂	Effective in textile effluent remediation	152
Pb	<i>Cocos nucifera</i>	Pb(COOH) ₂	Absorption of carcinogenic dye	153
Ag	<i>Croton sparsiflorus</i>	AgNO ₃	Effective against <i>S. aureus</i> , <i>E. coli</i> , <i>B. Subtilis</i> .	154
Ag	<i>Olea europaea</i>	AgNO ₃	Effective against drug resistance bacterial isolates	155

III. UPTAKE, TRANSLOCATION, AND ACCUMULATION OF NANOPARTICLES IN THE PLANTS

Uptake, translocation, and accumulation of NPs depend on the plant species and the size, kinds, chemical composition and stability of the NPs. The uptake, biotransformation and translocation of various NPs by a model plant has been demonstrated by Majumdar [33] in Fig. 2. The uptake, accumulation, and the translocation of natural organic matter (NOM), suspended fullerene C70 and MWCNT in rice plants were studied by Lin *et al* [34]. Occurrence of C70 in the form of black aggregates was reported. These aggregates were found more in the seeds and roots as compared to the stems and leaves of the rice. The author hypothesized that the presence of aggregates of NOM-C70 in leaves followed the transmission route of water and the nutrients through the xylem tissue. In the cell membrane specific ion transporters have been identified for NPs taken up by the plants [35]. The low surface friction of CNTs facilitates the flow of organic substances into the cytoplasm [36]. Interaction of ryegrass with NPs has been reported. The scanning electron microscopy studies confirmed the adsorption and aggregation of the NPs on the root surface [37].

TEM images of root cross-sections of the ryegrass also showed the presence of particles in the apoplast, cytoplasm and nuclei of the endodermal cells. Birbaum [38] observed that CeO₂ NPs applied on corn leaves, were absorbed by the leaves, but not translocated to new leaves. Zhu [39] reported the uptake of Fe₃O₄ NPs by

pumpkin seedlings in hydroponic culture using a vibrating sample magnetometer. NPs were detected in roots, stems, and leaves of the plants. It was interesting that no uptake was observed when plants were grown in soils and reduced uptake when grown on sand. It suggested that the uptake of the NPs depends on the growth medium this may be due to the adherence of the Fe₃O₄ NPs to the soil and sand grains. Uptake of NPs was also found to be species specific. Lima bean plants (*Phaseolus limensis*) did not absorb Fe₃O₄ NPs on treatment. Uptake and translocation of Cu NPs in mungbean (*Phaseolus radiata*) and wheat (*Triticum aestivum*) were investigated by Lee *et al.*, [40] in the agar growth medium. The authors observed that the Cu NPs could cross the cell membrane and agglomerate in the cells. *Cucurbita pepo* when treated with Ag NPs, the Ag concentration in the plant shoots was found to be 4.7 times higher in the plants than those treated with bulk Ag powder exposed to 10–1000 mg L⁻¹ Ag NPs [41]. There are reports that NPs in algae and tobacco are transmitted to the next trophic level [42, 43]. NPs accumulated in the cells may be transported by apoplast or symplast through plasmodesmata. However, the exact mechanisms by which plants take up NPs and plant specific accumulation of NPs is are still unknown and remain to be explored.

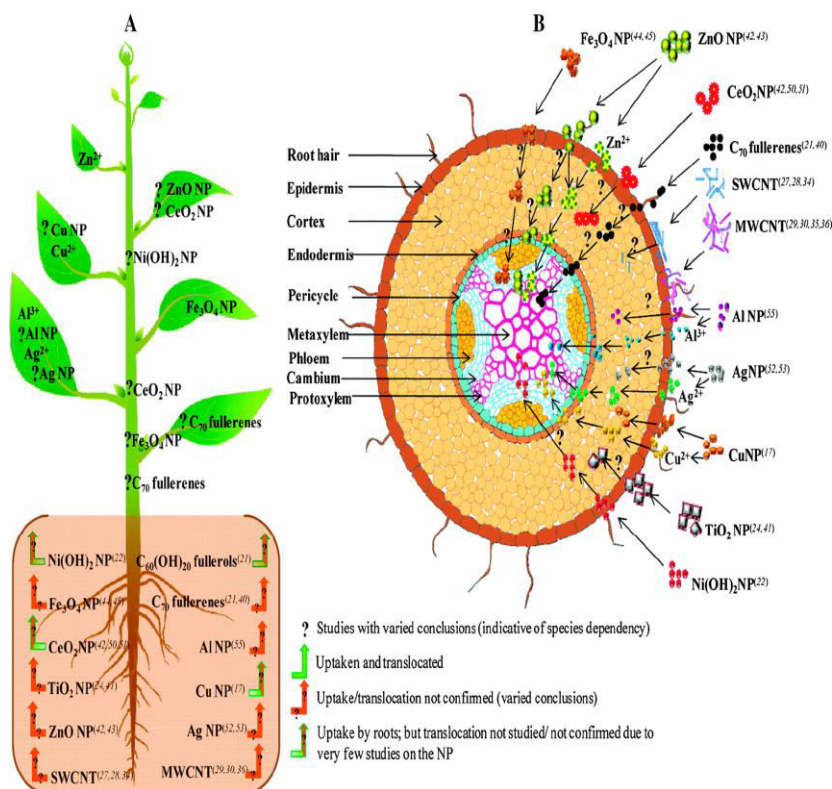


Fig. 2 Uptake, translocation, and biotransformation pathway of various nanoparticles in a plant system: a plant showing the selective uptake and translocation of nanoparticles; b transverse cross section of the root absorption zone showing the differential nanoparticle interaction on exposure. The superscripts depict the reference cited in the original article. Reprinted with permission³³. Copyright 2011 American Chemical Society

IV. NANOPARTICLES AS GROWTH PROMOTER

In recent years, the researchers have reported the effects of NMs on germination and growth with the goal to promote their use of agricultural applications. Interaction of NPs with plants caused various physical and physiological changes, depending on the properties of NPs. Effectiveness of NPs depends on their concentration and it varies from plant to plant (Table 2). Efficiency of NPs is determined by their chemical composition, size, surface area, reactivity, and the concentration at which they response positively [44]. NPs have both positive and negative effects on plant growth and development. However, this review deals with the positive roles played by NPs on seed germination, photosynthesis and plant growth. NPs commonly encountered in the agricultural field fall into following categories: carbon NMs, metal NPs and metal oxides NPs.

Effect of carbon nanomaterials on plants

Among the NPs, carbon NMs have acquired a significant place due to their unique mechanical, electrical, thermal and chemical properties. The tomato seeds when exposed to MWCNTs, seed germination and vegetative biomass increased significantly [44]. Author of this study hypothesized that penetration of the cell wall by NPs leads to the increase in water uptake by seeds which enhanced germination percentage.

Table 2. Positive role of nanoparticles at on plant growth and development.

NPs	Optimum concentration	Plant	Effects	Reference
<u>Nanoanatase TiO₂</u>	0.25%	<u>Spinacia oleracea</u>	Induction in enzyme activity	156
Alumina NPs	10mg/L	<u>Lemna minor</u>	Root length increased	157
Alumina NPs	0.3g/L	<u>Lemna minor</u>	Accumulation in biomass	157
<u>Serium oxide NPs</u>	500,1000,2000,4000 mgL ⁻¹	Corn, Alfalfa, Soybean	Significantly increased root and stem growth	70
Iron oxide NPs	0.5-.75 g/L	<u>Glycine max</u>	Improvement in yield and quality	72
Iron oxide NPs	50 ppm	<u>Vigna radiate</u>	Enhancement in biomass	158
CeO ₂ NPs	250 ppm	<u>Arabidopsis thaliana</u>	Biomass increased	159
CO ₃ O ₄ NPs	5g/L	<u>Raphanus sativus</u>	Increased root growth	160
<u>CuO NPs</u>	500mg/kg	<u>Triticum aestivum</u>	Biomass increased	161
G NPs	10 ug/mL	<u>Arabidopsis thaliana</u>	Increased root and shoot length, early flowering	56
Ag NPs	10-30 ug/mL	<u>Boswellia ovalifoliolata</u>	Increased germination and seedling growth	57
TiO ₂ NPs	1000 mg/L	<u>Triticum aestivum</u>	Increased in chlorophyll content	80
TiO ₂ NPs	.05-0.2 g/L	<u>Lycopersicum esculantum</u>	Net photosynthetic rate increased, enhancement in H ₂ O conductance	132
CNTs	40 ug/mL	<u>Lycopersicum esculantum</u>	Enhancement in germination and seedling growth	162
MWCNTs	50 and 200ug/mL	<u>Lycopersicum esculantum</u>	Plant height improved and number of flower increased	163
<u>ZnO NPs</u>	1.5 ppm	<u>Cicer arietinum L.</u>	Shoot and dryweight significantly increased	85
<u>ZnO NPs</u>	1000 ppm	<u>Arachis hypogea</u>	Increased stem and rood growth, high yield	164
Al NPs	2000mgL ⁻¹	Radish, Rape	Root growth improved	51
Au NPs	62,100,116 mgL ⁻¹	Cucumber, Lettuce	Significant increase on germination index	165
<u>ZnO NPs</u>	500 mgL ⁻¹	Soybean	Root growth increased	70

Sriniwasan and Sarawathi [45] reported that the single walled-CNTs (SWCNTs) act as nanotransporters for delivery of dye molecules and DNA into plant cells. In another report MWCNTs enhanced efficiency of water uptake as well as Ca and Fe nutrients uptake which increased the seed germination and plant growth [46, 47].

Seed germination increased in barley, soybean and corn when treated with MWCNTs, authors with the help Raman spectroscopy and TEM detected nanotube agglomerates inside the seed coat [48]. Oxidized MWCNTs increased cell elongation in root system and promoted dehydrogenase activity [49]. CNTs induced the root and shoot growth of wheat plants in light and dark conditions. It has been confirmed the presence of water soluble CNTs by SEM and fluorescence microscope inside the plants [50]. Lin and Xing [51] reported that MWCNTs enhanced 5-days root elongation in rye grass, rape and corn. Canas et al [52] reported that the exposure of SWCNTs at 0.16, 0.9 and 5 gL⁻¹ concentration enhanced the root growth of onion and cucumber seedlings.

Effect of metal nanoparticles on plants

The studies suggest that metal NPs increase plant growth and development. AgNPs increased the root length in maize and cabbage plants in comparison with AgNO₃ [53]. Au NPs influenced the number of leaves, leaf area, plant height and sugar and chlorophyll content that result in better crop yield [54, 55]. Au NPs have a significant role on seed germination and antioxidant system in *Arabidopsis thaliana* [56]. Au NPs improved seed germination in *Boswellia ovalifoliata* [57]. Biologically synthesized Ag NPs induced synthesis of protein and carbohydrate and decreased the total phenol content in *Baopa monnieri* [58]. Root length increased in barley exposed to AgNPs [59]. Spinach seeds soaked in a solution of Ti NPs increased fresh and dry weight as well as contents of total N, chlorophyll and protein in leaves [60]. More than two fold increase in height and fresh weight of duckweed was found when treated with Ti NPs at 0.5 gL⁻¹ conc. [61]. Biosynthesized Zn NP significantly enhanced shoot (10.8%), chlorophyll content (18.4%) and grain yield (29.5%) in pearl millet [62]. Almeelbi and bezbaruah [63] reported the effect of Fe NPs on spinach in hydroponic solution. The authors reported significant enhancement in plant growth and biomass by NPs. Interestingly Fe content in spinach roots, stem and leaves increased 11-21 times.

Effect of metal oxide nanoparticles on plants

A large number of studies on the effects of metal oxide NPs on germination and growth of plants have been documented. Nanosized TiO₂ promoted plant growth when seeds were soaked in NPs or sprayed with NPs [64]. Parsley seeds exposed to nano anatase, enhanced germination, root and shoot length and chlorophyll content of the seedling [65]. The germination rate of salvia improved when the seeds were treated with TiO₂ NPs [66]. Mixture of TiO₂ and SiO₂ NPs improved the nitrate reductase activity and stimulated the antioxidant system in soybean [67]. In spinach, chlorophyll formation, photosynthesis and plant dry weight increased when exposed to TiO₂ NPs [68, 69]. Root elongation was promoted at a particular concentration of ZnO NPs in soybean [70]. Iron oxide NPs enhanced root elongation in pumpkin [71]. In another experiment iron oxide NPs increased soybean pod and leaf dry weight [72]. ZnO NPs promoted seed germination, root and shoot length in the peanut plant [73]. Suriyaprabha [74] reported that seed germination increased by nano SiO₂ which provided better nutrient availability to maize seeds. Changbai larch (*Larix olgensis*) seedlings when exposed to nano SiO₂, NPs improved seedling growth and chlorophyll biosynthesis [75]. Plant growth and development improved by nano SiO₂ by increasing photosynthetic rate, transpiration rate, electron transport rate and other physiological parameters [76, 77]. ZnO NPs in lower concentration increased seed germination in wheat [78]. *Cyamopsis tetragonoloba* when exposed to ZnO NPs, improved plant biomass, root and shoot length, chlorophyll and protein synthesis and other growth parameters [79]. Seed germination, radicle and plumule growth of canola seedlings was stimulated by TiO₂ NPs [80]. Under water stress condition wheat plant growth is increased by TiO₂ NPs [81]. TiO₂ NPs increased plant growth by promoting chlorophyll formation and activities of Rubisco [82]. According to Gupta and Tripathi [83] TiO₂ NPs may be used for decomposition of organic compounds and production of H₂ as a fuel. 58.2 and 69.8% increase in fresh and dry weight and significant increase in chlorophyll content, photosynthetic rate and Rubisco activity was recorded in Spinach when treated with anatase TiO₂ NPs [84]. Burman [85] reported that foliar application of ZnO NP at 1.5 mg/L concentration increased biomass as compared to ZnSO₄ in chickpea. Fe₂O₃ NPs given to soybean by foliar application and soil route. Root elongation and photosynthetic potential significantly enhanced by foliar application of NPs but this enhancement was far less when NPs were given to plant via soil route which may be due to precipitation of Fe ions [86]. According to Singh et al [87] RuO₂ NPs enhanced the germination and early growth of the *Brassica* sps. The growth stimulating function of NPs on plants seems to be significant. Sincere field research is needed to study, promoting effects of these NPs on yields of some important crops. The mode of action of these NPs by which they take part in the growth and development of plants must also be explored.

V. NANOPARTICLES IN DISEASE SUPPRESSION

Viruses, bacteria, fungi and nematodes are mainly responsible for plant diseases resulting in decreased yield and poor quality of plant products. Various approaches to manage crop disease are being used including genetic breeding, cultural schemes with sanitation, host indexing, enhanced eradication protocols, new pesticide products, and integrated pest management. Several studies have reported that NPs can be used to suppress pathogens which increased crop growth. Jo et al [88] reported that Ag NPs in 200 mg/l conc. reduced 50%

colony formation of pathogenic fungi that caused disease in ryegrass. Lamsal et al [89] have also reported that application of Ag NPs enhanced the disease suppression. Combined activities of Ag NP with the fungicide flucanazole were found to be effective against *Candida albicans*, followed by *Phoma glomerata* and *Trichoderma* sps [90]. ZnO NPs reduced growth by 26% of *Fusarium graminearum* grown in mungbean broth agar [91]. MgO NPs exhibited significant antimicrobial activity due to strong interaction with a negative surface of bacterial membranes [92]. Chemically synthesized Cu NPs demonstrated higher pathogenic fungal inhibition in comparison to the fungicide bavistin [93]. Jo et al. [94] showed effective concentrations for inhibition of colony formation by silver compounds on *Bipolaris sorokiniana* was greater than that on *Magnaporthe grisea*. Silver compounds inhibited colony formation of *B. sorokiniana* by 50% at optimum concentration. Significant reduction in mycelial growth was observed from spores incubated with silver NPs [95]. Silver NPs greatly reduced the number of germinating fragments relative to the control at 24 hour incubation of spores with a 2.5 ppm solution of NPs. Field tests was also done with silver NPs (WA-CV-WA138) at various concentrations to determine antifungal activity. The highest inhibition rate for the growth of fungal pathogen on cucumber and pumpkins exposed to 100 ppm silver NPs [96].

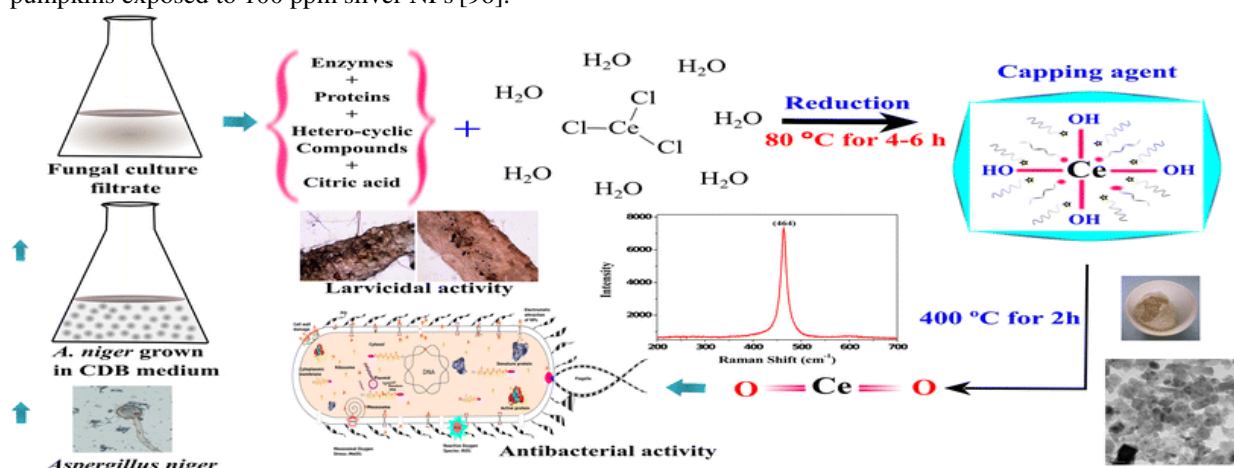


Fig 3. Biologically synthesized Cerium oxide nanoparticles (CeO_2 NPs) at a concentration of 10 mg/mL showed higher antibacterial activities against *Streptococcus pneumonia* and *Bacillus subtilis* and the NPs caused 100 % mortality on first instar of *Aedes aegypti* at 0.250 mg/L concentration after 24-h exposure. Reproduced with permission¹⁰³. Copyright 2015 Springer Science+Business Media

ZnO NP was found to be a good antibacterial agent, according to Ahmad et al ZnO NP reduced the cell number of *Salmonella typhimurium* and *Staphylococcus aureus* to zero within 8 and 4 hour. This antibacterial activity of ZnO NP can be used in food system as preservative agent [97]. Kamran et al [98] reported that the nanosilver and nano TiO_2 with a good potential may be used for removing of the bacterial contaminants in the tobacco plant. Ag NP exposure causes toxicity to bacteria. Ag NP treatment can prevent replication and protein synthesis [99]. Cui et al [100] reported the mechanism and antibacterial activity of Au NP against *E. coli*. NPs were demonstrated to decay membrane potential, decreased ATPase activity and inhibition of ATP at the cellular level. Tea extracts were used to prepare Ag NP which exhibited antibacterial activity against *Vibrio harveyi* [101]. Antibacterial activity of Ag NPs against *E. coli* was also reported by Marek et al [95]. These NPs were synthesized by extract and powder of *Curcuma longa* tubers. Au NPs synthesized by banana peel extract, exhibited antifungal activity against *C.albicans* [102]. Gopinath et al [103] in his report showed antibacterial and larvicidal activity of biologically synthesized CeO_2 NPs (Fig. 3).

VI. NANOPESTICIDE AND NANOHERBICIDE

Pesticides and herbicides are usually used in agriculture to get better crop yield and efficiency. But presently the negative aspects of conventional pesticides and herbicides on environment are under argument. The main disadvantages of pesticides are development of pathogen and pest resistance, decreases nitrogen fixation, reduces soil biodiversity, contributes to bioaccumulation of pesticides, pollinator decline and destroys habitat for birds [104]. Therefore, use of NPs resolve these problem to most extent, its application with herbicides reduces the amount of herbicides requirement for weed eradication. With the active ingredient and smart delivery system, herbicides are released in the soil according to the soil condition (Gruere *et al*) [105]. Ag NPs have pesticidal activity against pathogenic fungi, reported to have inhibitory effects on conidial germination of genus *Raffaelea* which causes mortality of oak trees [106]. On the other hand, Avermectin (pesticides which block neurotransmission in insect) has very short life span, with half-life of 6 hour because it cannot resist UV rays in field, its life span is reported to increase by the porous Si NPs with shell thickness of 15nm and pore diameter 4-5nm.

Table 3. Antimicrobial activity of biosynthesized nanoparticles.

NPs	Plants	Precursor	Findings	Reference
CuO	<i>Cassia alata</i>	CuSO ₄	Wide application in medicine.	147
Pd/ Fe ₃ O ₄	<i>Euphorbia condylocarpa</i>	PdCl ₂ & FeCl ₃ ·6H ₂ O	Magnetically recyclable catalyst	148
CeO ₂	<i>Gloriosa superba</i>	CeCl ₃	NPs have toxicological behavior	28
ZnO	<i>Camellia sinensis</i>	Zn(O ₂ CCH ₃) ₂ (H ₂ O) ₂	Effective against microbes	149
CuO	<i>Gum karaya</i>	CuCl ₂ ·2H ₂ O	Antimicrobial activity against <i>E. coli</i>	150
CuO	<i>Malva sylvestris</i>	CuCl ₂ ·2H ₂ O	Effective against both gram +ve & -ve bacteria	26
CuO	<i>Phyllanthus amarus</i>	CuSO ₄	Effective than rifampicin against <i>B. subtilis</i>	27
TiO ₂	<i>Oryza sativa</i>	TiO ₂ (OH) ₂	Synthesized TiO ₂ NPs highly potential photocatalyst.	151
Pd	<i>Catharanthus roseus</i>	Pd(OAc)	Effective in textile effluent remediation	152
Pb	<i>Cocos nucifera</i>	Pb(COOH) ₂	Absorption of carcinogenic dye	153
Ag	<i>Croton sparsiflorus</i>	AgNO ₃	Effective against <i>S. aureus</i> , <i>E. coli</i> , <i>B. Subtilis</i> .	154
Ag	<i>Olea europaea</i>	AgNO ₃	Effective against drug resistance bacterial isolates	155

Si NPs encapsulates Avermectin and preserves its capacity and secures from UV rays and release of these encapsulated pesticide by NP carrier have increased life span for about 30 days [104]. Gruere et al [105] reported nano- surfactant based on soybean micelles. The crop susceptible to glyphosate may be glyphosate resistant when these are applied with the nanotechnology-derived-surfactant.

The use of nano formulations may offer new ways to enhance the stability of biological agents. The role of NPs in insects and their potential for insect pest management has been reported [107]. Green synthesis of silver nanoparticle of *Tinospora cordifolia* showed maximum cidal effect against the head louse *Pediculus humanus* and fourth instar larvae of *Anopheles subpictus* and *Culex quinquefasciatus* [108]. Recently, researcher has concluded that nanoagrochemicals are generally nano reformation of existing pesticides and fungicides. Probably the nanoformulations are expected to enhance the solubility of poorly soluble active constituents, release the active constituents in a targeted fashion and resists premature degradation [109]. Nanopesticides significantly controlled delivery of pesticides, low chemical dose and high positive results. Silver NPs at 100 mg/ kg reduced mycelial growth and conidial germination on cucurbits and pumpkins against powdery mildew [110]. Phenolic suspension of hydrophobic alumina-silicate NPs are significantly effective against grasserie disease in *Bombyx mori* leaves [111]. It is also reported that Nano encapsulated pesticides are adsorbed on plant surface, helps in sustained release for longer time as compared to conventional pesticides that washed away in the rain [112].

Conventional methods to control the pathogens and pests have adverse effects on both the environment and economy of farmers. Therefore the NPs applications are gaining ever escalating demand for sustainable agriculture without disturbing the environment.

The studies conducted under non-sterile conditions make it clear that the increase in crop growth/yield is the result of reduced disease presence. This is possible either from the anti-pathogenic activity of the NP itself, or indirectly through the induction of key defensive pathways and metabolites within the plant.

VII. NANOFERTILIZERS

Nanofertilizers are the NMs which can provide nutrients to the plants or they assist to augment the activities of conventional fertilizers. Replacement of nanofertilizers for traditional fertilizer is beneficial as its application is to release nutrients into the soil steadily and in a controlled way, thus prevents water pollution [113, 114]. Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) NPs of 16 nm in size, synthesized by Liu and Lal [115], exhibited fertilizing effect on soybean. There are so many reports where application of nanofertilizer reflects positive effect in terms of good crop yield as well as environmental pollution. The application of NPs increased the growth rate and seed germination by 33% and 20% respectively, compared to regular P fertilizer. The result indicated that the roots of soybean can absorb hydroxyapatite NPs as an effective P nutrient source. Soil amended with metallic Cu NPs significantly increased 15 day lettuce seedling growth by 40% and 91% respectively [116]. Some studies focused on the characteristics of NPs also revealed that NPs can enter plant cells and transport DNA and chemicals inside the cell [117-119]. These studies provide a platform on which we can assume that NPs can also deliver nutrients to the plants as fertilizers. The nano-organic iron chelated fertilizers demonstrated high absorption, increase in photosynthesis and expansion in the leaf surface area [120]. Moreover, nanofertilizers have great impact on the soil as nanofertilizers can reduce the toxicity of the soil and decrease the frequency of fertilizer application [121]. De rosa [122] reported that in nanofertilizers, nutrients can be encapsulated by NMs, coated with a thin protective film or delivered as emulsions or NPs. Nano and subnano composites control the release of nutrients from the fertilizer capsule [123]. Urea modified hydroxyapatite nanoparticle- encapsulated *Gliricidia sepium* nanocomposite exhibited a slow and sustained release of nitrogen over time at 3 different pH values [124]. Manikandan et al reported that nanoporous zeolite used on N fertilizer might be used as alternate strategy to enhance the effectiveness of N used in crop production system [125]. Nanofertilizers due to their characteristic features have great role in sustainable agriculture [126]. Thus from the above mentioned findings we can articulate that the use of nanofertilizer leads to an increased efficiency of the micro and macro elements, reduces the toxicity of the soil and reduces the frequency of application of conventional fertilizers.

VIII. ROLE OF NANOPARTICLES IN PHOTOSYNTHESIS

Photosynthesis is the process by which plant converts solar energy into chemical energy. Only 2-4% of available energy in radiation is converted by plants is used in plant growth and development [127]. Researchers are trying to improve photosynthetic efficiency of plants by gene manipulation and other techniques. Nanotechnology has the potential to improve function of photosynthetic machinery. Embedded SWCNTs in the isolated chloroplast increased photosynthetic activity three folds higher than that of control. It also increased maximum electron transport rate [128]. SiO_2 NPs increase photosynthetic rate by changing the activity of carbonic anhydrase and synthesis of photosynthetic pigments [129, 130]. Nano TiO_2 increases the photosynthetic carbon assimilation by activating Rubisco that could promote carboxylation, reflecting increase in plant growth [131]. Net photosynthetic and transpiration rates are improved by TiO_2 NPs [132]. Au NPs and Ag nanocrystals can induce the efficiency of energy production in photosynthetic machinery [133]. Nano mesoporous silica compound (SBA) bound with photosystem II and increase activity of photosynthetic oxygen evolving reaction [134]. Ma et al [135] reported that nano- anatase- induced marker gene increased the activities of Rubisco activase reflected in the improvement of Rubisco carboxylation and high rate of carbon reaction of photosynthetic machinery. Thus the improvement of photosynthetic mechanisms by nano-genic approach may help to design artificial light-harvesting systems.

IX. NANOBIOSENSORS

NPs can be used as a diagnostic tool for detection of plant pathogens. However, this research is in initial stage in agriculture. NPs sometime used as a investigative tool to detect compounds which could be indicator of disease. Fundamentally biosensor is derived from the coupling of a ligand-receptor binding reaction to a signal transducer. It consists of a probe, bioreceptor and transducer. The interaction of analyte with bioreceptor is designed to produce an effect measured by transducer, which converts the information into electrical signal (Fig. 4). Lopez et al [136] reported that nano-chips are known for detecting single nucleotide changes of bacteria and viruses. These nano-chips contain fluorescent oligo capture probe by which hybridization can be detected. *Xanthomonas axonopodis* causes bacterial spot disease in Solanaceae plant. Yao et al [137] used fluorescence silica NPs in combination with antibody to detect this microorganism showing potential of NPs in disease detection. Karnal bunt disease in wheat was detected by nano-gold based immunosensor using surface plasmon resonance [138]. Research on nanosensors for detecting pathogens, is yet to be explored specially for its field application. It would be highly valuable for diagnosis and disease management. Nanosensors dispersed in the field can detect the presence of plant viruses, other crop pathogens and the level of soil nutrients [139, 140]. Mousavi reported that nano smart dust i.e. tiny wireless sensors and transponders can evaluate environmental pollution quickly [141]. Insects, disease, pathogens, chemicals and contaminants can be rapidly detected by portable nano devices and results in faster treatment [142]. Nanotechnology based devices will increase the use of sensors for real time monitoring of crops [143]. These intelligent systems thus monitor and minimize the use

of pesticides and antibiotics [144]. According to Mishra [145] due to very low concentration of biochemicals and the presence of very low amount of detectable virus and many fungal or bacterial infections, disease diagnosis is difficult. Application of nanobiosensor includes detection of urea, glucose, pesticide, monitoring of metabolites and detection of various microorganisms/pathogens [146]. Nanosensors offer the advantage of being small, portable, sensitive and they are accurate, reproducible and stable too, thus they can replace the conventional sensors. Soil temperature and moisture are very important indicators and play significant role in agriculture. With the help of microelectronic circuit, biosensors are able to sense and monitor the temperature and moisture of the soil [144]. It is now clear that nanobiosensors can be effectively used for sensing a wide variety of fertilizers, herbicides, pesticides, insecticides, pathogens and thus can support sustainable agriculture by enhancing crop productivity.

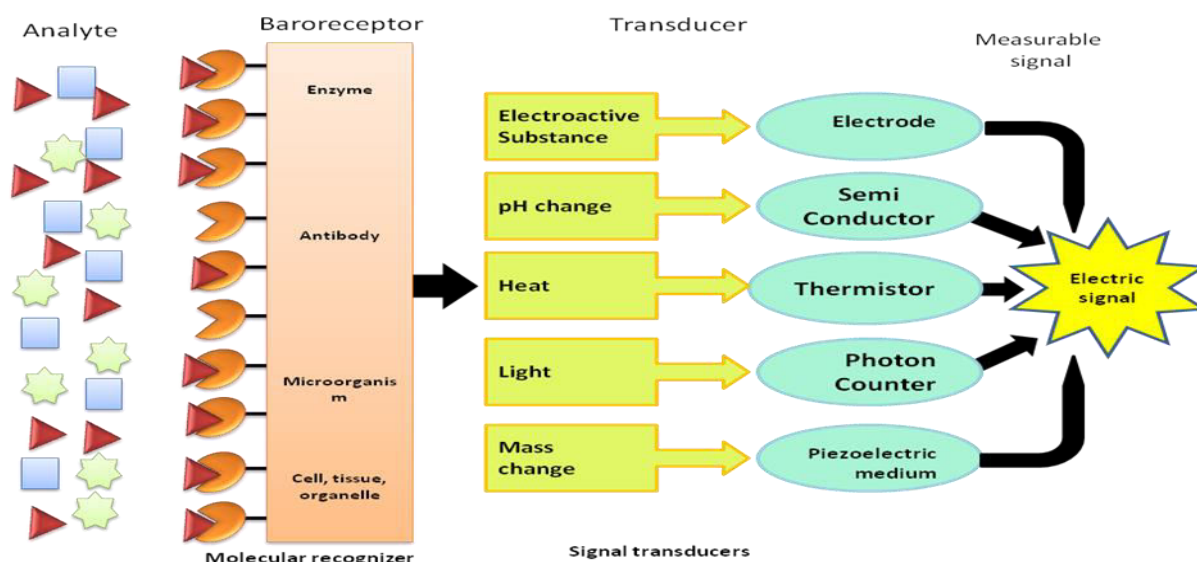


Fig. 4 Diagrammatic representation of generalised mechanism of Biosensor

CONCLUSION AND FUTURE ASPECTS

However, with the speedy progress in the study of phytotoxicity, uptake and accumulation of NPs in the past few years, we are still in the very early stage of this field and several questions with tremendous scientific or practical importance need to be addressed. Earlier studies have clearly demonstrated the activities of NPs in plant species, yet how and why different plant species display different resistance to NPs remains unexplored. How plant species and environmental factors will affect the uptake and accumulation of NPs is still to be investigated.

Genetic response of plants in the presence of NPs is also a topic of discussion. Different xylem structures may exhibit different route of uptake of NPs. Another important aspect is to realize the penetration route of NPs into vascular tissues. Solutes enter into vascular tissues, either through apoplast or symplast. Some studies with NPs explored the apoplastic pathway for entrance of NPs in plant tissues and cross membrane through plasmodesmata. More studies are required in the field to confirm this hypothetical view.

The concern on the toxicity of NPs in the environment has emerged during the last decade, with the increase of NPs industry and manifold applications. The potential uses and benefits of nanotechnology are enormous. With the help of nanotechnology maximization of output and minimization of inputs through better monitoring and targeted action is possible. The use of nanotechnology brings major benefits to farmers by food production and to the food industry through the development of novel products through food processing, preservation, and packaging. Other application of NMs in the field of agriculture include nanosensors/nanobiosensors for detecting pathogens and soil quality and plant health monitoring, nano enabled fertilizers for slow-release and efficient dosage of water and fertilizers, nanocapsules for agrochemical delivery, nanocomposites for plastic film coatings used in food packaging and antimicrobial application of NPs for preventing contamination. There has been significant interest in using nanotechnology to promote agriculture. The use of NMs for crop disease suppression has not been sufficiently explored. Use of Nano particles for delivery of anti-microbiological or drug molecules will be highly demanding in near future for therapy of all pathological sufferings of plants. The potential benefits of nanotechnology for agriculture and food need to be balanced against concerns for the soil, water and environment. Although this review displays the potential of NMs for different agricultural practices however, further investigation and research are needed to expand the application, possibilities and methodologies in agriculture.

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