

Review Article

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Nanotechnology and its Importance in Micronutrient Fertilization

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ABSTRACT

The increase in population and reduction of available land and water resources are major concern for agriculture to meet food requirement. The possible growth in agriculture can be achieved by increasing productivity through soil, water and nutrient management supported by an effective use of modern technology like nanotechnology. The small size, high specific surface area and reactivity of nano fertilizers compared to bulk fertilizers may increase the solubility, diffusion and availability of nutrients to plants and enhance crop productivity. Nanotechnology has provided the feasibility of exploring nanostructured materials as fertilizer carrier or controlled-release vectors for building of the so-called smart fertilizers, as new facilities to enhance the nutrient use efficiency and reduce the environmental pollution. Micronutrients like iron, zinc, copper and manganese have become yield-limiting factors and are partly responsible for poor food nutritional quality. Once added to soils, they react rapidly to form chemical precipitates, interact with clay colloids and organo-mineral matrix of soils. In high rainfall areas, they are significantly lost due to leaching. Thus, micronutrient use efficiency (MUE) is less than 5%. Micronutrient nanofertilizers may enhance the availability of these micronutrients to plants and increase the crop productivity. Since development and application of nanofertilizers are still at initial stages, there are few studies available on the effects and advantages of applying micronutrient nanofertilizers under field conditions. Any breakthrough on new crop-production stimulating mechanisms along with providing nutrients would be a milestone not only in nanotechnology research, but also in ushering another new “Green Revolution”.

Keywords

Nanotechnology,
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Introduction

Nanotechnology has the potential to revolutionize the agricultural and food industry with new tools for enhancing the ability of plants to absorb nutrients, molecular treatment of diseases, rapid disease detection,

etc (Anonymous, 2015a). Nanotechnology is seen as an important technology for future agriculture production. The word ‘nano’ is taken from Greek language meaning ‘dwarf’ refers to the dimensions on the order of magnitude 10^{-9} . It refers to a size range of 1 to 100 nm. Nanotechnology is the technology

that manipulates or self-assembles individual atoms, molecules or molecular clusters into structures to create materials and devices with new or vastly different properties (Nair *et al.*, 2010). The core of nanotechnology is, size and control. The smaller size, higher specific surface area and reactivity of nanofertilizers as compared to bulk fertilizers may increase the solubility, diffusion and availability to plants and hence enhance crop productivity. Nanotechnology has provided the feasibility of exploring nanoscale or nanostructured materials as fertilizer carrier or controlled-release vectors for building of the so-called smart fertilizers as new facilities to enhance the nutrient use efficiency and reduce the cost of environmental pollution (Chinnamuthu and Boopati, 2009).

History of nanotechnology

The concepts behind nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by American physicist Richard P. Feynman at an American Physical Society meeting at the California Institute of Technology (Caltech) on 29th December, 1959, long before the term nanotechnology was used.

Over a decade later, Professor Norio Taniguchi of the University of Tokyo coined the term nanotechnology in his explorations of ultra-precision machining.

The invention of scanning tunneling microscope in 1981 and the discovery of fullerene (C₆₀) in 1985 led to the emergence of nanotechnology.

American engineer, K. Eric Drexler developed and popularized the concept of Nanotechnology and founded the field of molecular nanotechnology in 1980.

Japanese physicist, Sumio Iijima invented Carbon nanotube in 1991.

Basic forms of attaining nanomaterials

Top-down

This approach usually involves breaking of big chunks of materials (physically or chemically) into smaller objects of desired shapes and sizes by either cutting or grinding, e.g. mechanical milling, ion implantation etc. These methods are usually not suitable for generating uniformly shaped nanoparticles. The nanoparticles produced may or may not have properties different from those of the bulk material they are produced.

Bottom-up

Also known as “self-assembly” involves building up of macro-sized complex systems by combining simple atomic level components material. The nanoparticles produced have properties different from those of the bulk material.

Physico-chemical properties of nanoparticles

Specific surface area

As the particle size decreases in nanoparticles, the proportion of atoms and molecules at the surface increases leading to a considerable enhancement in the specific surface area.

Surface charge

The surface charge density of nanoparticles is highly size-dependent and determines their dispersion/ stability and affects their mobility in the environment.

Surface charge for the spherical metal oxide nanoparticles showed a considerable increase in the surface charge of nanoparticles as the particle size decreases to diameters less than 10 nm.

Aggregation and agglomeration

Nanoparticles can readily form aggregates (loosely bound particles that are readily dispersed)/ agglomerates (rigidly bound) because they have relatively higher surface energy.

Dissolution

The solubility of solids depends on the surface tension, which is correlated with the specific surface area and also with particle size and as the surface tension of nanoparticles is large, their dissolution kinetics also increase.

Applications of nanotechnology (Anonymous, 2015b)

Energy storage

The development of effective energy producing, energy absorbing and energy storage products in more effective smaller devices like batteries, fuel cells and solar cells such as prototype batteries, nanorods and nanotubes, respectively, is possible through nanotechnology.

Defense and security

There are some nano-enabled approaches to counteract enemy threats such as missile attacks on satellites, stealth and camouflage coatings to protect battle tanks and air vehicles by misleading enemy, and reactive adsorbents for chemical warfare agents to protect humans. Nanosensors could be used for the detection of bombs, explosives, lethal toxic agents, etc. to protect our soldiers and human population from impending catastrophes likely to be caused by hostile action of our adversary or as an act of terrorism.

Metallurgy and materials

An approach based on nanosystems is promising for the production of fine grain

structured metals and high performance steel. In the past decade, progress in ferrous metallurgy has been characterized primarily by the development of nanotechnologies – in particular, the production of high quality materials used in electronics, optics, construction, the power industry, manufacturing, astronautics and elsewhere. The strength of the metal in the nanostate may be increased by a factor of 3-4, and the hardness by an order of magnitude, with improvement in the cold strength and great increase in the corrosion resistance.

Electronics

Nanotechnology could increase the capabilities of electronic devices while reducing their weight and power consumption such as improving display screens on electronics devices, increasing the density of memory chips, reducing the size of transistors used in integrated circuits.

Optical engineering and communication

Nanophotonics is the branch of nano-optics which deals with the optical methods to make lenses, microscopes, telescope and many other instruments by utilizing the property of light.

Biomedical and drug delivery

The current application of nanotechnology in medicine being developed involves employing nanoparticles to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to diseased cells, which allow direct treatment of those cells and reducing damage to healthy cells and allows for earlier detection of disease.

Agriculture and food

Nanotechnology in agriculture, results in higher crop yields and reduction in the use of

pesticides. Nanoparticles could be used for removing contaminants and detection of pathogens and also as nanosensors.

Clay nanocomposites are used to provide an impermeable barrier to gasses such as oxygen or carbon dioxide in lightweight bottles, cartons and packaging films. Storage bins are produced with silver nanoparticles embedded in the plastic.

The silver nanoparticles kill bacteria from any material that was previously stored in the bins, minimizing health risks from harmful bacteria.

Cosmetics and paints

Titanium and zinc oxide nanopowders are widely used in sunscreens and other creams and lotions. Nanotechnology can give both coatings and paints improved qualities making them of increased hardness, scratch, mould and bacteria resistance, easy clean and lasting.

Biotechnology

Nano-biotechnology refers to the use of nanotechnology to manipulate living organisms, as well as to enable the merging of biological and non-biological materials. This includes the use of nanotechnology to facilitate genetic engineering breeding programs, the incorporation of synthetic materials into biological organisms, and ultimately the creation of new life forms.

Textile

Nanotechnology improves fabric properties without increase in the weight, thickness or stiffness such as Ag-nanoparticles in fabric which kills bacteria making clothing odor-resistant.

Teflon and other polymer nanoscale fibres are used in some stain and wrinkle-resistant clothing.

Role of nanotechnology in agriculture

Soil studies

Nanotechnology helps in the characterization and weathering of soil minerals. Soils are complex mixtures of solids from millimeter to nanometer in particle size, which may contain moisture. It is now possible to understand these structures using techniques developed for nanotechnology such as Transmission Electron Microscopy and Atomic Force Microscopy. These techniques illustrate the organization of colloidal material in soils such as phyllosilicates, and humic acids and the discovery of new particles such as nanoparticles of iron oxides (Table 1a). High resolution transmission electron microscopy (HRTEM) is a unique and important technique, which provides information on local atomic structures by direct visualization of atom columns parallel to the electron beam. This can be useful for understanding inorganic materials in soils. Nanotechnology has also allowed atomic packing of phyllosilicates to be observed.

Precision farming

Precision farming has been a long-desired goal to maximize output (i.e. crop yields) while minimizing input (i.e. fertilizers, pesticides, herbicides, etc.) through monitoring environmental variables and applying targeted action. Although not fully implemented yet, tiny sensors and monitoring systems enabled by nanotechnology will allow enhanced productivity in agriculture by providing accurate information, thus helping farmers to make better decisions. There is also a potential for designing slow release fertilizers, which can release a specific nutrient solution suitable for an individual crop.

Nano-based products

Products such as nanofertilizers, nanofungicides and nanopesticides can be

produced through nanotechnology. Techniques at the nanoscale are also being applied in an attempt to enable the targeted delivery of pesticide applications. This includes the insertion of nanoscale active ingredients into pesticides and pesticide encapsulation.

Nanofertilizers can also be used as slow release fertilizers which will be made available to the plant of interest at appropriate time.

Crop improvement

Through the convergence of nano and bio techniques, it may be possible to improve the precision of genetic engineering breeding programs, thereby ensuring greater control in delivering new character traits to plant and crop varieties (ETC Group 2004). Researchers are attempting to use nanoparticles, nanofibres and nanocapsules to introduce foreign DNA and chemicals into cells (Friends of the Earth, 2008). Nanotechnology has also showed a new dimension in mutation research.

Nanofood

Potential applications include food that can alter its color, flavor, or nutrients to suit each consumer's preference or health requirements; filters that can take out toxins or modify flavors by sifting through certain molecules based on their shape instead of size; and packaging that can detect when its contents are spoiling, and change color to warn consumers.

There are containers being offered with coatings of nanosilver particles that can be used for storage of foods safely without spoilage. Nanocomposites are already available as packaging or in coatings on plastic bottles to control gas diffusion and prolong the lifetime of various products.

Water management

Nanoscale separation membranes can be used in low cost methods to produce potable water. Filters with aluminum oxide nanofibers which can remove viruses, bacteria, and protozoan cysts have been developed for water purification (Zhang 2003).

Photocatalysis degradation process has found popularity in the area of waste water treatment process as well as pesticide degradation. Rapid detection biosensors can also be used for detecting contaminants in water bodies.

Nanomaterials have also been used in the remediation of agricultural lands and groundwater contaminated by farm run-off.

Nanofertilizers

Nanofertilizers are nutrient carriers of nano-dimensions ranging from 30 to 40 nm (10^{-9} m or one-billionth of a meter) and capable of holding bountiful of nutrient ions due to their high surface area and release it slowly and steadily that commensurate with crop demand (Subramanian *et al.*, 2015).

Importance of nanofertilizers in plant nutrition

- High solubility and stability
- High effectiveness
- Time-controlled release
- Enhanced targeted activity with effective concentration
- Less eco-toxicity
- Safe, easy mode of delivery and disposal

They improve nutrient use efficiency (NUE), ion transport in soil-plant system and act as stimulating agents for plant growth and activate metabolic processes in plants.

Delivery systems of nanofertilizers

Nanoparticles have the potential to deliver nutrients to specific target sites in living systems. The loading of nutrients on the nanoparticles is usually done by (a) absorption on nanoparticles, (b) attachment on nanoparticles mediated by ligands, (c) encapsulation in nanoparticulate polymeric shell, (d) entrapment of polymeric nanoparticles, and (e) synthesis of nanoparticles composed of the nutrient itself (Fig. 1).

***In vitro* methods**

Aeroponics

This technique was first reported by Weathers and Zobel (1992). In this technique, plant roots are suspended in air and the nutrient solution is sprayed continuously. In this method, the gaseous environment around the roots can be controlled.

Hydroponics

This method was first introduced by Gericke (1937). The method is also commonly known as “solution culture” as the plants are grown with their roots immersed in a liquid nutrient solution. Volumes of nutrient solution, maintenance of oxygen demands, and pH are the factors that need attention while using this method of nutrient delivery. In this case, nutrient solution is flushed from one end and old solution is removed from the other end.

***In vivo* methods**

Soil application

Soil application is the most common method of nutrient supplement using chemical and organic fertilizers. The factors that need attention while choosing this method of fertilizer applications are how long the

fertilizer will last in the soil, soil texture, soil salinity, and plant sensitivities to salts, salt content, and pH of the amendment.

Foliar application

In this method, liquid fertilizers are directly sprayed onto leaves. It is generally used for the supply of trace elements. Uptake of iron, manganese, and copper may be more efficient with this method as compared to soil application where they get adsorbed on soil particles and hence are less available to root system (Taiz and Zeiger, 2010). As stomata and leaf epidermal cells are majorly involved in nutrient uptake, foliar application method can have agronomic advantage if used for nano-fertilizers.

Importance of Micronutrient Nanofertilizers

Zinc, iron, manganese and copper have become yield-limiting factors and are partly responsible for low food nutrition.

They are often added to the N, P, and K fertilizers at low rates ($<5 \text{ mgL}^{-1}$) as soluble salts for crop uptake. Micronutrients in these composite fertilizers usually provide enough nutrients and cause little environmental risks. However, plant-availability of the applied micronutrients may become low.

Once fertilizer micronutrients are added to soils, the trace elements react rapidly to form chemical precipitates, or interact with clay colloids and the organo-mineral matrix of soils, rendering them unavailable for synchronized uptake by plants during crop growth. Thus, the crop fertilizer-micronutrient use efficiency (MUE) is low, $<5\%$. In high rainfall areas, they are significantly lost due to leaching.

Micronutrient-containing nanoparticles could potentially improve plant growth by supplying

nutrients (Table 4). Nanofertilizers are used as smart delivery systems” in order to improve fertilizer formulation by minimizing nutrient loss and increased uptake in plant cell (Naderi and Danesh Shahraki, 2013). These “nano-fertilizers” have high surface area, sorption capacity, and controlled-release kinetics to targeted sites attributing them as smart delivery system.

Novel technologies for fertilizer micronutrients

Nanotechnology has progressively moved away from the experimental into the practical areas. The development of slow/controlled release fertilizers, on the basis of nanotechnology has become critically important for promoting the development of environment friendly and sustainable agriculture. Indeed, nanotechnology has provided the feasibility of exploiting nanoscale or nanostructured materials as fertilizer carriers or controlled-release vectors for building of so-called “smart fertilizer” as new facilities to enhance nutrient use efficiency and reduce costs of environmental protection (Chinnamuthu and Boopathi, 2009).

Nanoencapsulated micronutrients

As nutrient delivery systems, mesoporous aluminosilicates appear to have the potential for delivering micronutrients to soils or plant leaves as they have been used as carriers of nanoparticles (NPs) of CuO (Huo *et al.*, 2014) which may help to reduce the rate of release of micronutrients to plants.

Hollow core shell nanomaterials and nanostructures have become an important research area due to their potential applications in the field of agriculture which could serve as an excellent plant growth medium for supplying plant roots with additional nutrient ions and the nano-

formulated material release nutrients more slowly, satisfying plant root demand through the process of dissolution and ion exchange reactions.

Microcapsules have high loading efficiency and majority of the added nutrient remains encapsulated. Because the rates of loading in microcapsules are much higher, smaller amounts of carrier material per amount of nutrient units are needed.

Nanomaterials (NMs) and nanoparticles (NPs)

The physico-chemical properties of NPs can be drastically modified compared to the bulk material (Nel *et al.*, 2006). Engineered nanomaterials are semiconductor, metal and metal oxide-based materials- nanozinc, nanoiron and nanoscale metal oxides like ZnO, Fe₃O₄, CuO, and composites combining NMs with other NMs or with larger bulk-type materials (Lin and Xing, 2007). These composites present different morphologies such as spheres, tubes, rods and prisms (Ju-Nam and Lead, 2008).

Nanodevices

A nanodevice can be simply defined as any manufactured device whose dimensions are on the scale of 1-100 nm and whose properties exploit the unique properties of nanoscale materials. Microbial-based sensors have been used in the diagnosis of micronutrient deficiency and toxicity in soils. For instance, a genetically-modified microbial sensor was constructed and used to evaluate the immobilization and bioavailability of Zn in different soils (Maderova and Paton, 2013).

Nanofertilizers will combine nanodevices in order to synchronize the release of fertilizers with their uptake by crops, so preventing undesirable nutrient losses to soil, water and

air through direct internalization by crops, and avoiding the interaction of nutrients with soil, microorganisms, water, and air (DeRosa *et al.*, 2010).

Uptake, translocation and fate of nano-fertilizers in plants

The uptake and fate of nano-fertilizers in plant is a growing field of research interest. The uptake, translocation, and accumulation of nanoparticles depend on the plant species, age, growth environment, and the physicochemical property, functionalization, stability, and the mode of delivery of nanoparticles.

The entry of nanoparticles through the cell wall depends on the pore diameter of the cell wall (5–20 nm) (Fleischer *et al.*, 1999). Hence, nanoparticles or nanoparticle aggregates with diameter less than the pore size of plant cell wall could easily enter through the cell wall and reach up to the plasma membrane (Navarro *et al.*, 2008). Functionalized nanoparticles facilitate the enlargement of pore size or induction of new cell wall pore to enhance the uptake of nanoparticles. Several reports have discussed the uptake of nanoparticles into plant cell via binding to carrier proteins through aquaporin, ion channels, or endocytosis (Nair *et al.*, 2010). Further, nanoparticles can also be transported into the plant by forming complexes with membrane transporters or root exudates (Kurepa *et al.*, 2010). Various other studies reported that nanoparticles could enter through stomata or the base of trichome in leaf (Uzu *et al.*, 2010).

After entering the cell, nanoparticles can transport apoplastically or symplastically. They may be transported via plasmodesmata from one cell to the other (Rico *et al.*, 2011). In the cytoplasm, nanoparticles approach to different cytoplasmic organelles and interfere with different metabolic processes of the cell (Moore 2006).

Micronutrient nanofertilizers

Iron (Fe)

It is absorbed by roots as Fe⁺² and Fe⁺³. The sufficiency range of Fe in plant tissue is between 50 and 250 ppm.

Functions

Fe is a structural component of porphyrin molecules: cytochrome, heme protein, Fe-S protein and leghaemoglobin. These substances are involved in oxidation-reduction reactions in respiration and photosynthesis.

Fe is a catalyst to chlorophyll biosynthesis. It is a constituent of nitrogenase, the enzyme essential for N₂ fixation by N-fixing microorganisms.

Deficiency symptoms

Generally, when tissue Fe content <50 ppm, deficiency is likely to occur. Fe deficiency symptoms appear first in the young leaves, because Fe is not mobile in the plant.

- Young leaves develop interveinal chlorosis, progressing rapidly over the entire leaf.
- In severe cases, leaves turn entirely white and necrotic.

Case studies

Ghafariyan *et al.*, (2013) reported that low concentrations of superparamagnetic Fe-NPs significantly increased the chlorophyll contents in sub-apical leaves of soybeans in a greenhouse test under hydroponic conditions, suggesting that soybean could use this type of Fe-NPs as source of Fe and reduce chlorotic symptoms of Fe deficiency (Fig. 2).

The impact of using Fe-NPs was similar to that of an effective Fe source for the plants — Fe-EDTA at concentrations b 45 mg L⁻¹ as Fe.

Delfani *et al.*, (2014) reported that a foliar application of 500 mg L⁻¹ Fe-NPs to black-eyed peas significantly increased the number of pods per plant (by 47%), weight of 1000-seeds (by 7%), Fe content in leaves (by 34%), and chlorophyll content (by 10%) over those of the controls. Application of Fe-NPs also improved crop performance more than that by application of a regular Fe salt. The abovementioned parameters were increased by 28%, 4%, 45%, and 12%, respectively, under the Fe-NP treatment compared with these under treatment with a Fe salt. In addition, Fe-NPs significantly improved the beneficial effect of another nanofertilizer (Mg- NPs) on black-eyed peas.

Sheykhbaglou *et al.*, 2010 reported that from a controlled treatment and 4 levels of nano-iron oxide application (0.25, 0.5, 0.75 and 1 g L⁻¹), an application of 0.75 g L⁻¹ causes increase in dry pod and dry leaf weight of soybean on clay soil.

Zinc (Zn)

It is absorbed by roots as a cation (Zn⁺²) and as a component of synthetic and natural organic complexes. Its concentration in plants ranges between 25 and 150 ppm.

Functions

Zinc is important for the synthesis of tryptophane, a component of some proteins and a compound needed for the production of growth hormones (auxins) such as indoleacetic acid and gibberillic acid.

It is involved in enzyme systems and metabolic reactions.

It is necessary for the production of

chlorophyll and carbohydrates.

Deficiency symptoms

Deficiencies of zinc are usually associated with concentrations of less than 10 to 20 ppm. First symptoms of deficiency appear on the younger leaves. The symptoms are:

- Light green, yellow, or white areas between leaf veins.
- Eventually tissue necrosis in chlorotic leaf areas occurs.
- Shortening of stem or stalk internodes, resulting in bushy, rosette leaves.
- Premature foliage loss.
- There is malformation of fruit, often with little or no yield.

Case studies

ZnO-NPs have been one of the most widely used metal oxide NPs in the industry for several decades. Using the plant agar method, Mahajan et al (2011) observed that ZnO-NPs enhanced growth of mung bean and chickpea (*Cicer arietinum*) seedlings at low concentrations, for the mung bean seedlings, the best growth response for root (a 42% increase in length or 41% in biomass) and shoot (98% in length or 76% in biomass) was observed at a concentration of 20 mg L⁻¹ over those of the control; for the chickpea seedlings, concentration of 1 mg L⁻¹ caused significant increases in root (53% in length or 37% in biomass) and shoot (6% in length or 27% in biomass) growth as compared to those of the control.

However, decline in growth rates of roots and shoots were observed beyond these optimal concentrations (Fig. 4).

Lin and Xing (2007) reported that application of 2 mg L⁻¹ of ZnO-NPs enhanced root elongation of germinated radish (*Raphanus sativus*) and rape (*Brassica napus*) seeds over

those of the control (deionized or DI water only).

Prasad *et al.*, 2012 reported that application of 1000 ppm nanoscale ZnO to peanut recorded significant germination and seedling vigour index (Fig. 5).

Nanoscale ZnO at 1000 ppm also proved to be effective in improving root volume and root dry weight as well as pod yield and plant height, shelling percent and other biometric parameters (Fig. 6).

Yuvaraj and Subramanian (2014) reported that zeo zinc applied pot increased the chlorophyll SPAD readings by 48.55 and 42.36 followed by manganese core shell, 46.74 and 37.43, carbon sphere 46.45 and 36.28, ZnO 45.10 and 34.50, ZnSO₄ 45.70 and 39.16 in submerged and aerobic condition respectively and IAA oxidase activities by 139.7 and 122.6 followed by manganese core shell 122.5 and 118.4, carbon sphere 120.8 and 115.7, zinc oxide 118.5 and 112.1, ZnSO₄ 114.3 and 110.5 (Fig. 7).

Except for a few of these articles cited above, almost all other reports regarding effects of Zn-NPs on organisms claimed that Zn-NPs were inhibitory/toxic to plants/crops. Boonyanitipong *et al.*, 2011 reported that nano-ZnO showed toxicity on rice roots which was apparent from root length and number of roots. Higher concentration show reduction effect on root length started from 100 mg L⁻¹ and greatly inhibited at concentrations 500 and 1000 mgL⁻¹, with longer soaking time inducing inhibition of root growth (Fig. 3).

Copper (Cu)

Plants absorb Cu⁺² and as a component of either natural or synthetic organic complexes. Normal Cu concentration in plant tissue ranges between 5 to 20 ppm.

Functions

- Lignin is a constituent in cell walls that imparts strength and rigidity, essential for erect stature of plants. Several enzymes (polyphenol oxidase and diamine oxidase) important to synthesis of lignin contain Cu.
- Cu is part of the enzyme cytochrome oxidase that catalyzes electron transfer in the transfer of electrons in respiration.
- Important in carbohydrate and lipid metabolism.

Deficiency symptoms

Deficiencies of Cu are usually associated with concentration of less than 5 ppm. Symptoms of deficiency first appear on the young leaves.

- Young leaves become yellow and stunted.
- In advanced stages, necrosis along leaf tips and edge appears
- Lodging, wilting and increased incidence of disease is observed due to reduced lignification with low Cu.

Case studies

A 3-day incubation study using a type of waterweed (*Elodea. densa planch*) indicated that low concentrations (<0.25 mg L⁻¹ as Cu) of Cu-NPs stimulated plant photosynthesis rate by 35% compared with that of the control (without Cu) (Nekrasova *et al.*, 2011).

Shah and Belozerova (2009) reported that soil amended with metallic Cu-NPs (130 and 600 mg kg⁻¹) significantly increased 15-day lettuce seedling growth by 40% and 91%, respectively.

Buu *et al.*, (2013) reported that application of nanometal Cu powder dose of 0.08 g ha⁻¹ increases chlorophyll content and other basic growth parameters and crop yield as compared to other doses of 0.20 g ha⁻¹ and 0.32 g ha⁻¹ (Table 2 and Fig. 8).

Table.1 Methods of nanoparticle preparations and applications			
Nanomaterial	Synthesis method	Remarks	Reference
Inorganic AgO, TiO₂, ZnO, CeO₂, Fe₂O₃, FePd, Fe–Ni Silica	Physical: Arc-discharge, high energy ball milling, laser pyrolysis Chemical: electrochemical, reverse precipitation	Delivery of biomolecules, biosensors, pesticide degradation	Oskam 2006
Clay Montmorillonite layered double hydroxides	Physical: exfoliation co-precipitation	Delivery of pesticides, fertilizers, plant growth promoting factors	Lakrainid <i>et al.</i> , 2000
Organic Carbon nanotubes	Physical: Arc-discharge, laser ablation Chemical: sonochemistry,	Biocatalysts, sensing Delivery of DNA and pesticides	Yu <i>et al.</i> , 2009
Polymeric <i>Natural</i> Cellulose, Starch, Gelatin, Albumin, Chitin, Chitosan <i>Synthetic</i> Dendrimers Polyethylene oxide Polyethylene glycol Polyalklycyanoacrylates	Chemical: suspension, emulsion, dispersion -precipitation	Biocompatible, biodegradable, drug delivery, delivery of DNA/RNA Delivery of diagnostic agents, pesticides, delivery of DNA/RNA	Liu <i>et al.</i> , 2008

Table.1a Effect of various concentrations of nano-iron oxide on some agronomic traits in soybean			
Nano-iron oxide (g L ⁻¹)	Pot dry weight (g)	Leaf+pod dry weight (g)	Yield (g m ⁻²)
0	0.41	32.35	60.94
0.25	0.42	42.35	76.78
0.5	0.44	42.45	90.22
0.75	0.48	45.84	88.33
1	0.45	42.32	80.39

Table.2 Basic growth parameters and crop yield of nanometal-treated soybean with 0.08g ha⁻¹ Nanometal Cu Dose

Parameters	Control	Cu
Chlorophyll content	27.0 ± 0.9	29.1 ± 0.6
Number of nodules/root	13.1 ± 1.6	19.7 ± 4.4
Number of pods/plant	76.2 ± 16.4	81.1 ± 18.1
Weight of 1000 grains (g)	162.2 ± 3.1	169.2 ± 2.8
Crop yield (ton/ha)	2.33 ± 0.06	2.59 ± 0.08

Table.3 Nutritional and yield responses of rice to Mn hollow core shell loaded Zn

Parameters	Submerged		Aerobic	
	Control	Core shell	Control	Core shell
Shoot zinc content (mg kg⁻¹)	30.42	36.73	27.87	32.52 NS
Grain yield (g pot⁻¹)	150.2	237.8	127.2	182.8
Straw yield (g pot⁻¹)	336.8	359.2	210.8	290.3
Total yield (g pot⁻¹)	550.9	597.0	446.2	473.1

Table.4 Nanoparticles for better seed germination and plant growth

Nanoparticle	Influence On Plant Growth	Reference
Nanoscale titanium dioxide (TiO₂)	Promotes photosynthesis and growth of spinach	Yang <i>et al.</i> , 2006
Nano-SiO₂ and TiO₂ Mixture	Hastens germination and growth in soybean	Lu <i>et al.</i> , 2002
1000 ppm nano-ZnO (25 nm)	Results highest chlorophyll content, higher seedling vigour, early vegetative growth and significant pod yield of peanut	Prasad <i>et al.</i> , 2012
Nano-Si	Improves salinity stress on tomato seed germination	Haghighi <i>et al.</i> , 2012
Carbon nanotubes (CNTs)	Enhance root growth of onion and cucumber	Yang and Watts, 2005

Table.5 Possible risks of nanomaterials	
Nanomaterials	Possible Risks
Carbon nanomaterials, silica nanoparticle	Pulmonary inflammation, granulomas, and fibrosis
Carbon, silver and gold nanomaterials	Distribution into other organs including the central nervous system
Quantum dots, carbon and TiO ₂ nanoparticles	Skin penetration
MnO ₂ , TiO ₂ , and carbon nanoparticles	May enter brain through nasal epithelium olfactory neurons
TiO ₂ , Al ₂ O ₃ , carbon black, Co, and Ni nanoparticles	May be more toxic than micron sized particles

Figure.1 Schematic representation of different nanodevices for delivery of pesticides, fertilizers or nucleic acids (a) adsorption on nanoparticle; (b) attachment on nanoparticle mediated by different ligands; (c) encapsulation in nanoparticulate polymeric shell; (d) entrapment in polymeric nanoparticle

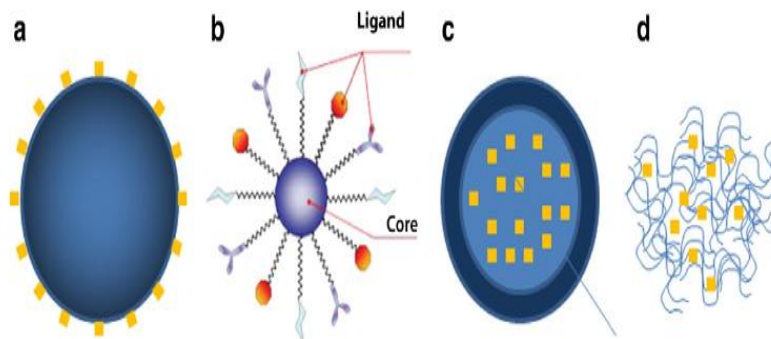


Figure.2 Iron foliar application effect on leaf chlorophyll content of black-eyed pea

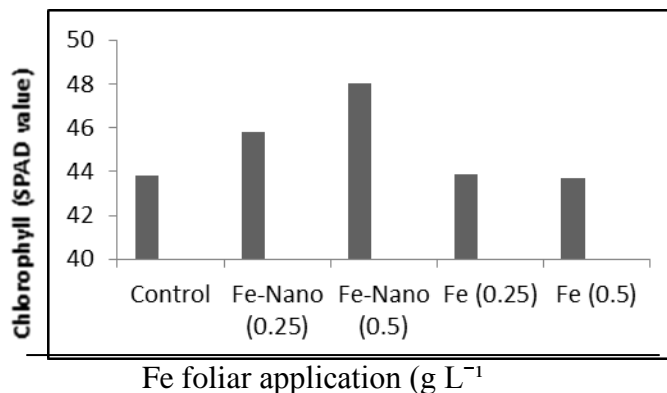


Figure.3 Soil Zn deficiency in Indian soils (Alloway, 2008b)

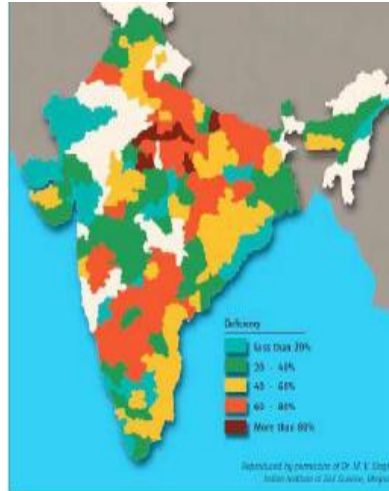


Figure.4 Response of roots and shoots of (a) mung and (b) gram seedlings to nano-ZnO doses. Zhao *et al.*, (2013) reported that application of 400 and 800 mg kg⁻¹ ZnO-NPs to a soil mixture enhanced cucumber (*Cucumis sativus*) growth. The results showed that the plant root dry mass was 1.1 and 1.6 times higher than those of the control although the dry weight of the fruits was slightly increased by only 0.6 and 6% compared to those of the control. Application of ZnO-NPs also increased the contents of starch (by 1.1–1.6 times), glutelin (by 0.9–2 times), and Zn (by 1.7–2.5 times) in the harvested cucumber fruits. Further, there were no adverse effects of ZnO-NPs observed on any growth-related parameters

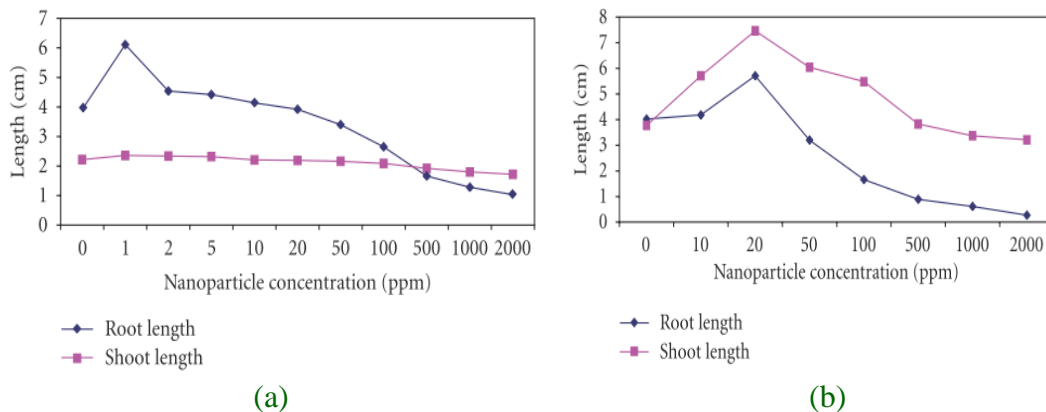


Figure.5 Seeds showing differences in germination and root growth A) after three days and B) nine days after the treatment

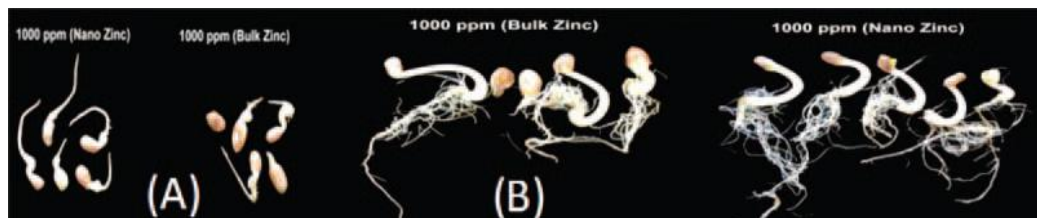


Figure.6 A) Higher root growth of peanut plant after nanoscale ZnO treatment (1000 ppm). The plants were uprooted after 110 days. B) Pot culture experiment showing higher plant growth after ZnO treatment (1000 ppm), after 110 days

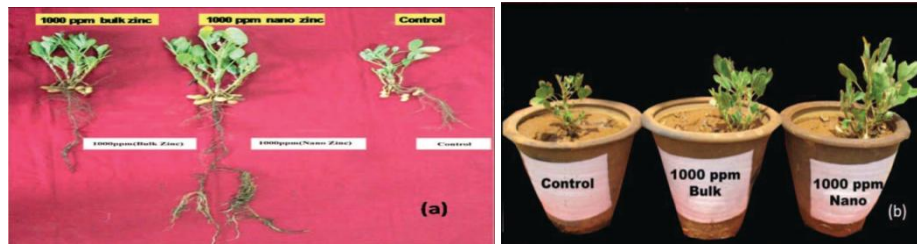


Figure.7 Effect of nanoscale ZnO (N) and bulk ZnSO₄ (B) concentrations on peanut plant root, stem growth and pod yield



Figure.8 Influence of nanometal Cu powder doses on germination of nanometal-treated soybean seeds

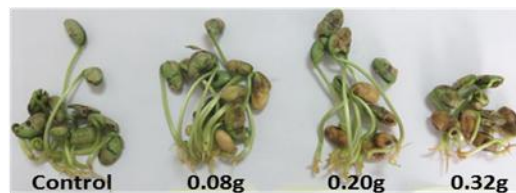
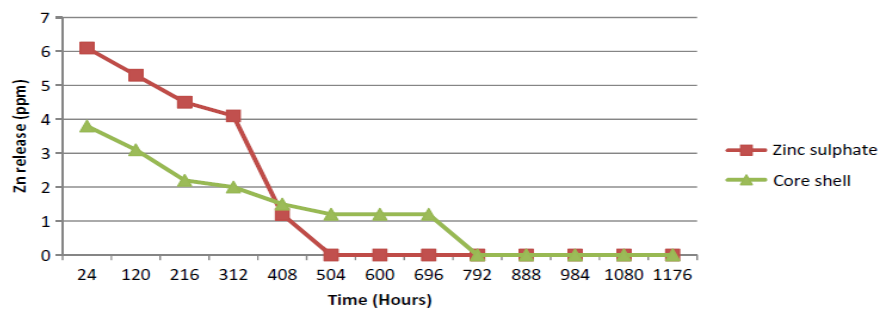


Figure.9 Release pattern of Zn from ZnSO₄ and Mn hollow core shell



Manganese (mn)

Plants absorb Mn^{+2} and low- molecular-weight organically complexed Mn. Its concentration in plants typically ranges from 20 to 500 ppm.

Functions

- Activates several important metabolic reactions.
- Aids in chlorophyll synthesis in photosynthesis because it is essential to electron transfer through chlorophyll to reduce CO_2 to carbohydrate and produce O_2 from H_2O .
- Accelerates germination and maturity.
- It activates several enzymes that synthesize several amino acids and phenols important to lignin production.
- Increases availability of P and Ca.

Deficiency symptoms

Mn deficient plants contain < 15 to 20 ppm Mn. Mn is immobile in the plant, so younger leaves initially exhibit deficiency symptoms.

- There is chlorosis of younger leaves and slower growth.
- Mn deficiency produces interveinal chlorosis in most crops.

Case studies

Pradhan *et al.*, (2013) reported that metallic Mn-NPs were a better micronutrient source of Mn than the commercially-available $MnSO_4$ salt. Pradhan and colleagues observed that Mn-NPs enhanced growth of mung bean (*Vigna radiata*) and augmented its photosynthesis. The mung bean seedlings were incubated for 15 days in an inert media (perlite) with Hoagland solution in growth chambers. Application of Mn-NPs at 0.05 mg L^{-1} produced the maximum growth enhancement over that of the controls

(without Mn) in root length (by 52%), shoot length (by 38%), number of rootlets (by 71%), fresh biomass (by 38%), and dry biomass (by 100%). In comparison with seedlings treated with $MnSO_4$ salt, these parameters were enhanced with the use of Mn-NP by 2%, 10%, 28%, 8%, and 100%, respectively. Interestingly, application of $MnSO_4$ exhibited an inhibitory effect on the plant growth at concentration of 1 mg L^{-1} while the response was still positive at this level with the application of Mn-NPs.

Yuvaraj and Subramanian (2015) reported that 0.5 mg manganese hollow core shell loaded with $ZnSO_4$ delivered to the rhizosphere increased the grain and straw yields by 30 and 27%, respectively of rice grown under both submerged and aerobic systems (Table 3).

Biozar nanofertilizer in Iran

Biozar Nano-Fertilizer has been designed and produced in Iran to improve the fertility of soils and various agricultural plants. Produced by the knowledge-based Fanavar Nano-Pazhooheh Markazi Company Biozar Nano-Fertilizer (2015), it has been made from various useful and local microorganisms. The fertilizer is a combination of organic materials, micronutrients (iron, zinc and manganese nanoparticles), macromolecules and substances that increase soil fertility. In addition, the bacteria used in the fertilizer are able to produce growth hormones. It reduces the consumption of nitrogen and phosphate fertilizers.

The product can be used in all crop and garden products. The company claims that Biozar Nano-Fertilizer decreases the consumption of chemical fertilizers containing nitrogen or phosphate by 50-80 percent and it increases productivity by up to 10-40 percent with higher quality.

According to the company's CEO, about 2-3 kilos of biologic fertilizer is currently used per hectare. This is very small compared with chemical fertilizers, which is about 100-300 kilos per hectare. The application of the product decreases environmental hazards.

Nanotechnology and risk

In a publication in November 2004, the ETC (Action Group on Erosion, Technology and Concentration) stated that "the merger of nanotech and biotech has unknown consequences for health, biodiversity and the environment". Since there is no standardization for the use and testing of nanotechnology, products incorporating the nanomaterials are being produced without check. The ability for these materials to infiltrate the human body is well known, but there is really no information on the effects that they may have (Table 5).

The use of nanotechnology in agriculture is significantly important as it directly affects humans (Bouwmeester *et al.*, 2009). Nanoparticle fertilizers may contaminate the soils, waterways and toxins may be released to the environments. Nano-fertilizers enable nanoparticles to enter in the food chain allowing their distribution in every organism related to the food chain. As all substances, from arsenic to table salt, are toxic to plants, animals, or humans at some exposure level, this would not limit their use in various applications which are designed keeping in mind the critical exposure concentration. As discussed in most of the studies regarding the use of nanoparticles for promoting growth of plants with a focus on using lower concentrations of nanoparticles, it can be argued that it will pose insignificant health and environmental damage.

In conclusion, increasing agricultural productivity is necessary to meet the ever increasing food demand, but keeping in mind

the damage to the ecosystem, new environmental friendly approaches need to be considered. With the current application and advancements soon to come, nanotechnology will have a great impact on agriculture science. Nanoscale or nanostructured materials as fertilizer carrier or controlled-release vectors for building of the so-called smart fertilizers can enhance the nutrient use efficiency and reduce the cost of environmental pollution. Nano-fertilizers can precisely release their active ingredients in responding to environmental triggers and biological demands. Both in vitro and in vivo methods can be used for nanofertilizer delivery to the plants. However, the uptake, translocation, and fate of nanoparticles in plant system are largely unknown.

Micronutrient research should focus on enhancing the bioavailability of these fertilizers to address leaching or soil fixation issues. Additional research on the toxicity of a newly developed nanofertilizer should be conducted. There should be collaboration among developed and developing countries, public and private sectors, research institutions and international organizations to contribute more efficiently towards the new agricultural production technology. Any breakthrough on new crop-production stimulating mechanisms other than providing nutrients would be a milestone not only in nanotechnology research, but also in ushering another new "Green Revolution".

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