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Review

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Nanofertilizer for Precision and Sustainable Agriculture: Current State and Future Perspectives

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ABSTRACT

The increasing food demand due to the rising global population has prompted the large-scale use of fertilizers. Due to resource constraints and low use efficiency of fertilizers, the cost to the farmer is increasing dramatically. Nanotechnology offers a great potential to tailor fertilizer production with the desired chemical composition, improve the nutrient use efficiency that may reduce environmental impact and boost the plant productivity. Furthermore, controlled release and targeted delivery of nanoscale active ingredients can realize the potential of sustainable and precision agriculture. A review of nanotechnology-based smart and precision agriculture is discussed in this paper. Scientific gaps to be overcome, and fundamental questions to be answered for safe and effective development and deployment of nanotechnology are addressed.

KEYWORDS: *Nanofertilizer, nanotechnology, smart and precision agriculture, nanoparticle aerosol technology, plant-nutrition, agrochemicals*

1. INTRODUCTION

The world's agricultural zones are facing a wide spectrum of challenges such as stagnation in crop yields, low nutrient use efficiency, declining soil organic matter, multi-nutrient deficiencies, shrinking arable land, water availability, and a shortage of labor due to an exodus of people from farming.[1, 2] Data compiled by the UN's Food and Agriculture Organization indicates that depletion and degradation of land and water pose serious challenges to producing enough food and other agricultural products to sustain livelihoods and meet the needs of the world's ever increasing population.[3] Nanotechnology, designing ultra-small particles having exceptional properties, such as surface area to volume size ratio, and enhanced optoelectronic and physicochemical properties, compared to their bulk counterparts,[4] is now emerging as a promising strategy to promote plant growth and productivity.[5-8] This idea is part of the evolving science of precision agriculture, in which farmers make use of technology to efficiently utilize water, fertilizer, and other inputs. Precision farming makes agriculture more sustainable by reducing waste and energy demand.[9] In agriculture, nanotechnology and its derivative outcomes are being evaluated for various applications such as nanoscale sensors for sensing nutrients, pesticides, and contamination; post-harvest processing of agriculture products for improved shelf life; nanoscale pesticides for effective control of plant diseases; smart and target delivery of biomolecules and nutrients; agronomic fortifications; water purification, nutrient recovery, smart fertilizers and their delivery.[4, 5, 8, 10-14] In this review, we focused on nanotechnology for smart fertilizers, herein termed "nanofertilizers".

Fertilizers provide nutrients needed by the plants for optimal productivity. Farmers typically apply fertilizers through the soil, either by surface broadcasting, sub-surface placement, or mixing with irrigation water. However, a large portion of fertilizers applied using these methods is lost to the atmosphere or surface water bodies, thereby polluting ecosystems.[15, 16] For example, excess nitrogen is lost through volatilization as NH_3 or emission as N_2O or NO, or through NO_3 leaching or runoff to water bodies. In contrast, excess phosphorus becomes "fixed" in soil, where it forms chemical bonds with other elements such as Ca-P, Mg-P, Al-P, Fe-P and Zn-P, and become unavailable for uptake by the plants. Eventually, rain washes the nitrogen and phosphorus compounds into waterways such as rivers, lakes and the sea, where they can cause serious pollution problems.[16] Fertilizer use worldwide is increasing, along with global population growth. Currently, farmers are using nearly 85 percent of the world's total mined phosphorus as fertilizer, although the plants can uptake only about 42 percent of the applied phosphorus.[17] If this scenario persists, the world's supply of phosphorus could run out within the next 80 years, affecting agricultural productivity.[17, 18] In the United States, trends from

1978 to 1987 suggest that metropolitan-influenced counties experienced a decline in crop-land of 77%.[19, 20] To meet the food demand, farmers apply more chemical fertilizers, which eventually affects soil and environmental health, and reduces natural resources. Some crops can be grown under artificial conditions using hydroponic techniques, but the cost (in energy and dollars) is approximately 10 times that of conventional agriculture. Such systems are neither affordable nor sustainable for the future.[21] Therefore, it is necessary to develop sustainable strategies that result in more nutritious and enhanced crop production by minimizing the use of resources and fertilizers. In contrast to conventional fertilizer use, which involves 80-140 or more kilograms of inputs per hectare under intensive production systems, nanotechnology focuses on the use of smaller quantities. Moreover, nanoscale fertilizer may have potential to minimize nutrient losses through leaching, and avoid rapid changes in their chemical nature, thus enhancing nutrient use efficiency and addressing fertilizer environmental concerns.

It is worth noting that the definition of "nanofertilizer" is debatable. In the literature related to nanotechnology application in agriculture, nanofertilizer is used for both materials of a physical diameter between 1 and 100 nm in at least one dimension (e.g., ZnO nanoparticles), and those existing at the bulk scale, with more than 100 nm in size, but that have been modified with nanoscale materials (e.g., bulk fertilizer coated with nanoparticles). Therefore, in this review, the term "nanofertilizer" refers to true nanomaterials and nano-enabled bulk materials used as fertilizers. Due to their unique properties, nanoparticles may influence plant's metabolic activities to different degrees, compared to conventional materials, and have the potential to mobilize native nutrients such as phosphorus in the rhizosphere.[22, 23] A comparative schematic of fertilization strategies attempted in the past, and a hypothesized nanotechnology-based agri-input is illustrated in **Figure 1**.

In the following sections, recent literature relevant to nanoscale material/nanoparticles/nanocomposites used for plant nutrition as nanofertilizers is reviewed. The discussion is presented systematically, to allow a better understanding of both fundamental and applied aspects of nanofertilizers for sustainable and precision agriculture.

2. NANOFERTILIZERS

Nanofertilizers are nutrient fertilizers composed, in whole or part, of nanostructured formulation(s) that can be delivered to the plants, allowing efficient uptake or slow release of active ingredients. Conventional bulk fertilizers have low plant uptake efficiencies, and thus, larger amounts have to be applied. Two main challenges of the low nutrient uptake efficiency for nitrogen and phosphorus-based fertilizers are the rapid changes into chemical forms that the plants do not take up, and runoff, leaching, or atmospheric losses. The resultant effects are emission of harmful greenhouse gases (such as certain oxides of nitrogen), and eutrophication, with negative consequences for soil and environmental health. Therefore, it is critical to develop smart fertilizers that are more readily uptake by the plants. Nanotechnology is one possible route for sustainably and precisely attaining this objective, for which reason scientists are actively researching a range of metal and metal oxide nanoparticles for use in plant science and agriculture.[5] However, environmental health and safety aspects of nanotechnology should also be considered, and it is crucial to determine the toxicity/biocompatibility of nanofertilizers.[24-27] Since nanoscale particles are smaller in dimension compared to bulk particles, the plants can absorb them with different dynamics than bulk particles or ionic salts, which presents an added advantage.[26,28,29,30]

A number of inorganic, organic, and composite nanomaterials have been tested on various the plants, to assess their potential impact on plant growth, development, and productivity. A brief summary of the nanoparticles used as nutrients/fertilizers and validated on agriculturally important crops is presented in **Table 1**. In order to be on focus, we have limited this article to the technical aspects of nanofertilizers and their application. For information regarding aspects of the commercial and socioeconomic impacts of nanofertilizers, readers are directed to a Perspective recently published in this journal.[12] Since, the effects of nanoscale materials and corresponding plant responses depend on various factors related to nanoscale properties, soil, and environment, the table included the information on the type of nanoparticles, nanoscale property, mode of nanoparticle delivery, tested plants, and studied responses. In the following sub-sections, we discuss specific examples of nanoparticles used as nanofertilizers or nano-nutrients.

2.1. Nitrogen. Nitrogen (N) is one of the key nutrients, categorized as primary macronutrient; it is, however, deficient in most agriculture soils. Although, the atmosphere consists of more than 78% of N, plants cannot use N in its atmospheric form. The plant needs specific chemical forms of N namely, nitrate and ammonium. All commercial N fertilizer manufacturing begins with a source of hydrogen gas and atmospheric N that are reacted to form ammonia, in a reaction known as Haber-Bosch process.[31] Nitrogen fertilizers clearly make a very essential contribution to maintaining adequate supply of nutritious food by influencing plant growth and development.[31] The N in urea, a commercial N fertilizer, vanishes approximately 75% soon after application, due to rapid volatilization and leaching. The current N fertilizers, therefore face the problem of low utilization efficiency (<20%), whereby loss of N in the environment causes eutrophication and greenhouse gas increase.[32] Recently, a group from the Sri Lankan Institute of Nanotechnology developed an advanced N nanofertilizer using urea coated hydroxyapatite nanoparticles (rod-shaped structures, average aspect ratio 10), for targeted delivery and slow release of N.[33] Urea - hydroxyapatite nanoparticles were selected due to their chemical compatibility, and rich N and phosphorus sources, respectively. The nanohybrid of urea-modified hydroxyapatite, synthesized with N weight of 40%, releases N 12 times slower than conventional urea. Moreover, field trials with rice showed that slow release properties of the nanohybrid resulted in better yield at a 50% lower concentration of urea (**Figure 2)**. A subsequent goal would, therefore, to be optimize the nanoscale N fertilizer to maximize its potential in a range of arable soil types by following quantitative –structural area relationship models.[11]

2.2. Phosphorus. Along with N, phosphorus (P) is essential to all living organisms. More than 90% of globally mined P is used for food production. Rock phosphate (RP) is the starting raw material used to manufacture most commercial phosphate fertilizers available in the market. Global RP reserves are very limited, and according to the geological estimates, will last only the next 100 years. However, the consumption rate of P fertilizer will not remain at the current level, due to increased global population. Therefore, the price of P fertilizer is consistently going up, and market availability and accessibility for P fertilizer are stepping down. According to a global P research initiative, RP prices spiked 800 percent compared to the previous decade (*http://phosphorusfutures.net/*). The major concerns for P fertilizers are low use or uptake efficiency, and rapid conversion of the plant-usable P into less available forms. Additionally, there are environmental concerns of eutrophication (increased N and P levels in water).[34, 35] In the past, different approaches, such as phosphorus-solubilizing bacteria, phosphatase- and phytase-producing fungi, organic acid-producing microorganisms, and vesicular-arbuscular mycorrhiza, have been investigated for enhancing P uptake. However, the success of phosphorus-mobilizing microorganisms has been limited due to low soil organic carbon, which limits the supply of energy to P-mobilizing microorganisms, and high evaporation of water from surface soils. This adversely affects the survivability of nutrient mobilizing microorganisms.[36]

Nanotechnology and nanoscience researchers are looking for opportunities that enhance P uptake efficiency, slow release of the fertilizer, long-term stability in plant-usable P forms, and mobilization of native P to plants. Tarafdar et al.,[37] synthesized fungal-mediated P nanoparticles using tri-calcium phosphate as a precursor salt. They confirmed using electron dispersive spectroscopy that 62% (by atom) was P, in 28 nm size. Subsequently, Liu and Lal[38] synthesized carboxy-methyl cellulose (CMC)-stabilized hydroxyapatite nanoparticles of 16 nm, and investigated their effect on soybean. In a greenhouse experiment, the authors applied these nanoparticles in soil, and found that treated soybean increased phenological growth rate by 33% **(Figure 3 A),** and yield by 18%, relative to plants treated with a conventional P fertilizer. Mechanistically, the hydroxyapatite nanoparticles have relatively weaker interactions with soil components than charged ions of conventional P fertilizer, thus facilitating P uptake by the plant, relative to conventional P.[38] However, further studies will be required to understand the uptake efficiency with time under various agricultural soil types having variations in pH, ionic state, organic carbon, and water content. A recent report on P nanofertilizer, a water-phosphorite suspension of 60-120 nm obtained from natural raw phosphorite by ultrasonic dispersion, gave promising results upon seed treatment. The nano P enhanced morphometric indices of corn plants in greenhouse and field tests; the fresh yield increases from 2.4% to 2.2 fold, and the corn yield increases from 14.5 to 24.1%. The improvement in crop production quality by a set of indices from 0.3% to 2.6 fold was noted.[39]

It is often reported that total soil P is adequate, but not in the plant-usable form, so that farmers always need more P fertilization. To address the issue, zinc nanoparticles were used to mobilize native P (a plant-unavailable P form) into plant-available P to enhance its use efficiency. Enzymes such as phosphatase and phytase require Zn as a cofactor. It was found that foliar application of ZnO nanoparticles increased the activities of these enzymes, resulting in about 11% increase in P uptake by the legumes and cereals, without the addition of any external P fertilizer (**Figure 4**).[40-42] Increased native P mobilization and uptake by plants also improved plant growth, biomass, yield and nutritional quality of cereals and legumes **(Figure 3 B)**. Similar results of plant growth and development in response to ZnO nanoparticles exposure along with P supplements were observed on cotton plants by Venkatachalam et al.[43] ZnO nanoparticles with P supplementation increased biomass, photosynthetic pigments and proteins in cotton, exhibiting a protective role against oxidative damage by increasing the activities of antioxidant enzymes.[43] Magnetite (Fe_3O_4) nanoparticles were also found to be capable of mobilizing native P in soil.[23] In summary, attempts to improve P uptake by generating P-based nanoparticles, or to stimulate native P mobilization by nanoparticle micronutrients (such as Zn and Fe), not only improve plant growth and development, but also address environmental consequences of P-induced eutrophication and limited P availability.

2.3. Zinc. Zinc (Zn) is a micronutrient required for plant's growth and development.[44] Zinc deficiency is ubiquitous in arable soils because availability of Zn for plant uptake is restricted in the root zone.[45] This causes Zn deficiency in cereals and legumes growing on potentially Zn-deficient soils. The low human dietary bioavailability of Zn from plant-based diets causes its deficiency worldwide, and may impair growth and immune functions. Due to ultra-small size and high surface area to volume size ratio, Zn nanoparticles, applied either as foliar spray or root placement, can be transported efficiently in the plant system.[45-48] Recently, Subbaiah et al[30] sprayed 25 nm ZnO nanoparticles on maize foliage and observed that the nanoparticles positively influenced plant growth, yield, and Zn content in the maize grains. Notably, about 36 ppm Zn was recorded in the grains of plants sprayed with 100 ppm ZnO nanoparticles.[30] The increased Zn content may, thus, help to address Zn deficiency in human/animal nutrition. The authors concluded that the accumulation of Zn in various plant parts depends on nanoparticle concentration, particle solubility, plant's ability to uptake the nutrient, and size and delivery of the nanoparticles. Previously, our group reported that nanoparticles exposed to plants through foliar application (aerosol spray) can be uptake efficiently and translocated to the different plant parts.[49, 50] Moreover, uptake of nutrients (either nano or bulk) by plant largely depends on the surface biophysical state and its interaction with plant type.[29] Furthermore, the elemental distribution studies by ICP-MS showed that Zn was distributed in all plant parts, including seeds. It is unclear what the nature of this Zn was, although it has been observed previously that ZnO nanoparticle-exposed plants contain more ions than particles, suggesting transformation of the ZnO nanoparticles, either before, or after entry, into the plant.[46, 51-53] The distribution of ions depends on nanoparticle properties, such as solubility, stability and dissolution kinetics; plant age, plant species, and exposure concentration vs. uptake of nanoparticles. However, the concentration of Zn in the seeds/edible plant parts has been found to be within the limit of the dietary recommendation for humans.[54]

ZnO nanoparticles not only increase Zn biofortification, but also improve nutritional quality. In tomato, ZnO nanoparticles (100 ppm exposure concentration and 25 nm particle size) increased lycopene content by 113% over the control.[48] Lycopene is an antioxidant, an important nutritional parameter in tomato fruits. However, the mechanism behind nanoparticle-induced lycopene biosynthesis is still unknown. In addition, Zn nanoparticles were also used, in a composite with CaO and chelators, for the nutritional enrichment of food. For example, Zn-Fe_2O_4 nanostructured powder, produced by flame spray pyrolysis that can control chemical composition and surface area, were demonstrated to possess superior sensory qualities in reactive food matrices at equivalent solubility to the commercial counterpart, and do not affect the color/texture of the product.[55] Thus, nanostructured powders may be used for the fortification of color-sensitive foods, such as extruded artificial cereal grains, chocolate- drinks, and fruit yogurts.[56]

Furthermore, ZnO nanoparticles have also been used to improve the uptake of native nutrients from the soil. Recently, Raliya et al.,[41] used biosynthesized ZnO nanoparticles to enhance native phosphorus uptake in mung bean. The level of resultant P uptake in mung bean was 10.8% more than control plants. Mechanistically, it was found that ZnO nanoparticles (mean diameter 25 nm and concentration 10 ppm) enhanced the activities of phosphorus-mobilizing enzymes, such as acid and alkaline phosphatases, enzymes involved in transforming complex forms of phosphorus (i.e. Ca-P, Fe-P, Al-P, Zn-P) into the plant available form (**Figure 4**)[40, 41]. Tarafdar et al.,[42] tested Zn nanofertilizer (average Zn particle size between 15 nm and 25 nm) on a cereal crop, pearl millet (*Pennisetum americanum* L.). Compared to the control plants, they observed significant improvements in the plants' phenological growth, chlorophyll content, total soluble leaf protein (38.7 %), and plant dry biomass (12.5%), in 6 weeks old plants under natural field conditions. Moreover, grain yield at crop maturity was improved by 37.7 % due to foliar application of Zn nanofertilizer.[42] The various studies using Zn/ZnO or Zn-composite nanomaterials are of significant agricultural importance (provided the nanomaterials are of optimized properties, discussed in subsequent section) for improving plant growth, development, and productivity, but also for addressing the challenges of Zn malnutrition by agronomic fortification.[29, 57]

2.4. Iron oxide. Iron (Fe) is an essential dietary nutrient, and is important for crop growth and development. Iron is involved in chlorophyll biosynthesis, and required for certain enzyme functions, notably, heme–proteins (e.g., cytochromes–found in chloroplast and mitochondria) and involved in electron transfer system.[58] Therefore, the primary symptom of Fe deficiency is chlorosis in young plant leaves that affects normal physiological function and nutritional quality.[59] The most abundant form of Fe in soils is ferric oxide (Fe_2O_3) or hematite, which is extremely insoluble; thus Fe uptake by the plant is often low. Conventionally, Fe uptake is dependent on the plant's ability to reduce Fe^{3+} (ferric) to the Fe^{2+} (ferrous) form, and remove it from the complex or chelating compound (often phytosiderophores). Considering the food chain, Fe deficiency not only affects plant growth and development, but also leads to Fe deficiency in animals and humans.[56, 60] Therefore, it is important to increase the use efficiency of Fe fertilizers. Iron oxide nanoparticles have been widely used for various applications including catalysis and medicine.[61] Previous studies showed that Fe oxide nanoparticles delivered to plants through soil or foliar spray can be uptake and transported in corn[62], pumpkin[63] and watermelon.[49, 64] Fundamental studies on the use of Fe oxide nanoparticles on various crops including lettuce[23], wheat[65], clover[66], soybeans[67, 68], rice[69], peanut[70] show that Fe nanoparticles improve several agronomic traits, including grain yield, nutritional quality, Fe biofortification, biomass, and biochemical parameters such as chlorophyll content, photosynthesis, light absorption and nitrogen and phosphorus metabolism. The findings based on magnetization studies suggest that iron oxide nanoparticles can be taken-up by plants as intact particles, and that they eventually undergo dissolution in the plant to affect plant development. Thus, Fe nanoparticles may be an ideal substrate to complement or replace traditional chelator-based iron fertilizers. However, results are limited by various factors such as type of soil, soil chemistry, plant species, plant age, nanoparticle exposure concentration, and physicochemical properties, and thus, require continuous validation with a diverse range of crops, and in various arable soils, as well as subsequent effects on the food chain.

2.5. Silica (Si/SiO/SiO_2/Silicon). Upon literature survey based on Google Scholar, PubMed, and Web of Science, the oldest report of nanoparticle influence on plant growth and development was found to be from 2004.[71] These researchers shook roots of 200-year old Changbai Larch (*Larix olgensis*) seedlings in nanostructured silicon dioxide (TMS). They observed that 0.5 ppm TMS promoted seedling growth. Reports of abiotic stress tolerance in plants due to silicon (or silica nanoparticles) have been reported by other groups. For example, nano silica conferred tolerance in tomato plants grown under salinity stress[72] as well as tolerance against drought in wheat.[73] Furthermore, it also enhanced photosynthetic rate, biomass production, grain yield, and maintained leaf water content. Mechanistically, silica nanoparticles form a binary film in the cell wall that provides osmotic adjustments. Silica nanoparticles also stimulate antioxidant enzymes, leading to resistance against biotic and abiotic stresses, and resulting in better seedling growth[71, 74, 75] In addition, Si nanoparticles reduce sodium uptake and translocation, while increasing potassium uptake and translocation under salt stress.[76, 77] Salinity and drought are major challenges in agriculture that limit crop production. Therefore, the beneficial impacts of silica and silicon nanoparticles on plant growth and development can potentially address adverse effects of climate changes that such as uneven rainfall, and rising temperatures that lead to enhanced evaporation of water from the soil surface.

2.6. Titanium (TiO_2- Rutile/Anatase). Since its commercial production, TiO_2 has been used as a pigment, in paints, and in sunscreens due to its photocatalytic water-splitting under UV light.[78] The photocatalytic activity of nanoscaleTiO_2 converts light energy into electrical or chemical energy under sunlight. Therefore, scientists see the potential to enhance photosynthesis while using engineered TiO_2 nanoparticles; it is one of the most studied nanoparticles for investigating plant responses to seed germination, plant growth, plant pest management, pesticides degradation, advanced water purification, and sensor technology to detect pesticide residues.[79] TiO_2 nanoparticles have been tested on various crops such as lettuce[23], spinach,[80-82] *lemna minor*,[83] tomato,[28] wheat,[84] watermelon,[49] beans,[85] and millets.[86, 87] These studies conclude that TiO_2 nanoparticles increase a) plant biomass/yield, b) chlorophyll content, c) photosynthetic activity, d) nutrient contents, and e) germination rate. However, the plant responses depended on plant type, exposure concentration, and nanoscale properties. The main reason for enhanced physiological activities is thought to be due to increase in nitrogen metabolism and RuBISCO, a key photosynthetic enzyme activity that leads to more CO_2 assimilation.[82, 88-91] The studies demonstrate that exposure of plants to TiO_2 nanoparticles enhances growth by increasing photosynthesis/light absorption.[48, 79, 83, 85, 88, 92] However, it remains to be seen whether TiO_2 nanofertilizers can be produced by the fertilizer industry and acceptable to farmers, considering that it is not an essential element for plants.

2.7. Carbon-based nanomaterials. Carbon is a major constituent of all living things; carbon bonds with other atoms and provides the structure to biomolecules, i.e. protein, carbohydrates, and fat. Plants also use carbon in the form of carbon dioxide during photosynthesis, to convert photo-energy into carbohydrates.[93] Plants use carbon for their own growth and development, and also for providing nourishment to other living organisms. Farmers use manure or decomposing plant biomass in farm field/garden to fertilize plants due to its rich carbon source.[93, 94] Thus, it is clear that plant growth and carbon are intrinsically linked, regardless of the carbon source - carbon dioxide from the air or organic carbon in soil.

Engineered carbon nanomaterials (1D, 2D or 3D) such as graphene, fullerenes, and carbon nanotubes have attracted considerable attention, due to their exceptional physicochemical properties and stability. It has also been reported that carbon nanotubes can be taken-up by plants, to influence growth and development.[95-98] A range of studies have been reported on the positive influence of carbon nano materials/structures on plants (**Figure 5)**. These studies conclude that carbon nanomaterials increase root length, stimulate seed germination, and plant biomass.[99-103] Most of the available literature report best outcomes with carbon nanotubes (SWCNT>MWCNT>CNT), followed by fullerenes, and graphene. For further details on carbon-based nanomaterials, readers are directed to recently published review articles on carbon nanomaterial application in agriculture by Vithanage et al.,[104] Mukherjee et al.,[105]; Zaytseva and Neumann.[106] These articles discussed the contrasting effects of carbon nanostructures on agriculturally important plants.

3. SYSTEMATIC STUDY: SYNTHESIS, DELIVERY, INTERACTION and FATE

The influence of nanomaterials on plants depends greatly on the intrinsic properties, and extrinsic interactions, of the nanoparticles. This is, presumably, one reason among many, that the literature has shown contrasting results from the same class of particles. For examples, TiO_2 nanoparticles exposure to corn seeds delayed germination,[107] whereas they show non-significant effect on rice seed germination [108], and improved seed germination of wheat.[84] In the following sections, we discuss some of the factors needed to be examined, while comparing a nanoparticle type and its influence on plants.

3.1. **Synthesis of nanoparticles/nanofertilizer.** Direct fabrication or synthesis of nanoscale materials is becoming increasingly important in life sciences, medical, agricultural, environmental, and related emerging applications. While some nanomaterials are available commercially, there is need for stringent control on resultant particle characteristics and customization of samples, especially when new application areas are to be developed. Nanomaterials are regularly being synthesized by both 'wet' methods such as, sol-gel, hydrothermal, homogeneous precipitation, biosynthesis using enzyme and protein template and reversed micelles methods)[28, 109-113] and 'dry' synthesis approach such as aerosol-based processes[114-119], ranging from single element nanoparticles, oxide semiconductors, other metal oxides, metals, metal alloys, polymers, doped and composite nanoparticles. A basic scheme of nanomaterial synthesis from bottom-up or top-down approach is illustrated in **Figure 6**. Nanoparticles to be used as fertilizers require a synthesis approach capable of producing mass scale particles with controlled physicochemical properties at low cost. To this end, a comparative summary of different methods for nanoparticle synthesis is summarized in **Table 2**.

3.2. Nanoparticles delivery, uptake, translocation, and biodistribution. In general, agrochemicals are delivered to plants in three ways – seed treatment, soil amendment, or foliar spray. Engineered nanoparticles have several consequences when applied via the soil, particularly when particles are mixed in the soil – the exposure and localized concentration of the particles become much higher than the indirect exposure during foliar spray or subsequent translocation to the roots that contribute significantly lower amounts to plant sinks. Moreover, high exposure concentrations may influence soil or rhizosphere microbial communities,[120-123] and induce agglomeration or aggregation as a result of soil physico-chemical properties that may limit the particle uptake by plants.[124-126] Comparative investigations of nanoparticles delivery to plants by spraying on the leaves vs. soil amendment indicate that foliar application has significant advantages for nanoscale nutrient uptake.[48-50, 68] Furthermore, lab-scale experiments demonstrated that an effective aerosol spray helps to generate monodisperse particles and avoid soft agglomeration during foliar application.

Foliar application of nutrients and pesticides has been practiced for years.[127] As a matter of principle, soil application or seed treatment of the fertilizer is done on the basis of nutrient deficiency in the soil, whereas, foliar (aerosol) application is done based on nutrient deficiency symptoms exhibited by plants.[128] The major consequence for foliar applications are that they require higher leaf area index, low exposure dose, potentially multiple applications times, and timing of the application based on weather, to avoid loss of nutrients.[129] An aerosol of engineered nanoparticles inhaled by the human or other animals may cause toxicity. However, this outcome is dependent on the particle concentration in the atmosphere, weather conditions of the day/time, exposure concentration, and physico-chemical properties of the particles.[25, 27, 130-133] To ensure safe foliar application of nanofertilizers, it is recommended to use appropriate personal protection equipment such as mask, gloves and eye protection.[134-136]

In the aerosol, particles maintain effective particle size, monodisperse and relatively more stable than particles in conventional suspension spray or soil application that undergo agglomeration as a result of particle – particle or particle–soil interaction.[49, 50] Nanofertilizer properties are particularly important for foliar delivery, whereby size exclusion may limit uptake via the stomatal pathway.[137] It has been demonstrated that stomatal uptake is enhanced through control of nanofertilizer particle size combined with an aerosol delivery method as illustrated in the past.[50] Furthermore, it was shown that foliar delivery of iron and magnesium nanofertilizers to pea (*Vigna unguiculata*) caused significant positive effects on plant growth and development.[138] Similarly, aerosol-mediated nanoparticle delivery, penetration, and translocation in watermelon[49,50] and tomato[28] have also been demonstrated (**Figure 7)**. The results revealed that nanoparticles of diameter less than 100 nm generated by an aerosol process enter the leaf through the stomatal pathway, passing through the phloem, and reaching the root of watermelon plants. It is worth noting that in many cases, plant parts are analyzed for studying nanoparticle transport using ICP-MS technique which analyzes ions, not the particles. However, many other studies also have supported their ICP-MS data with microscopic or X-ray spectroscopic studies of plant parts, to demonstrate the presence of actual particles. However, a major limitation of the electron microscopy of plant tissue is non-representative results due to imaging of very tiny fraction of the whole plant[48, 50, 139] Aerosol-mediated foliar application increases uptake of nanoparticles by circumventing the cuticle, the primary barrier of the plant cell[49, 50] The subsequent transport of nanoparticles from shoot to root is then achieved by the vascular systems – phloem transport pathways, a bidirectional pathway along the photosynthate gradient. Cellular transport of nanoparticles is carried out by both the apoplast and symplast pathways. The apoplast pathway favors transport of larger particles (~200 nm), while the symplastic pathway favors smaller (< 50 nm) particles **(Figure 8)**.[140]

3.2.1. Target delivery and controlled release of nanoscale material to plant. Since the advent of use the of nanomaterials in different applications, they have been extensively used in nanomedicine, where the nanoparticles are used either as therapeutic agents, or as target drug delivery vehicles.[141] Similarly, nanomaterials can be tailored for precise delivery to plants.[10, 13, 49, 50, 63] However, the desired progress for target or localized delivery of nanoscale nutrient or nanofertilizer is yet to be made. Torney et al.,[142] used mesoporous silica nanoparticles of 3 nm pore size for the delivery of a gene and its chemical inducer into isolated tobacco plant cells and intact leaves. Subsequently, gold nanoparticle capping was used to avoid the leaching out of the loaded gene and its inducer at the non-specific site. Similarly, aptamers, oligonucleotide or peptide molecules that bind to specific target molecules, can be potentially used for the surface functionalization of nanofertilizer, where the nutrient in the nanostructure is released in response to plant signals in the rhizosphere.[143, 144] The future possibilities for target delivery of essential nutrients, pesticides, and genetic materials using nanomaterial will offer new possibilities in the agricultural revolution.[144, 145]

3.2.2. Nanoscale Enabled Food-Energy-Water Nexus – A Futuristic Perspective. Regional to global demands for food, energy, and water (FEW) will place a range of significant resource limitations and pressures that will require the development of new alternative methods and technologies. Strategic developments and investments to address these realities must be underpinned by fundamental understanding of the interconnectivity of the FEW nexus, if successful management, including technology development, is to be achieved, at any scale. In the context of FEW systems, there are tremendous opportunities to create novel approaches, including new technologies, for optimizing linkages between these systems. These include utilizing treated wastewater for agricultural purposes, enhancing crop yields, and recharging aquifers, while being less energy intensive (or even net neutral). Sustainable energy and resource harvesting from wastewater management processes necessitates a shift from the current centralized wastewater management to a scientifically robust controlled decentralized framework. We propose an integrated systems approach, illustrated in **Figure 9** with the following perspectives to address the FEW nexus for sustainable agriculture: a) Anaerobic digester (for energy harvesting) coupled to a microbial electrochemical cell (for "green" production of disinfectants such as peroxides); b) Utilization of nitrogen and phosphorous rich discharges for the production of nanofertilizers through novel aerosol methodologies; c) Water discharge (from step described in a) reuse and as-produced nanofertilizers (from step b) for use in hydroponic and conventional soil-based agricultural systems; d) Managed discharge from the agricultural system to a natural soil aquifer treatment system, and reuse of the treated water; and e) Novel sensor-based network to monitor and integrate processes for real-time and simulation-based systems optimization and control.

3.3. Transport Models for Nutrient Uptake in Plants. There are several studies that have used models to address the uptake of nutrients and their transport in different regions of the plant. The uptake process includes the movement of nutrient ions through the soil toward the root surface, transport of ions through the membranes of root surface cells, radial transport of ions toward the root xylem vessels, and transport in the xylem and distribution of ions in the above ground parts of the plant. [146] Many recent studies have combined the model of nutrient uptake for a single root (mesh of root hairs) with the rate of root growth to predict total nutrient uptake over a period of time. The water and solute movement through soil is described by the Richards equation and the convection–dispersion equation in most of the recent models. Different empirical relations have been used in the models to address the nutrient uptake at the root's surface. In many models, nutrient uptake has been described by the Michaelis-Menten equation.[147, 148] Uptake increases with increasing nutrient concentration in a curvilinear fashion approaching maximum uptake. Kinetic parameters of the Michaelis-Menten equation vary with plant species, plant age, soil temperature and other parameters. Therefore, for modelling, these parameters need to be determined separately by controlled experiments, often posing a challenge, and is a scientific gap that needs to be addressed.

The initial nutrient transport models in plant tissues were of steady state source-sink type, with flow driven by osmotically generated pressure gradient.[149, 150] Diffusional transport of nutrients has generally been neglected in most of these models, as they have been considered to be insignificant, relative to convective transport in the main bulk flow. However, diffusion is significant near the vessel boundaries as the convective flux is nearly zero. The more recent models include a diffusive transport term in the transport equation.[151] Most models in the literature address only one or two aspects of the fertilizer-to-crop transport pathway. Also, many parameters used in the models such as Michaelis-Menten kinetic parameters need to be determined separately by experiments for different plant types, which poses major challenges. Although numerous models have been developed to predict the uptake of nutrients; there is a glaring gap in the present literature, hence opportunities for extending these models to address nanoparticle uptake and transport in plants.

5. FUTURE PREPECTIVES

Owing to the unique physico-chemical properties of nanostructures, their use as agrochemicals (fertilizers or pesticides) for plant growth and protection is consistently being explored. Most recently funded projects and future research calls appear to be focusing more on designing safer nanomaterial for effective responses, while being environmentally friendly. Nanotechnology research in agriculture is still at a rudimentary stage, but evolving swiftly. However, before nanofertilizers can be used on-farm for a general farm practice, there is a need for better understanding of their modes of function according to the regulatory frameworks, can be developed to ensure safe uses of such agrochemicals.

The United States Food and Drug Administration has already issued guidelines for the use of nanomaterials in animal feed.[152] Manufacturers are also adding engineered nanoparticles to foods, personal care, and other consumer products. Examples include silica nanoparticles in baby formula, titanium dioxide nanoparticles in powdered cake donuts, and other nanomaterials in paints, plastics, paper fibers, pharmaceuticals and toothpaste.[153-156] Many nanoparticle properties are considered to be of potential risk to human health, viz. size, shape, crystal phase, solubility, type of material, and the exposure and dosage concentration.[24, 133, 157] Expert opinions indicate that food products containing nanoparticles available in the market are probably safe to eat, but this is an area that needs to be more actively investigated.[12, 158-160] Addressing these issues will require further studies to understand how nanoparticles behave within the human body, once exposed through nano-food. Researchers need to conduct life cycle assessments of nanoparticles impact on human health and the environment, and develop strategies to assess and manage any risks they may pose, as well as finding sustainable ways to manufacture nanoscale materials to be used in agriculture.

Some of the major concerns regarding nanoscale technology and its use in agrochemicals that need to be addressed are summarized below.

1. Scaling up the synthesis/manufacturing/designing of safe nanomaterials that are environmentally benign and sustainable for agricultural production. Also, designing novel nanoparticles for controlled release and enhanced nutrient uptake rate.
2. Characterizing nanostructures, formulations or emulsions, for detailed understanding of nanoscale properties with respect to size, shape, chemical composition, crystal phase,

porosity, hydrophilicity/hydrophobicity, surface charge, stability, dissolution, agglomeration/aggregation, and valence of the surface layer.

3. Establishing precise delivery of nanomaterials, uptake rates, and investigating the metabolic fates of nanomaterials.
4. Developing nanoscale particles that can act as both fertilizers and pesticides, which provide sustained release and stability for plant protection management.
5. Understanding nano-bio-interactions, transport, and fate of nanoscale materials in the plant and food chain, including the solubility and durability of nanomaterials in the plant, soil, and environment.
6. Optimizing nanomaterial dose-response concentrations for a wide range of crops. For this, long-term studies, including life cycle, trans-generational, and trophic transfer investigations are required.
7. Optimizing nanoparticles parameters/characteristics, in particular, relationships among exposure concentration, dose metrics (number concentration v/s surface area concentration), and their impacts. Here, it is important to address the question related to inter-linked characteristics, for example, a given mass of smaller nanoparticles are more toxic than larger size of same species, but no significant difference observed if normalized by the surface area.
8. Understanding human and environmental exposure to engineered nanoscale particles via dietary uptake or food chain contamination.
9. Understanding potential environmental risks and development of mitigation strategies. Studying the basis of contradictory results and their reproducibility *vs*. reliability regarding the effect of engineered nanoparticles in plants using quantitative structure-activity relationship.
10. Developing common strategies/goals among the leading institutes/countries to test laboratory scale nano-products in real farm applications for broader technology validation and translation.
11. Establishment of educational and outreach programs along with research projects to bridge the community/users and scientists to address potential customer (farmers) concerns.

In summary, the world's population is expected to exceed nine billion by 2050[3] and this will result in great need to produce more food. Scientists are working to develop new ways to meet this rising global demand for food, energy, and water, and to do so without increasing the strain on natural resources. Nanotechnology represents a promising solution to these challenges. The development and use of nanofertilizers can be a potential strategy for promoting plant growth, development, and productivity. Nanotechnology-based fertilizers hold promise as smart delivery systems for plant nutrients; fundamental properties such as size, surface area, crystal phase, surface capping of nanomaterials, not only control nutrient dissolution and reactivity, but also control material behavior during application. While recent reports indicate that nutrient use efficiency can be enhanced through nanoscale packaging, compared to conventional fertilizers, the development and use of rationally designed nanoscale macro and micro nutrient fertilizer technologies remain nascent. Currently, there is pressing need for improving nano-synthesis and delivery capabilities for next generation fertilizers, and their use in agricultural systems.

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Notes

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Table1. Nanomaterials that influence plant growth and development

Type of NP	NP property		Mode of treatment Plant	Plant	Observation
	Size (nm)	Concentration (ppm)			
ESSENTIAL PLANT NUTRIENT					
Carbon Carbon based NPs (CNT, Graphene) MWCNT; SWCNT; Fullerol	1.5 - 5	5-500	Nutrient media and Foliar uptake; Seed treatment	Tomato[102, 161, 162]; Tobacco[99, 101, 162] Wheat[163]; Gram[103, 164] Bitter melon[165] Saltmarsh cordgrass[166] Soybean[102, 167, 168] Corn, Barley, rice, switchgrass[102, 168]	- Promote upregulation of stress related genes; Promote *in vitro* growth and biomass - Enhanced root elongation - Improving crop yield and seed quality - Reduce heavy metal toxicity and stress
Nitrogen Urea HA	< 200	50 Kg/ha	Soil exposure	Rice[11, 33]	- Slow release of nitrogen - Improved rice yield
Phosphorous CaPo4, CMC – HA, Phosphorite Zn induced P	<50	10-100	Soil and foliar applications	Cotton[43]; Pearlmillets[42] Beans[38, 40, 41] Wheat, Rye, Pea, Barley, Corn, Buckwheat, Radish, Cucumber[39]	- Protect against oxidative stress - Mobilize native P and enhance uptake - Enhances plant growth and yield
Magnesium MgO	<10	15	Foliar	Clusterbean[169]	- Improving biomass, chlorophyll content & phenological growth
Manganese	20	0.1 - 1	Seed	Mung bean[170]	- Improve nitrogen uptake and metabolism
Copper Cu-Chitosan	>10	100 -1200	Foliar & seed treatment	Corn[22], Tomato[171]	- Enhanced seedling growth, plant biomass and biochemical activities
Zinc ZnO	20-30	10 - 2000	Foliar application Seed application	Peanut[172] Beans[29, 40, 41, 47] Tomato[48] Cotton[43] Maize[30]	- Increase yield potential and plant growth - Enhance phytohormone level and plant growth - Help reduce drought stress and improve agronomic fortification
Iron Iron Oxide	10-100	1.5-4000	Foliar Spray	Wheat[65]; Watermelon[49, 64] Clover[66]; Soybean[67, 68, 173] Rice[69]; Tomato[174] Peanut[70]; Corn[62] Pumpkin[63]	- Enhance photosynthesis rate, chlorophyll content, biomass, grain yield & nutritional quality - Improving plant growth - Enhance nutrient absorption by enhancing microbial enzyme activity in rhizosphere

Type of NP	**NP property**		**Mode of treatment Plant**	**Plant**	**Observation**
	Size (nm)	**Concentration (ppm)**			
NON-ESSENTIAL PLANT NUTRIENT					
Titanium TiO_2	5-100	200-600	Seed, soil and foliar exposure	Spinach[80-82, 88-92, 175] *Lemna minor*[83] Tomato[48, 174] ; Wheat[84] Watermelon[49]; Mung bean[85]; Moth bean[87] Pearl millet[87] Clusterbean[86, 87]	• Increased plant biomass and photosynthetic activity. • Enhanced biochemical enzyme activity and light absorption by chloroplast; Increase photosynthesis, RuBISCO activity and carbon fixation • Increased germination rate. • Enhanced nitrogen metabolism
Cerium CeO	8 -30	0.1-250	Irrigation; Seed/root	Tomato[176, 177] *Arabidopsis thaliana*[178, 179] Cilantro[180]; Wheat[181]	• Improved plant growth and yield • Improved physiological and Molecular response • Increase stress tolerance enzyme activity
Indium In_2O_3	20-70	250	Seed/root	*Arabidopsis thaliana*[179]	• Improved physiological and molecular response
Silver Ag	5-25	1 -10	Hydroponics, Soil	Poplars[182] *Arabidopsis thaliana*[182] Clover[66]	• Influence phyto-stimulatory effect • Increase nutrient absorption by enhancing microbial activity in rhizosphere
Upconverson nanophosphore	n/a	10	Sprouts exposure	Mung bean[183]	• Promote plant growth
Silica Si SiO SiO_2	8-15	5-800	Soil irrigation, Seed & Root exposure	Tomato[72, 184] Wheat, Lupin[185] *Larix olgensis*[71]	• Help overcome from salinity stress and enhance plant growth • Enhance germination and growth Enhancement in total protein and chlorophyll content. • Promoted seedling growth and quality
Cobalt ferrite	n/a	1 – 1000	Root exposure	Tomato[186]	• Promote root growth

n/a = values not reported; Note: Superscript numbers are the corresponding reference citation of the study.

Table 2: A comparative summary of nanoparticle synthesis approaches[187]

Features	Nanoparticle synthesis methods			
	GAS PHASE	**LIQUID PHASE**		**SOLID PHASE**
	Aerosol	Biological	Chemical	Physical
Advantages	• Single step,Good control over particle size and shape • Synthesis of controlled nanocomposite • Monodispersity within a few percent & scalable • Passivation of the surface	• Environmentally benign • Surface coating with natural macro and micro biomolecules • Biocompatible	• Precise control on morphology of the metal nanoparticles	• Rapid and scale up synthesis
Limitations	• Large aggregates could be formed	• Rate of particle synthesis is low • Need natural resources • Broad polydispersity and poly shape	• Surface coating with harmful chemicals • Comparatively lesser bio-compatible	• Broad polydispersity and poly shape

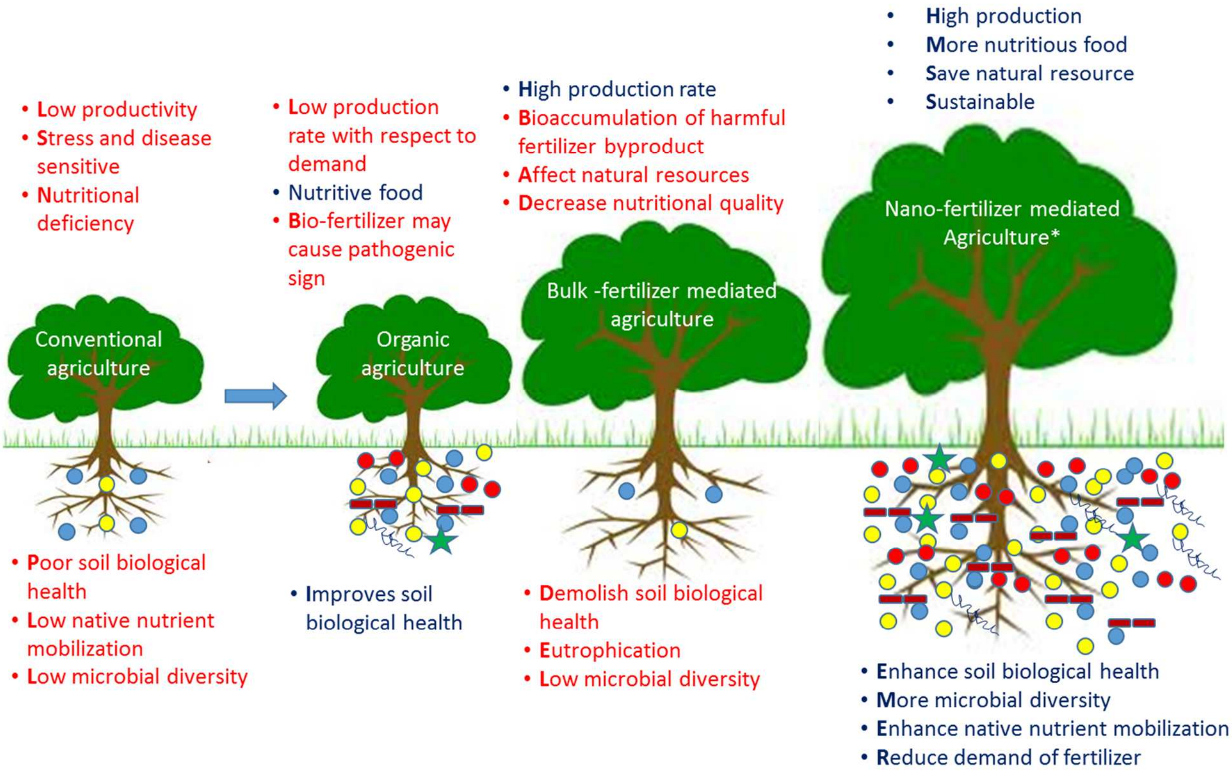


Figure 1. Comparative analysis of possible pros and cons of conventional approach with respect to nanotechnology mediated agriculture production. The impact on the rhizosphere as well as environment is elucidated; red color text represents potential negative impacts of a technology. * = Note that influence of nanofertilizer further depends on the plant growth and soil rhizosphere is depends on nanoparticle type, composition and exposure concentration.

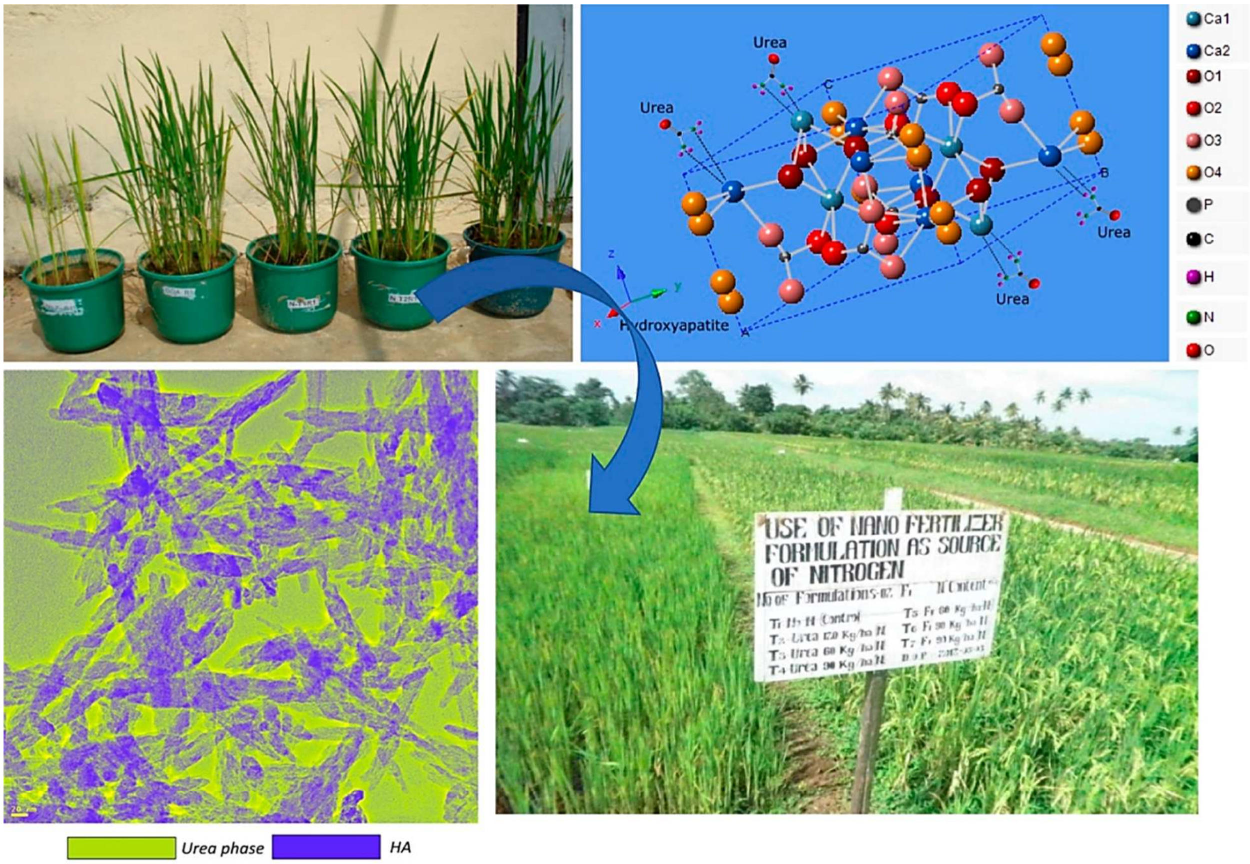


Figure 2. Nanotechnology based slow releasing nitrogen fertilizer. (A) and (C) Nanohybrids of urea-hydroxyapatite rod shape nanostructure and molecular level structural depiction (B) and (D) pot and field experiment with the synthesized nanohybrids. *The figure is adapted from reference* [11] *with Copyright permission from American Chemical Society.*

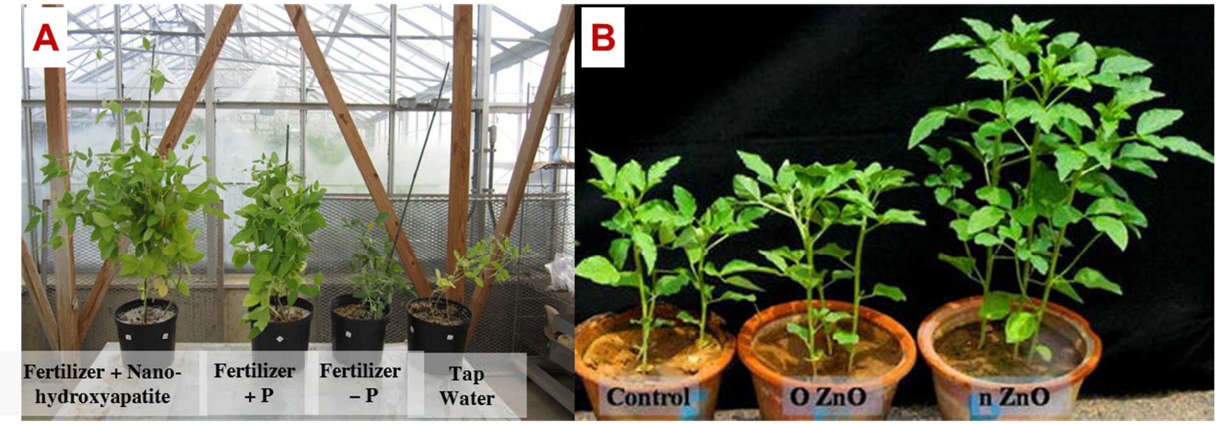


Figure 3. Phosphorus fertilization using nanoscale technology. (A) Growth of 6 week old soybean plants treated with nanoscale hydroxyapatite and compared with other P sources and control. [38] (B) Phenotypic growth of cluster bean after 4 weeks of germination, treated with ZnO nanoparticles and compared with its bulk counterpart and control [40]. Here, ZnO nanoparticles increase P mobilizing enzyme activities and enhance native P mobilization in rhizosphere and P uptake by the plant without any additional P fertilization [41]. *Figure 3 A adapted from Reference 29 with due copy right permission under CC license; and Figure 3 B adapted from reference 31 due copy right permission from Springer.*

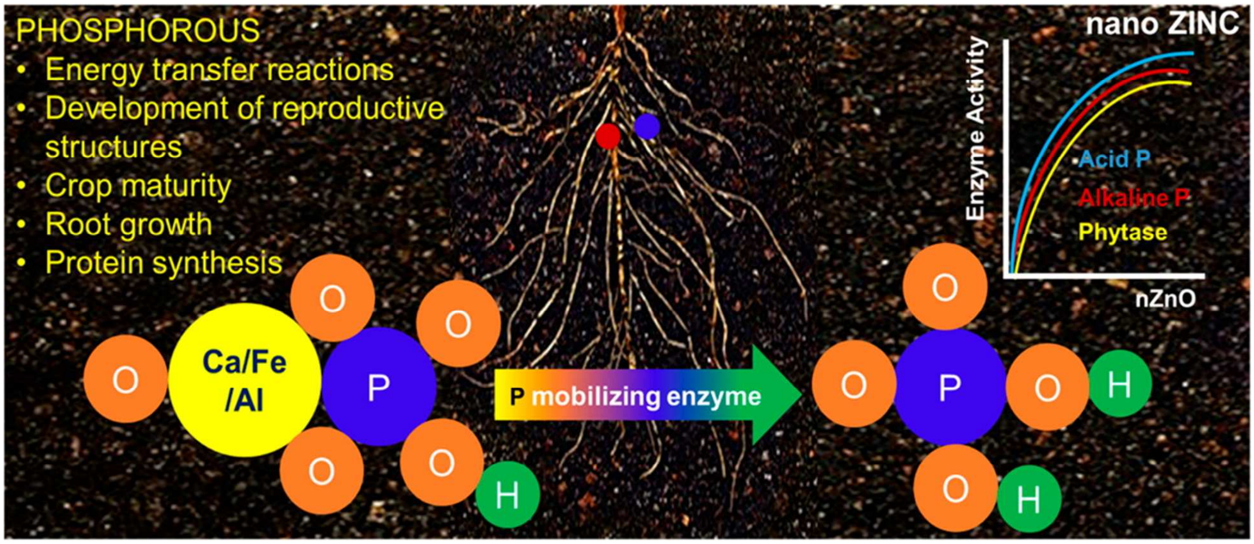


Figure 4. Mechanism of the influence of ZnO nanoparticles on native P mobilization in the rhizosphere and uptake by plants. Zinc ion act as a cofactor for P-mobilizing enzymes, and their activity was found to be increased as a result of ZnO nanoparticle treatment. Furthermore, enhanced P uptake by mung bean plants evidenced the influence of the ZnO nanoparticles on native nutrient mobilization. *Adapted from reference* [41]*with Copyright permission from American Chemical Society*

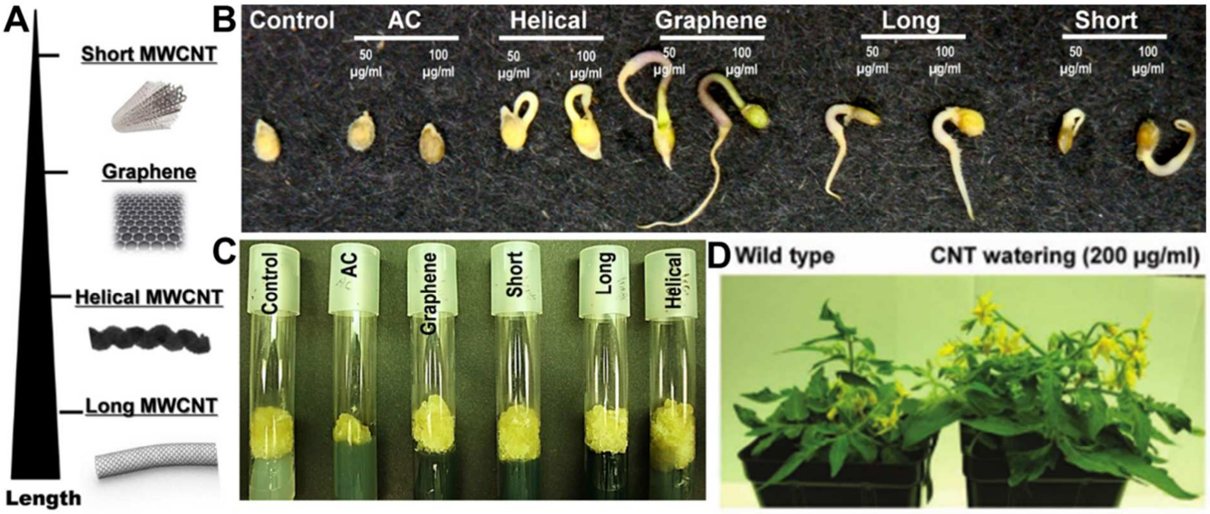


Figure 5. Carbon based nanomaterials and their influence on the plant growth – *in vitro* and *in vivo*(A) Different type of carbon nanostructure; (B); phenotype of tomato seeds after five days of carbon nanoparticles exposure C) Carbon nanoparticles induce tobacco callus culture growth; (D) Effect of CNT on the phenotype of tomato plants, wild type – is a control whereas, CNT watering means CNT was exposed with watering to the plants. *Abbreviation*: control media (Control), activated carbon (AC), helical MWCNTs (Helical), graphene, long MWCNTs (Long), and short MWCNTs (Short); CNT: Carbon Nano Tube.*The Figure A-C adapted with copyright permission from reference* [162] *with permission from IOP Publishing ltd and the Figure D adapted from reference* [161] *with a copyright permission from Wiley-VCH Verlag GmbH & Co.*

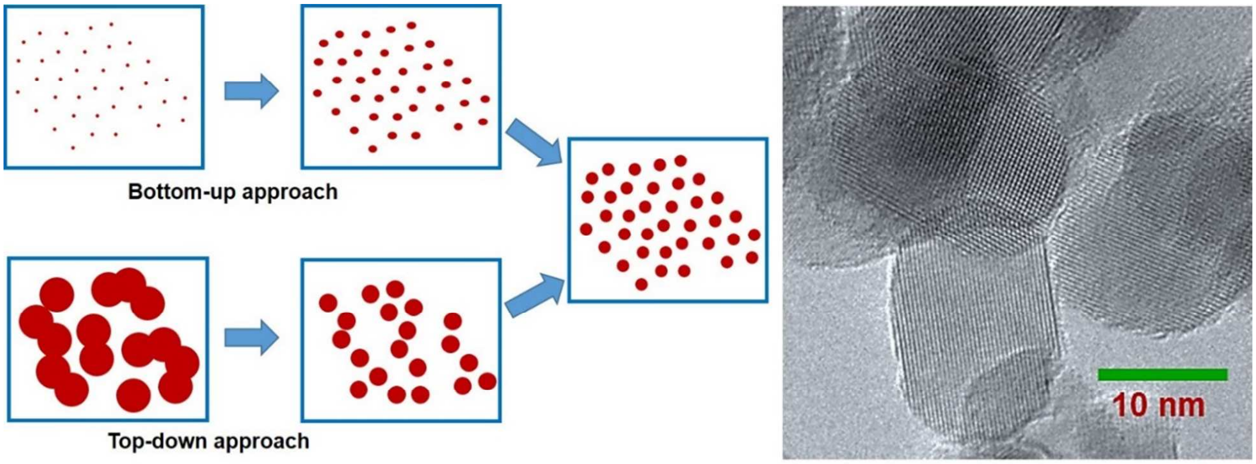


Figure 6. Synthesis of nanoparticles. Principally, two methods, Bottom up approach (molecules form clusters and eventually stable cluster or particles) and top-down approach (breakdown of big particles into small particles) are used to engineer nanoscale particles with controlled physico-chemical properties.

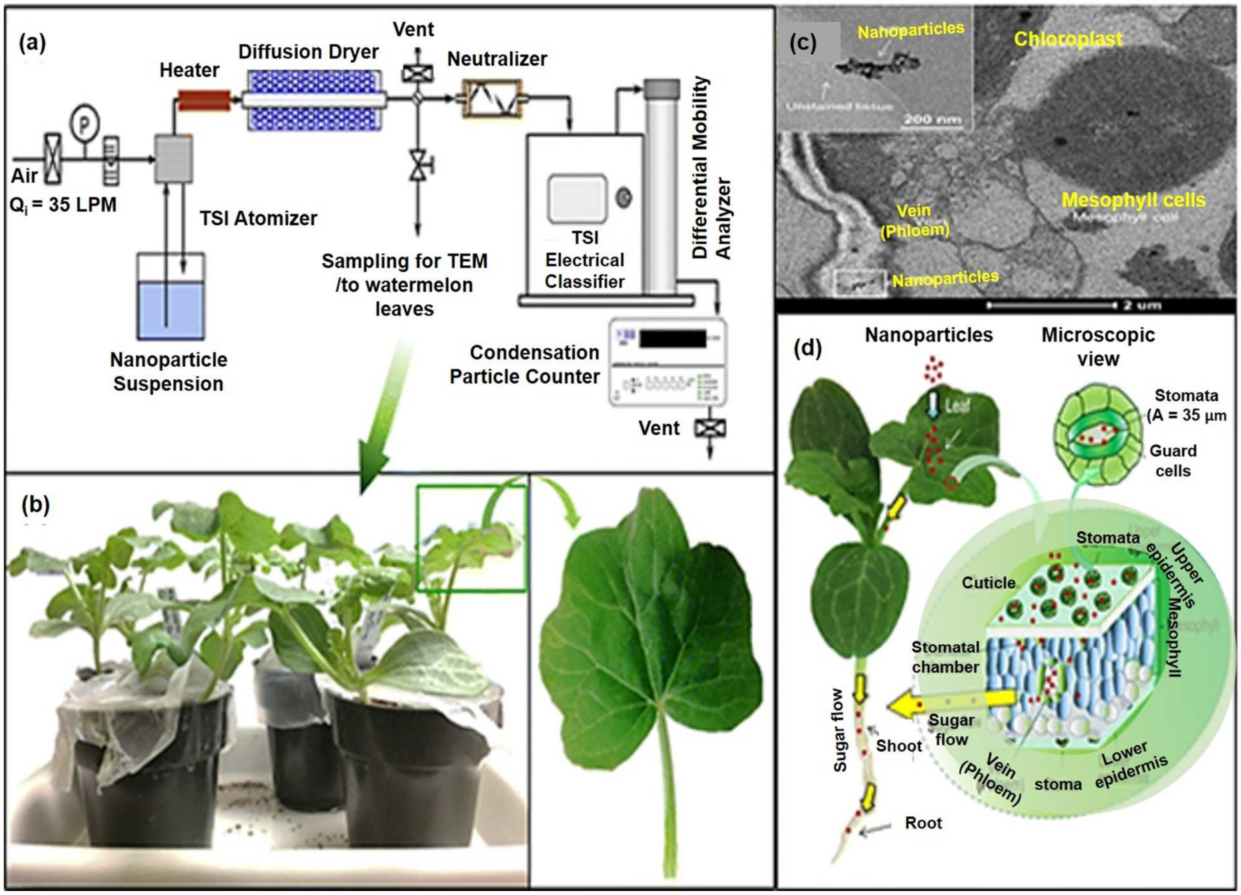


Figure 7. Aerosol mediated NP delivery to a watermelon plant (a) Schematic diagram of experimental setup (b) watermelon plants used in this work, inset b- typical watermelon leaf (c) TEM micrograph showing the presence of NPs inside the leaf after applying nanoparticles for three days, (d) Schematic diagram of nanoparticle transport inside watermelon plants. *Adapted and modified from reference* [49].

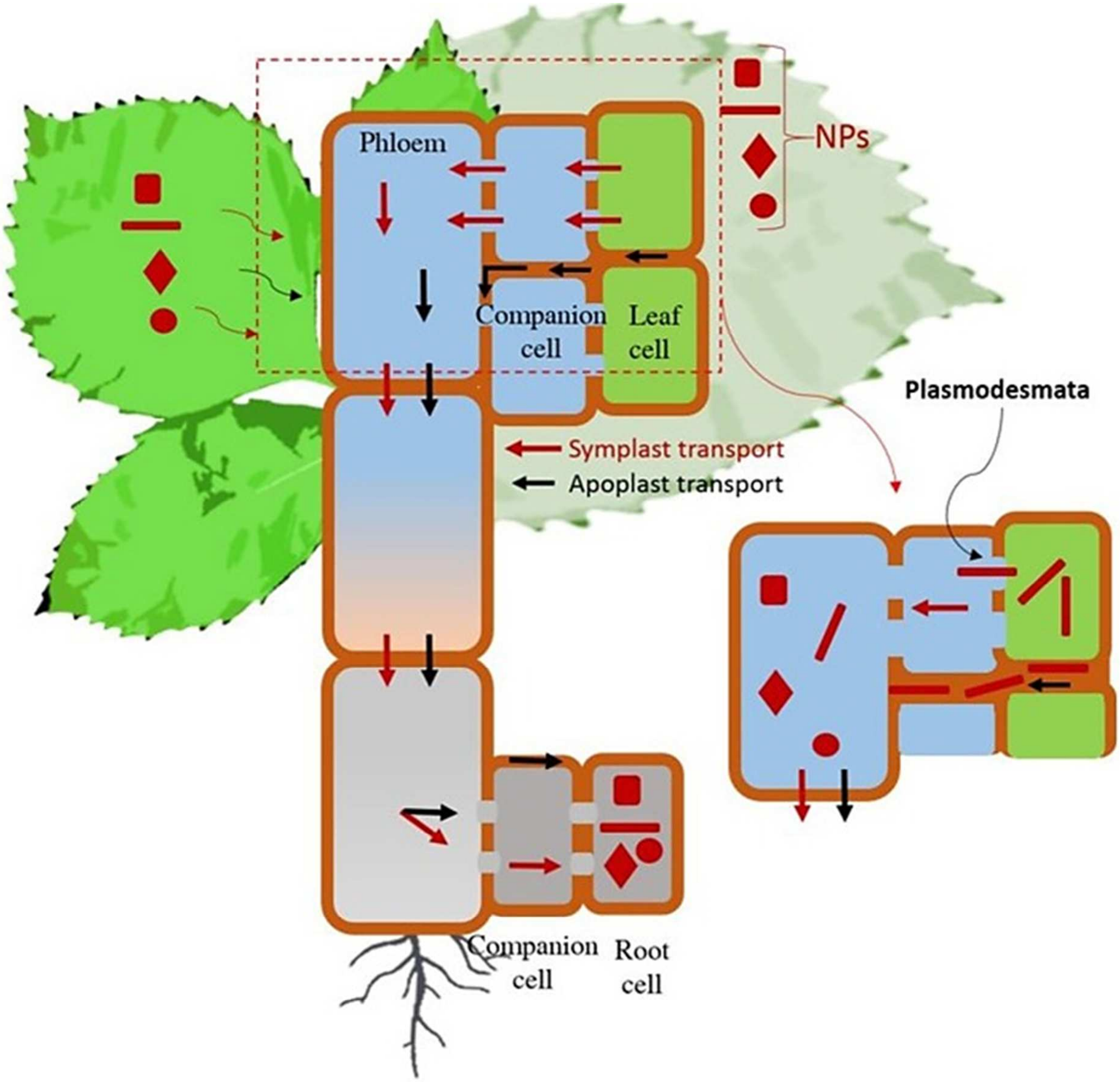


Figure 8. Mechanistic understanding of nanoparticle transport within plant cells. Representation describes how nanoparticles transport through apoplast and symplast pathway in plants cells along with pressure gradient or mass flow of photosynthate product. Inset represent the favorable transport of nanostructure (rod shape) more through apoplast than symplastic pathway. NPs: nanoparticles. Color gradient in the phloem represents mass concentration of photosynthate with nanoparticles. *Adapted from reference* [50] *with due copy right permission under CC license.*

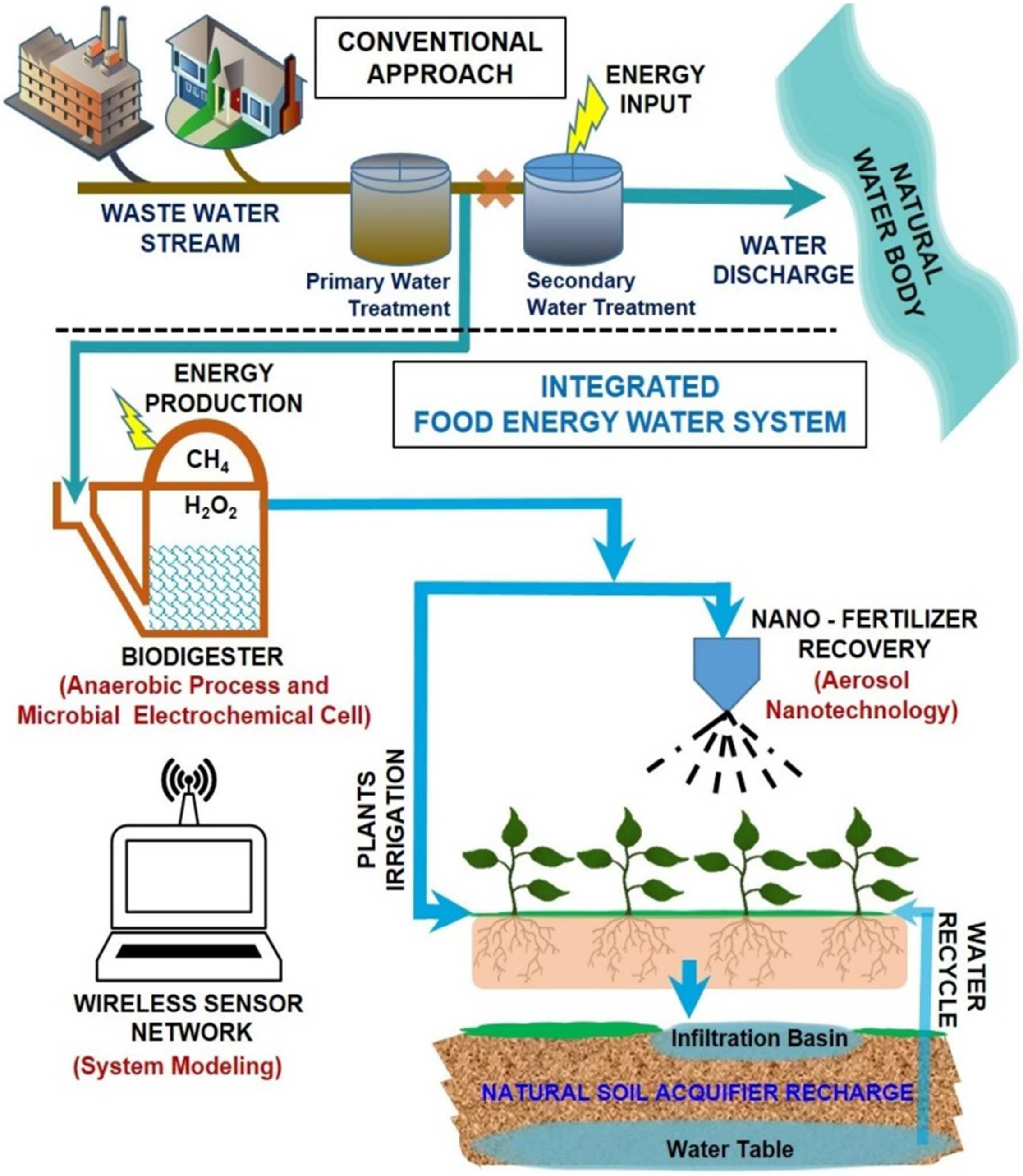
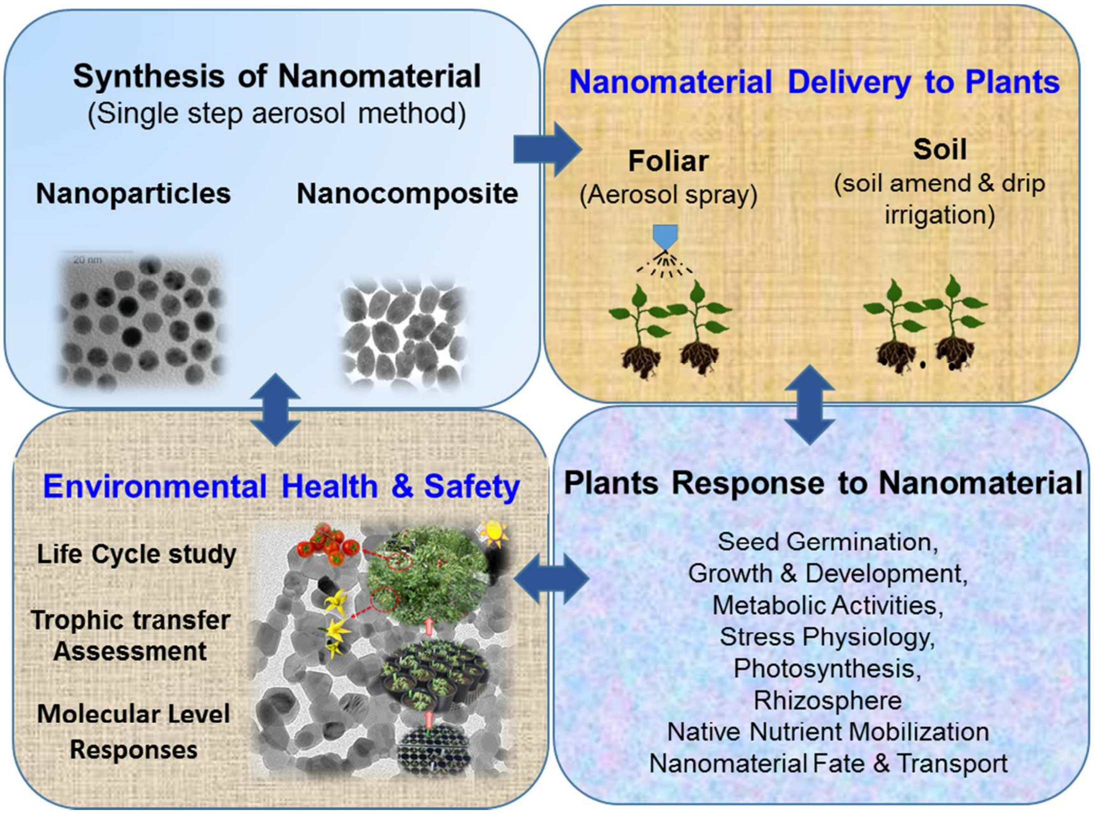


Figure 9. Illustration of various unit processes and their interconnectivity to realize the concept of sustainable agriculture by addressing food-energy-water nexus. In this illustration, propose four basic concepts – a) water and energy recovery from wastewater; b) nano-enabled agricultural processes; c) sustainable water reuse and aquifer recharge; d) nanotechnology-based sensing and system integration and modeling.

TOC Figure



TOC Figure: Nanofertilizer and its implication in agriculture: a systematic investigation.

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