Chapter

Polymeric Nanocomposite-Based Agriculture Delivery System: Emerging Technology for Agriculture

Mohammad Ashfaq, Neetu Talreja, Divya Chuahan and Werayut Srituravanich

Abstract

The increasing global population has forced the agricultural area to enhance the yield of crop, thereby fulfilling the requirements of people. The advancement has led to synthesis of nanomaterials with different size, shapes, and biocompatibility aspects towards specific applications like agriculture. Several nanomaterials such as metal, metal oxide, carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, and its derivatives have shown potential ability for augmenting the yield of crops and protect crops against pathogens. However, these nanomaterials required smart delivery system that might easily deliver the nanofertilizers in a controlled manner. In this context, the incorporation of nanotechnology and polymer science might be developing newer technology with minimal usage and maximum effectiveness for improvement of crops. The incorporation of nanomaterials in polymeric composites offers newer approaches for agricultural delivery system that might provide various advantages such as higher stability, solubility, uniform distribution, and controlled release. Moreover, nanomaterials have potential ability for advancement in the genetic engineering. Herein, we discuss the role of nanomaterials in the growth of the plant, polymeric nanocomposite materials for agriculture delivery system with the advancement in the genetic engineering, and future prospects of these polymeric-nanocomposite materials in agriculture.

Keywords: nanomaterials, polymeric composite, nanofertilizers, delivery system

1. Introduction

Nanomaterials (NMs) have attracted great interest especially in the field of agriculture that enhanced productivity of crops with lesser cost and waste [1, 2]. NMs offer sustainable effectiveness in the field of agriculture including protection and production of crops [3]. The significant advancement and development of the newer agricultural technologies is sturdily required because of continuously increasing food requirements globally [4]. The global food production must be increased around 70–100% by 2050 to achieve the demand of growing population [5, 6]. In this context, the agriculture promoted from various innovative technologies such as hybrid species, synthesis chemicals, and biotechnological developments [7]. However, continuous production of agricultural crops might be one of the great challenges due to the lack of nutrients/changes in climates. To overcome such issues related with the loss of production or improvement in the yield of crops, farmers continuously used agrochemicals. Nonetheless, excessive use of these agrochemicals leads to deterioration of soil, degradation of agro-ecosystems, and environmental problems [8, 9]. In this context, NMs have a technological advancement, might be transformed and allied sectors that provides newer agricultural tools for the management of stresses (biotic and abiotic), detection of diseases, improved nutrients absorption ability, and translocation ability. On the other hand, NMs might help to understand agricultural biology as well as interaction of nanomaterials with plants, thereby enhancing the nutritional value as well as productivity of the crops. However, the exact role of NMs in agriculture still remains a concern.

Numerous NMs including carbon-based nanomaterials (single-walled carbon nanotubes (SW-CNTs), multi-walled carbon nanotubes (MW-CNTs) [10, 11], carbon nanofibers (CNFs), graphene and fullerenes [12–15], metal and its oxide-based nanomaterials [16–18], magnetized iron (Fe) nanoparticles [19], aluminum oxide (Al_2O_3) [20], copper (Cu) [21], gold (Au) [22, 23], silver (Ag) [24, 25], silica (Si) [26], zinc (Zn) nanoparticles and zinc oxide (ZnO) [27–29], titanium dioxide (TiO_2) [30], and cerium oxide (Ce_2O_3) [31], etc.) and bio-composite nanomaterials have been developed. These NMs are efficiently used in the field of agriculture for production and protection of crops [32–35]. However, phytotoxicity, degradation of soil, large-scale production, agglomeration, and effective delivery system still remain a concern. On the other hand, CNFs have the potential ability to deliver micronutrients in plants and the release of micronutrients (Cu/Zn nanoparticles) in a controlled manner. However, CNFs also required polymeric delivery system for real applications [34]. In this context, polymeric nanocomposite has emerged as one of the most promising tools for the delivery of micronutrients and agrochemicals in the plant system [36].

Several polymers such as polyvinyl alcohol (PVA), chitosan, polyvinyl-pyrrolidone (PVP), starch, hyaluronic acid (HA), poly(lactic-co-glycolic acid) (PLGA), poly-lactic acid (PLA), etc. have been used as a carrier for delivery system for various biological applications due to their high biocompatibility, biodegradability, nontoxicity, cost-effectiveness, and excellent film forming ability [37–39]. Various processes such as cross-linking, emulsion formation, and self-assembly have been used for the synthesis of polymeric nanocomposite that facilitate controlled release of agrochemical/micronutrients within the plants. The encapsulation of nanomaterials by using polymeric matrix also aided advantages to enhance effectiveness of the nanomaterials, decreasing cellular toxicity and environmental contaminations [40]. On the other hand, smart polymeric materials and delivery system have the potential ability to deliver the genes/biomolecules/micronutrients within the plants and also protect viruses and pathogens [41, 42]. This book chapter focuses on the various nanomaterials and polymeric composite that augment the plant growth and interaction of nanomaterials with plants, genes/biomolecules/micronutrient delivery and discuss the advancement of genetic engineering by using nanomaterials.

2. Emergence of engineering nanomaterials (ENMs)

The advancement has led to the synthesis of engineering nanomaterials (ENMs) of various sizes and shapes [43]. This advancement in the synthesis routes offers great interest to develop unique characteristics against specific end applications like production and protection of crops [18, 44, 45]. Interestingly, these ENMs have been used in various applications such as medicine, environmental science, and sensors. Nonetheless, nanomaterial use in agriculture mainly for improvement in crop yield and crop protection is an under-explored research area. On the other hand, preliminary studies suggested that nanomaterials incorporated with polymers or polymeric composite have the potential ability to improve germination of seeds and growth of the plants, protection of crops, detection of pathogens, and detection of pesticide. The synthetic polymers also play a crucial role in agriculture because of polymeric materials that are pH-sensitive [46], temperature-sensitive [47], and climatic responsive that might be beneficial for growth of the plants such as mulches, shelters, and greenhouses (for fumigation, irrigation, and controlling water distribution) [48]. The ideal polymers for agricultural applications should have various properties such as stability, transmission, permeability, and weather ability, which is one of the important concerns nowadays [49]. In this context, functionalization of the polymers or polymeric composites has received significant consideration for the production of newer polymeric composites with improved characteristics [50]. **Figure 1** shows schematic representation of nanomaterials and their agricultural applications.

Several polymeric nanomaterials like chitosan, PVA, lipids, and PLGA are used in agriculture for augmenting the growth and protection of plants. The uptake and efficiency of the nanomaterials vary with the species, discussed later in the text.

In general, reactive nanomaterials exhibit various end applications due to their active functional groups and characteristic ability of polymers. Therefore, ENMs might be successfully utilized in different end applications including agriculture.

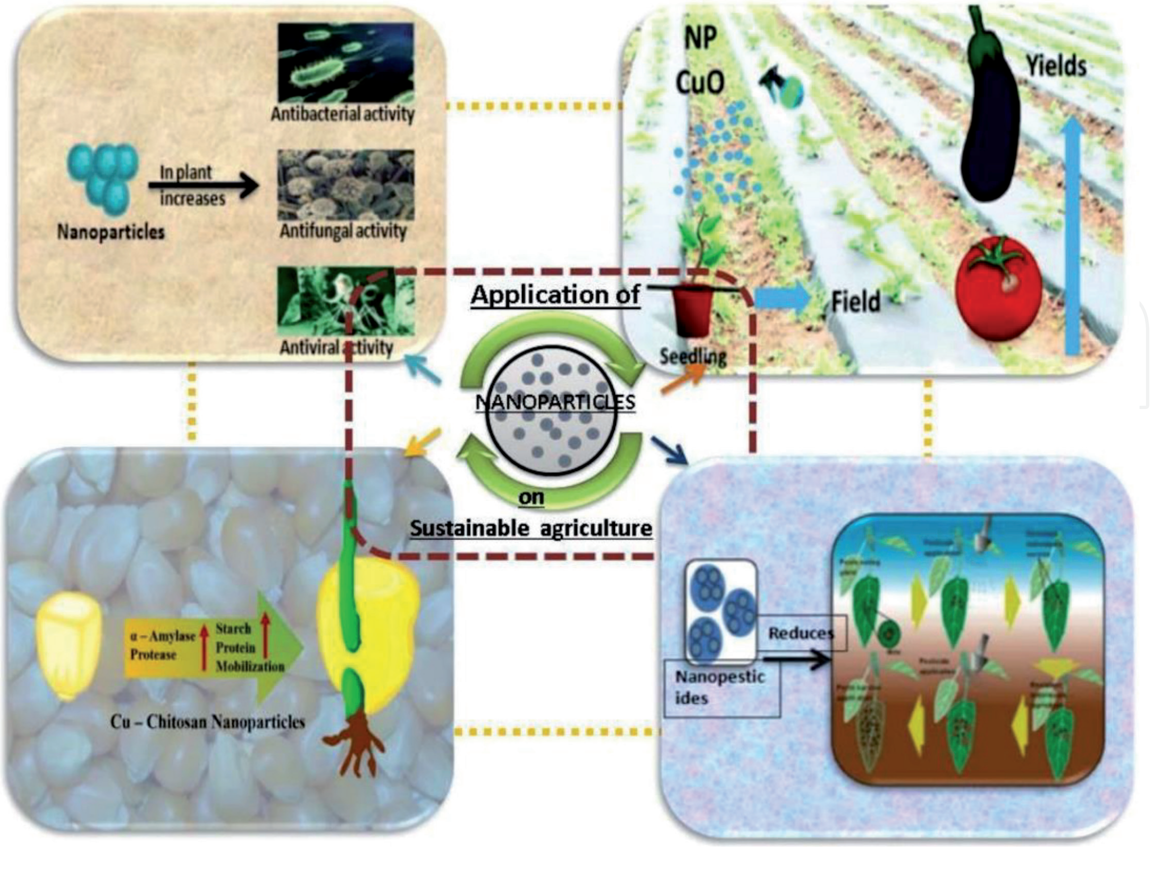

Figure 1.
Schematic representation of nanomaterials and its agricultural applications. Reprint permission Prasad et al. [7], copyright © 2017 Prasad, Bhattacharyya and Nguyen creative commons attribution license (CC BY).

3. Polymeric composites

Polymers are mainly used for the controlled release of agrochemicals such as insecticides, pesticides, fungicides, germicides, and growth stimulants. There are various factors such as cost, climate condition, controlled release, simple formulation, biocompatibility, and biodegradability involved in alteration in polymers for targeted system or applications. Moreover, thermal stability, thermal plasticity, glass-transition state, nature of polymers, melting point, its compatibility with biologically active molecules, and desired shape and size of the product still remain a concern. On the other hand, these polymers have the potential ability to control the release rate and rate of biodegradability, thereby being effective in various end applications, mainly medicine and agriculture [51]. The control release behavior of the polymeric formulation is one of the most important advantages in the delivery system like medicine, agrochemicals, and micronutrients.

Usually, the controlled release system is mainly divided into two groups; (1) encapsulation of active molecules/agrochemicals/micronutrients by using polymeric matrix and (2) polymeric matrix and active molecules/agrochemicals/micronutrients enclosed and formation of macromolecular backbones. Several polymers (natural, synthetic, and synthetic elastomers) such as carboxymethyl cellulose [52], cellulose acetate phthalate [53], gelatin [54], chitosan [55], gum Arabic [56], polylactic acid (PLA) [57], poly-butadiene, poly-lactic-glycolic acid (PLGA) [58], polyhydroxyalkanoates (PHAs) [59], polyvinyl alcohol (PVA) [60], polyacrylamide [61, 62], and polystyrene, etc., [63] are extensively used in various delivery systems. Among all of them, natural polymers are extensively used for controlled release of drugs/agrochemicals because of their low cost and being biodegradable. Moreover, controlled release rate might be tuned by using different molecular weight-based polymers and cross-linking of different polymers; therefore, polymeric composites are efficiently used in various biological applications. Recently, nanomaterials have been used as nanofertlizers, nanopesticides, and nanomaterials for genetic advancement, treatment of plant disease, and improved growth of the plants.

In general, polymers encapsulated with various materials including metal nanoparticles, carbon-based nanomaterials, biological molecules, agrochemicals, pesticides, insecticides, etc. with controlled release behaviors enhance the biocompatibility of the materials and are easy for applicability and thereby effectively used in various end applications, mainly medicine and agriculture [7].

3.1 Metal-polymer composites

The metal nanomaterials such as Cu, Zn, Fe, titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), aluminum nitride (AlN), boron nitride (BN), and zinc oxide (ZnO), etc. are extensively used for the plant growth and protection of crops. Usually, nanomaterials are synthesized for providing the controlled release delivery system for agrochemicals that enhanced solubility and protecting biologically active molecules against early degradation, thereby enhancing effectiveness of agrochemicals even at lower doses. However, these metal-based nanomaterials accumulate on the root and translocate less within the shoot and leave. Moreover, agglomeration, instability, and difficulty to use directly in land still remain a concern. In this context, the continuously increasing demands of the hybrid materials provide newer technological breakthrough for various end applications such as medical, environment, sensors, and agriculture. There are various existing materials such as plastics, metals, ceramic, and polymers that cannot achieve technological requirements for different applications. Usually, hybrid nanomaterials containing various nanomaterials as a filler with the polymeric matrix have great interest because of various advantages like high biocompatibility, controlled release, stability, and nontoxicity. The most important dominating approach for synthesis of metal-polymer composite by using metal/metal oxide encapsulates with polymers produces the desired product. The enhancements of material characteristic by using filler-polymer interactions at the interface as well as the uniform dispersion of the nanomaterials within the polymeric matrix. Usually, there are three approaches to achieve these requirements: (1) alteration of fillers/nanomaterial properties, (2) alteration of polymer properties by functionalization or formation of co-polymers, and (3) developing desired properties with the hybrid materials/polymeric nanocomposite. On the basis of agricultural applications, polymeric coating or polymeric nanocomposite is important, as higher concentration of nanomaterials might cause some extent of toxicity within the plants [64, 65].

3.2 Carbon-polymer composites

Carbon-based nanomaterials exhibited various end applications such as environmental remediation, sensors, drug delivery, antibacterial agents, crop protection, and growth regulator of the plants due to unique characteristics, mainly optical, electrical, mechanical, and thermal properties. The significant development has been done in the synthesis of carbon-based nanomaterials such as activated carbon, activated carbon fibers, CNTs, CNFs, graphene, and fullerenes, which have great interest in agriculture due to their possibility as a growth stimulant and protection of crops [66–79]. Moreover, these carbon-based nanomaterials, mainly CNTs, and CNFs, have the potential ability to penetrate seed coat as well as translocation ability within the plants from root to shoot to leaves. Several reports suggested that CNTs and CNFs efficiently translocate within the plants. These studies suggested that carbon-based nanomaterials acted as a growth stimulant with increasing the uptake of water and nutrients. Interestingly, CNFs hold metal nanoparticles and the release of metal nanoparticles in a control manner. These metal nanoparticles like Cu, Zn, and Fe also acted as micronutrients for the plants; therefore CNFs acted as a carrier for micronutrient delivery. Moreover, CNFs increase the water uptake ability, germination rate, and nontoxicity even at higher concentration of dose and therefore are used as a growth stimulant of the plants. In a recent study, Gupta et al. suggested that the CNFs are used as a carrier to deliver acylated-homoserine lactone in chick pea plants [34]. The study suggested that CNF-acylated homoserine lactone-based composite increased the plant growth as well as stress tolerance ability. The CNFs might be new generation fertilizers that enhance growth of the plants and defense regulator, also. However, direct application of the carbon-based nanomaterials still remains a concern. To overcome such issues, carbon-based nanomaterials are encapsulated with polymeric composite for agricultural delivery system. Kumar et al. synthesized bi-metallic (Cu/Zn) nanoparticle-dispersed CNFs encapsulated with PVA-starch composite to produce polymer-bi-metal-carbon (PBMC) composite [33]. The produced PBMC polymeric composite is effectively use as a fertilizer that enhances the growth of the plants. The releases of micronutrient (Cu/Zn) from CNFs, as well as polymeric composite in a controlled manner. The study also suggested that the release of micronutrients from PBMC is relatively slow in comparison with CNFs due to encapsulation of polymers. Moreover, CNFs efficiently translocated with the plants through root to shoot to leaves. The produced biodegradable PBMC-based formulation carrying Cu/Zn-CNFs (micronutrients) unwraps newer approach on the application of nanomaterials in agricultures. **Figure 2** shows the

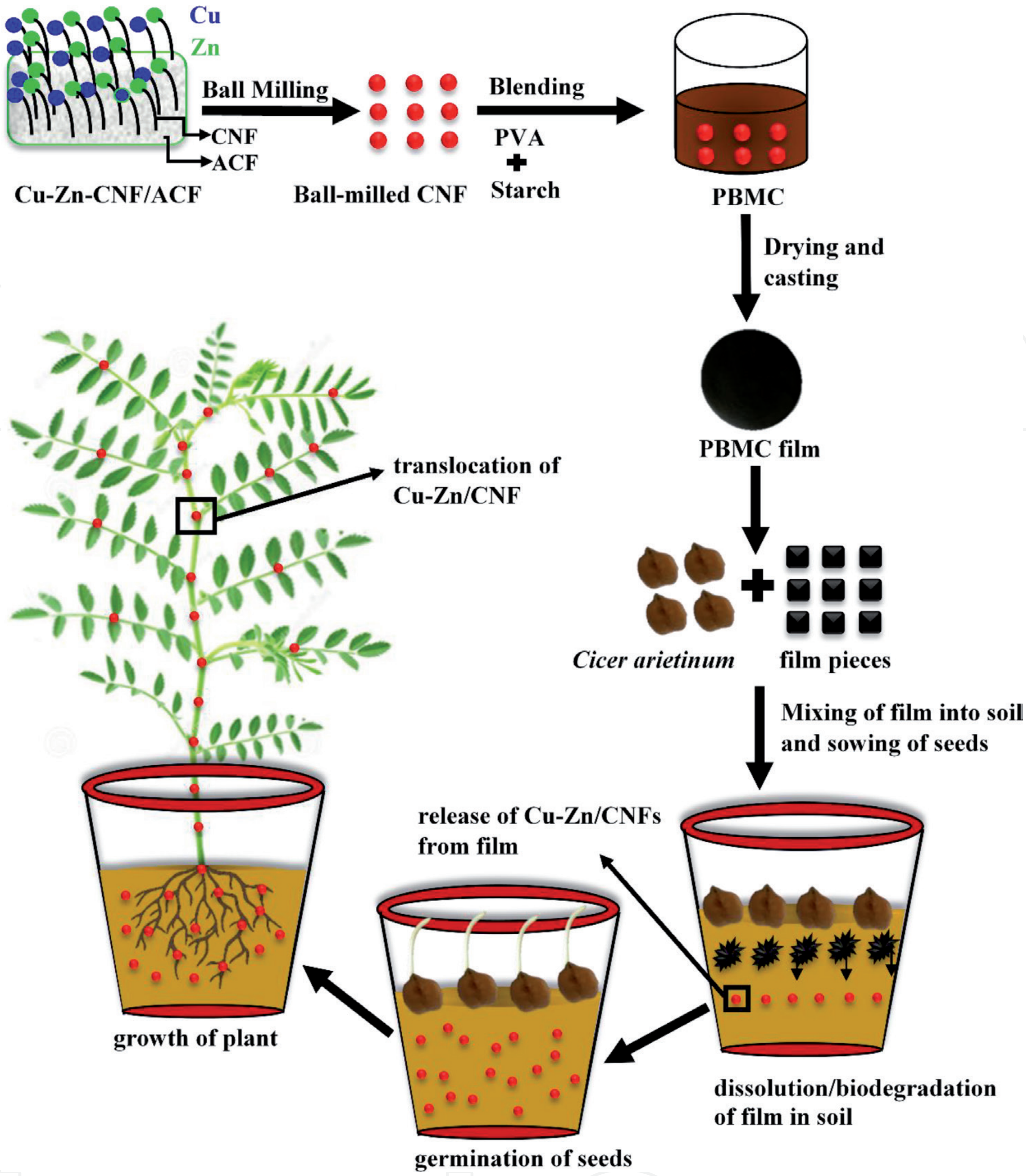

Figure 2.
A schematic representation of synthesis of Cu/Zn-CNF-dispersed polymeric composite and its agricultural application. Reprinted with permission (Kumar et al.), copyright © 2018, Springer Science Business Media, LLC, part of Springer Nature [33].

schematic representation of synthesis of Cu/Zn-CNF-dispersed polymeric composite and its agricultural application.

4. Interaction of polymeric nanocomposite with plants

Interaction of polymeric nanocomposite with plants (accumulation, uptake, and translocation), depends on various factors such as shape, size, surface charge, stability, chemical nature, functional group, and species of the plants. The cell-wall of the plants is one of the major sites of interaction with nanomaterials/other micronutrients. The cell-wall does not permit any foreign particles including nanomaterials/other micronutrients because it acts as a physical barrier. The plant cell-wall contains phosphate, hydroxyl, carboxylate, sulfhydryl, and imidazole groups that produce complex biomolecules, thereby selective translocation and uptake. There are two main properties that affect the uptake and translocation of nanomaterials/other micronutrients: (1) surface charge and (2) size. The surface charge of the nanomaterials/other micronutrients is one of the important parameters. The negatively charged nanomaterials/other micronutrients might favor translocation and uptake within the plants due to negatively charged plant cell-wall. The negatively charged nanomaterials/other micronutrients and plants do not attract each other, thereby easily uptake and translocation of the materials. On the other hand, positively charged nanomaterials/other micronutrients and negatively charged plant cell-wall attract each other, thereby accumulating on the root surface. The metal nanoparticles are positively charged, thereby having high accumulation and less translocation ability. Moreover, these metal nanoparticles also show phytotoxicity at higher concentration due to accumulation [17, 80–83].

The size of the nanomaterials/other micronutrients is one of the important factors for uptake and translocation. The smaller size (20–200 nm) favors the uptake and translocation within the plants. Moreover, carbon-based nanomaterials like CNTs and CNFs ~500 nm or less easily translocate within the plants due to their movement across the epidermis to cortex to vascular bundle. The nanomaterials are translocated to root to shoot to leaves through cell-wall network and plasmodesmata. The capillary action and osmotic forces are also one of the driving forces of translocation of nanomaterials within the plants. Additionally, the types of nanomaterials and chemical composition also affect the uptake and translocation within the plants. The functionalization and coating of nanomaterials alter the adsorption and accumulation ability within the plants. Some of the nanomaterials might accumulate at Casparian strip, whereas another translocate with symplastic routes towards shoot and root [84].

Recently, carbon-based nanomaterials like CNTs and CNFs acted as carriers for genes/micronutrients/biomolecules within the cells. Various are studies performed to understand the exact mechanism behind the nanomaterial uptake and translocation [81]. The larger sized nanomaterials are unable to penetrate cell-walls; however, a study on *Arabidopsis thaliana* leaf suggested the creation of endocytosis-like structure in plasma membrane [85]. Liu et al. suggested that water-soluble SW-CNTs with ~500 nm (length) were exposed on *Nicotiana tabacum*. The water-soluble SW-CNTs are able to penetrate through rigid and integral cell wall [86].

In general, several factors including surface charge, size, chemical nature, and surface coating influence the uptake and translocation ability within the plants [87]. Moreover, functionalization of nanomaterials with chemical/polymer might change the properties of materials, thereby easily translocating within the plants [88, 89].

5. Polymeric nanomaterial improved genetic engineering

Genetic engineering of the plant system is basically efforts of environmental sustainability, synthesis of product, and engineering of agricultural crops; therefore, advancement of genetic engineering is essential for growing population. The gene editing includes various techniques to use for accurately modifying the genome sequence. The emergence of gene editing is an exciting approach especially for agriculture scientist because of the simple process and accuracy that are able to develop improved variety of crops (addition of valuable traits and deletion of antagonistic traits). With the help of genome editing/genetic engineering, researchers continue to focus on the improvement in the yield of the crops with adverse conditions such as changes in climate. Usually, the cell-wall of the plants represents as a physical barrier; therefore, delivery of biomolecules/genes is difficult compared with animal system [90, 91]. Usually, two modes of transformation of genes exist in plants system: (1) cargo delivery that depends on the delivery techniques and (2) regeneration by using transformed plants that depends on the tissues, optimization of the protocols, and complicated hormone mixtures. However, the existing technologies have a lot of limitations such as less transformation, high toxicity, and DNA integration into host genome. The grand challenges of genes/biomolecules cargo delivery within the plants system due to the presence of rigid and multi-layered plant-cell wall, thereby slower transformation of genes/biomolecules within the plants. To overcome such issues, two approaches have been developed and used for transformation of genes/biomolecules within the plants: (1) *Agrobacterium*-mediated delivery system and (2) biolistic particle delivery (DNA bombardment). However, these strategies also have various drawbacks/limitations such as species dependence (changing the species changed the transformation efficiency), required regeneration from tissues, thereby time consuming and less efficiency, and *Agrobacterium*-mediated genes/biomolecule transformation might introduce foreign genetic materials. The *Agrobacterium*-mediated genes/biomolecules might cause disruption of genes/poor/unstable gene expression due to the random DNA integration. The DNA integration might be prevented by using nonintegrated viruses or plasmid deficient in transfer DNA insertion [90, 92]. Therefore, these two strategies are more preferred tools in comparison with other conventional methods. In this context, nanotechnology might be an alternative tool to resolve such issues associated with the existing delivery system.

Various nanomaterial-based plant delivery systems focus on the synthesis of nanomaterials, agrochemical delivery system, micronutrient delivery system, translocation of nanomaterials that augmented the growth of plants by using metal-based nanoparticles, CNTs, CNFs, quantum dots, graphene and its derivatives, and fullerenes. On the other hand, some nanomaterials exhibited phytotoxicity due to the oxidative stress and vascular blockage, damaging the structural DNA. Recently, Demirer et al. [90] developed nanomaterial-mediated biomolecule delivery system for gene expression and silencing of the plant system. For this, grafting of DNA on covalently functionalized pristine SW-CNTs and MW-CNTs was done to produce effective DNA delivery with strong expression of protein in mature *Eruca sativa* (arugula) leaves. The DNA is delivered in plant nucleus with the CNTs and also silencing of functional gene, separately. The grafting of DNA is done on CNTs due to the π-π stacking; the SDS is replaced by adsorption DNA by using the dialysis process. The produced DNA-CNT-based delivery system is comparable to *Agrobacterium*-mediated delivery system. The study also suggested that the produced CNT-based delivery system efficiently expresses protein in arugula protoplasts (cell-wall free) with the transformation (85%) efficiency.

Zhao et al. [93] developed nanoparticle-mediated genetic transformation. For this, they formed the complex of DNA-nanoparticles and delivered into the pollen grains by using magnetic force. The produce approaches to be moderate with insignificant toxicity, genetically stable and transformed plants. These studies suggested that nanomaterial-based delivery system plays a significant role in the advancement in the genetic engineering of the plant system.

In general, genetic engineering of the plant system is more complicated compared with animal system. The approach of the genes/biomolecule transformation within the plants still remains a concern due to the multi-layer and rigid cell-wall. There is lack of effective delivery of the diverse genes/biomolecules within the plant system without damaging the tissues. The nanotechnology might be an alternative tool in the advancement of the genetic engineering in plant systems that resolve such delivery challenge of genes/biomolecules, thereby increasing the utility of genetic engineering.

6. Conclusion and future prospects

Polymeric nanocomposites own distinct features of biodegradability and biocompatibility, which makes it an ideal material to be used in crop protection and micronutrient delivery in the agriculture field. The reactive nanomaterials have been used in various applications because of their functional groups and characteristics; therefore, ENMs might have the potential ability to be used in different applications including agriculture. Moreover, encapsulation of polymers with different nanomaterials like metal/metal-oxide and carbon-based nanomaterials enhanced the controlled release behaviors, biocompatibility, and simple use. Therefore, they are efficiently used in various applications mainly in agriculture. Additionally, uptake, accumulation, and translocation ability of the nanomaterials mainly depend on surface charges, size, and chemical nature of the materials. On the one hand, polymeric coating of nanomaterials might change the functionality and surface charge; therefore, polymeric composite might efficiently translocate within the plants. With regard to advancement in the genetic engineering, nanomaterials might be alternative tools that efficiently delivered genes/biomolecules. Therefore, polymeric nanocomposite enhances the utility of genetic engineering in plant system. As discussed in the text, CNFs is the next generation fertilizer that can easily deliver micronutrients and biomolecules within the plant. However, transformation of these research into field, some issues must be discuss or detailed studies required; (1) cost of the nanofertilizers, (2) safety concern like health/environmental toxicity, and (3) easy applications. We need to do more research in such agricultural areas for easy applicability in the field.

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References

[1] Fraceto LF et al. Nanotechnology in agriculture: Which innovation potential does it have? Frontiers in Environmental Science. 2016;**4**(20):1-5

[2] Parisi C, Vigani M, Rodríguez-Cerezo E. Agricultural nanotechnologies: What are the current possibilities? Nano Today. 2015;**10**(2):124-127

[3] Khot LR et al. Applications of nanomaterials in agricultural production and crop protection: A review. Crop Protection. 2012;**35**:64-70

[4] de Oliveira JL et al. Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: Prospects and promises. Biotechnology Advances. 2014;**32**(8):1550-1561

[5] Mortensen DA et al. Agriculture in 2050: Recalibrating targets for sustainable intensification. Bioscience. 2017;**67**(4):386-391

[6] Tilman D et al. Global food demand and the sustainable intensification of agriculture. Proceedings of the National Academy of Sciences. 2011;**108**(50):20260-20264

[7] Prasad R, Bhattacharyya A, Nguyen QD. Nanotechnology in sustainable agriculture: Recent developments, challenges, and Perspectives. Frontiers in Microbiology. 2017;**8**:1014-1014

[8] Nair R. Grand challenges in agroecology and land use systems. Frontiers in Environmental Science. 2014;**2**(1):1-4

[9] Aktar MW, Sengupta D, Chowdhury A. Impact of pesticides use in agriculture: Their benefits and hazards. Interdisciplinary Toxicology. 2009;**2**(1):1-12

[10] Zaytseva O, Neumann G. Carbon nanomaterials: Production, impact on plant development, agricultural and environmental applications. Chemical and Biological Technologies in Agriculture. 2016;**3**(1):17

[11] Yuan Z et al. Novel impacts of functionalized multi-walled carbon nanotubes in plants: Promotion of nodulation and nitrogenase activity in the rhizobium-legume system. Nanoscale. 2017;**9**(28):9921-9937

[12] Chichiricco G, Poma A. Penetration and toxicity of nanomaterials in higher plants. Nanomaterials (Basel). 2015;**5**(2):851-873

[13] Lin S et al. Uptake, translocation, and transmission of carbon nanomaterials in rice plants. Small. 2009;**5**(10):1128-1132

[14] Mukherjee A et al. Carbon nanomaterials in agriculture: A critical review. Frontiers in Plant Science. 2016;**7**:172-172

[15] Ghosh M et al. MWCNT uptake in *Allium cepa* root cells induces cytotoxic and genotoxic responses and results in DNA hyper-methylation. Mutation Research. 2015;**774**:49-58

[16] Chen H. Metal based nanoparticles in agricultural system: Behavior, transport, and interaction with plants. Chemical Speciation & Bioavailability. 2018;**30**(1):123-134

[17] Rastogi A et al. Impact of metal and metal oxide nanoparticles on plant: A critical review. Frontiers in Chemistry. 2017;**5**(78):1-16

[18] Gogos A, Knauer K, Bucheli TD. Nanomaterials in plant protection and fertilization: Current state, foreseen applications, and research priorities. Journal of

Agricultural and Food Chemistry. 2012;**60**(39):9781-9792

[19] Rui M et al. Iron oxide nanoparticles as a potential Iron fertilizer for peanut (*Arachis hypogaea*). Frontiers in Plant Science. 2016;**7**:815-815

[20] Burklew CE et al. Effects of aluminum oxide nanoparticles on the growth, development, and microRNA expression of tobacco (*Nicotiana tabacum*). PLoS One. 2012;**7**(5):e34783-e34783

[21] Belava VN et al. The effect of silver and copper nanoparticles on the wheat-*Pseudocercosporella herpotrichoides* pathosystem. Nanoscale Research Letters. 2017;**12**(1):250-250

[22] Tsi Ndeh N, Maensiri S, Maensiri D. The effect of green synthesized gold nanoparticles on rice germination and roots. Advances in Natural Sciences: Nanoscience and Nanotechnology. 2017;**8**(3):035008

[23] Siddiqi KS, Husen A. Engineered gold nanoparticles and plant adaptation potential. Nanoscale Research Letters. 2016;**11**(1):400-400

[24] Sharma J et al. Role of silver nanoparticles in treatment of plant diseases. In: Patra JK, Das G, Shin H-S, editors. Microbial Biotechnology, Application in Food and Pharmacology. Vol. 2. Singapore: Springer Singapore; 2018. pp. 435-454

[25] Kim SW et al. Antifungal effects of silver nanoparticles (AgNPs) against various plant pathogenic fungi. Mycobiology. 2012;**40**(1):53-58

[26] Korndörfer GH, Lepsch I. Chapter 7 effect of silicon on plant growth and crop yield. In: Datnoff LE, Snyder GH, Korndörfer GH, editors. Studies in Plant Science. Amsterdam: Elsevier; 2001. pp. 133-147

[27] Gangloff WJ et al. Mobility of organic and inorganic zinc fertilizers in soils. Communications in Soil Science and Plant Analysis. 2006;**37**(1-2):199-209

[28] Mortvedt JJ. Crop response to level of water-soluble zinc in granular zinc fertilizers. Fertilizer Research. 1992;**33**(3):249-255

[29] Rajiv P, Rajeshwari S, Venckatesh R. Bio-fabrication of zinc oxide nanoparticles using leaf extract of *Parthenium hysterophorus* L. and its size-dependent antifungal activity against plant fungal pathogens. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2013;**112**:384-387

[30] Wang Y et al. The application of nano-TiO(2) photo semiconductors in agriculture. Nanoscale Research Letters. 2016;**11**(1):529-529

[31] Zhang W et al. Uptake and accumulation of bulk and nanosized cerium oxide particles and ionic cerium by radish (*Raphanus sativus* L.). Journal of Agricultural and Food Chemistry. 2015;**63**(2):382-390

[32] Ashfaq M, Verma N, Khan S. Carbon nanofibers as a micronutrient carrier in plants: Efficient translocation and controlled release of Cu nanoparticles. Environmental Science: Nano. 2017;**4**(1):138-148

[33] Kumar R, Ashfaq M, Verma N. Synthesis of novel PVA–starch formulation-supported Cu–Zn nanoparticle carrying carbon nanofibers as a nanofertilizer: Controlled release of micronutrients. Journal of Materials Science. 2018;**53**(10):7150-7164

[34] Gupta GS, Kumar A, Verma N. Bacterial homoserine lactones as a nanocomposite fertilizer and defense

regulator for chickpeas. Nanotechnology in Environmental Science. 2019;**6**: 1246-1258

[35] Omar RA et al. Impact of nanomaterials in plant systems. In: Prasad R, editor. Plant Nanobionics, Advances in the Understanding of Nanomaterials Research and Applications. Vol. 1. Cham: Springer International Publishing; 2019. pp. 117-140

[36] Jarosiewicz A, Tomaszewska M. Controlled-release NPK fertilizer encapsulated by polymeric membranes. Journal of Agricultural and Food Chemistry. 2003;**51**(2):413-417

[37] Chen BZ et al. In vitro and in vivo assessment of polymer microneedles for controlled transdermal drug delivery. Journal of Drug Targeting. 2018;**26**(8):720-729

[38] Zhang JN et al. Development of a BDDE-crosslinked hyaluronic acid based microneedles patch as a dermal filler for anti-ageing treatment. Journal of Industrial and Engineering Chemistry. 2018;**65**:363-369

[39] Chen BZ et al. Self-implanted tiny needles as alternative to traditional parenteral administrations for controlled transdermal drug delivery. International Journal of Pharmaceutics. 2019;**556**:338-348

[40] Oliveira HC et al. Nanoencapsulation enhances the post-emergence herbicidal activity of atrazine against mustard plants. PLoS One. 2015;**10**(7):e0132971

[41] Roy I, Gupta MN. Smart polymeric materials: Emerging biochemical applications. Chemistry & Biology. 2003;**10**(12):1161-1171

[42] Priya James H et al. Smart polymers for the controlled delivery of drugs: A concise overview. Acta Pharmaceutica Sinica B. 2014;**4**(2):120-127

[43] Talreja N, Kumar D. Engineered nanoparticles' toxicity: Environmental aspects. In: Hussain CM, Mishra AK, editors. Nanotechnology in Environmental Science. 2018. DOI: 10.1002/9783527808854.ch23

[44] Mazzaglia A, Fortunati E, Kenny JM, Torre L, Balestra GM. Nanomaterials in plant protection. In: Axelos MA, Van de Voorde MH, editors. Nanotechnology in Agriculture and Food Science. 2017. DOI: 10.1002/9783527697724.ch7

[45] Hong J, Peralta-Videa JR, Gardea-Torresdey JL. Nanomaterials in agricultural production: Benefits and possible threats? In: Sustainable Nanotechnology and the Environment: Advances and Achievements. American Chemical Society (ACS); 2013. pp. 73-90

[46] Kocak G, Tuncer C, Bütün V. pH-responsive polymers. Polymer Chemistry. 2017;**8**(1):144-176

[47] Kim Y-J, Matsunaga YT. Thermo-responsive polymers and their application as smart biomaterials. Journal of Materials Chemistry B. 2017;**5**(23):4307-4321

[48] Kasirajan S, Ngouajio M. Polyethylene and biodegradable mulches for agricultural applications: A review. Agronomy for Sustainable Development. 2012;**32**(2):501-529

[49] Pascoli M et al. State of the art of polymeric nanoparticles as carrier systems with agricultural applications: A minireview. Energy, Ecology and Environment. 2018;**3**(3):137-148

[50] Van Beilen JB, Poirier Y. Production of renewable polymers from crop plants. The Plant Journal. 2008;**54**(4):684-701

[51] Roy A et al. Controlled pesticide release from biodegradable polymers. Central European Journal of Chemistry. 2014;**12**(4):453-469

[52] Davidson DW, Verma MS, Gu FX. Controlled root targeted delivery of fertilizer using an ionically crosslinked carboxymethyl cellulose hydrogel matrix. Springerplus. 2013;**2**:318-318

[53] Mukherjee R, De S. Preparation, characterization and application of powdered activated carbon-cellulose acetate phthalate mixed matrix membrane for treatment of steel plant effluent. Polymers for Advanced Technologies. 2016;**27**(4):444-459

[54] Wilson HT, Amirkhani M, Taylor AG. Evaluation of gelatin as a biostimulant seed treatment to improve plant performance. Frontiers in Plant Science. 2018;**9**:1006-1006

[55] El Hadrami A et al. Chitosan in plant protection. Marine Drugs. 2010;**8**(4):968-987

[56] de Oliveira JL et al. Geraniol encapsulated in chitosan/gum arabic nanoparticles: A promising system for pest management in sustainable agriculture. Journal of Agricultural and Food Chemistry. 2018;**66**(21):5325-5334

[57] Chang Y-N, Mueller RE, Iannotti EL. Use of low MW polylactic acid and lactide to stimulate growth and yield of soybeans. Plant Growth Regulation. 1996;**19**(3):223-232

[58] Gao H et al. Enhanced plant growth promoting role of mPEG-PLGA-based nanoparticles as an activator protein PeaT1 carrier in wheat (*Triticum aestivum* L.). Journal of Chemical Technology & Biotechnology. 2018;**93**(11):3143-3151

[59] Voinova ON et al. Microbial polymers as a degradable carrier for pesticide delivery. Applied Biochemistry and Microbiology. 2009;**45**(4):384-388

[60] Russo R et al. Alginate/polyvinylalcohol blends for agricultural applications: Structure-properties correlation, mechanical properties and greenhouse effect evaluation. Macromolecular Symposia. 2004;**218**(1):241-250

[61] Paradelo R, Basanta R, Barral MT. Water-holding capacity and plant growth in compost-based substrates modified with polyacrylamide, guar gum or bentonite. Scientia Horticulturae. 2019;**243**:344-349

[62] Lee SS et al. Synergy effects of biochar and polyacrylamide on plants growth and soil erosion control. Environmental Earth Sciences. 2015;**74**(3):2463-2473

[63] Nussinovitch A. Beads and special applications of polymers for agricultural uses. In: Polymer Macro- and Micro-Gel Beads: Fundamentals and Applications. New York, NY: Springer New York; 2010. pp. 231-253

[64] Ponnamma D et al. Synthesis, optimization and applications of ZnO/polymer nanocomposites. Materials Science and Engineering: C. 2019;**98**:1210-1240

[65] Kumar S et al. Nano-based smart pesticide formulations: Emerging opportunities for agriculture. Journal of Controlled Release. 2019;**294**:131-153

[66] Afreen S et al. Carbon-based nanostructured materials for energy and environmental remediation applications. In: Prasad R, Aranda E, editors. Approaches in Bioremediation: The New Era of Environmental Microbiology and Nanobiotechnology. Cham: Springer International Publishing; 2018. pp. 369-392

[67] Ashfaq M et al. Cytotoxic evaluation of the hierarchical web of carbon micronanofibers. Industrial & Engineering Chemistry Research. 2013;**52**(12):4672-4682

[68] Ashfaq M, Khan S, Verma N. Synthesis of PVA-CAP-based biomaterial in situ dispersed with Cu nanoparticles and carbon micro-nanofibers for antibiotic drug delivery applications. Biochemical Engineering Journal. 2014;**90**:79-89

[69] Ashfaq M, Verma N, Khan S. Copper/zinc bimetal nanoparticles-dispersed carbon nanofibers: A novel potential antibiotic material. Materials Science & Engineering. C, Materials for Biological Applications. 2016;**59**:938-947

[70] Ashfaq M, Verma N, Khan S. Novel polymeric composite grafted with metal nanoparticle-dispersed CNFs as a chemiresistive non-destructive fruit sensor material. Materials Chemistry and Physics. 2018;**217**:216-227

[71] Khare P et al. Carbon nanofibers containing metal-doped porous carbon beads for environmental remediation applications. Chemical Engineering Journal. 2013;**229**:72-81

[72] Kumar D, Talreja N. Nickel nanoparticles-doped rhodamine grafted carbon nanofibers as colorimetric probe: Naked eye detection and highly sensitive measurement of aqueous Cr^{3+} and Pb^{2+}. Korean Journal of Chemical Engineering. 2019;**36**(1):126-135

[73] Sankararamakrishnan N, Chauhan D, Dwivedi J. Synthesis of functionalized carbon nanotubes by floating catalytic chemical vapor deposition method and their sorption behavior toward arsenic. Chemical Engineering Journal. 2016;**284**:599-608

[74] Saraswat R et al. Development of novel in situ nickel-doped, phenolic resin-based micro–nano-activated carbon adsorbents for the removal of vitamin B-12. Chemical Engineering Journal. 2012;**197**:250-260

[75] Sharma AK et al. Preparation of novel carbon microfiber/carbon nanofiber-dispersed polyvinyl alcohol-based nanocomposite material for lithium-ion electrolyte battery separator. Materials Science & Engineering. C, Materials for Biological Applications. 2013;**33**(3):1702-1709

[76] Singh S et al. Preparation of surfactant-mediated silver and copper nanoparticles dispersed in hierarchical carbon micro-nanofibers for antibacterial applications. New Biotechnology. 2013;**30**(6):656-665

[77] Talreja N, Kumar D, Verma N. Removal of hexavalent chromium from water using Fe-grown carbon nanofibers containing porous carbon microbeads. Journal of Water Process Engineering. 2014;**3**:34-45

[78] Talreja N, Verma N, Kumar D. Carbon bead-supported ethylene diamine-functionalized carbon nanofibers: An efficient adsorbent for salicylic acid. Clean–Soil, Air, Water. 2016;**44**(11):1461-1470

[79] Bhadauriya P et al. Synthesis of yeast-immobilized and copper nanoparticle-dispersed carbon nanofiber-based diabetic wound dressing material: Simultaneous control of glucose and bacterial infections. ACS Applied Bio Materials. 2018;**1**(2):246-258

[80] Pérez-de-Luque A. Interaction of nanomaterials with plants: What do we need for real applications in agriculture? Frontiers in Environmental Science. 2017;**5**(12):1-7

[81] Rico CM et al. Interaction of nanoparticles with edible plants and their possible implications in the food chain. Journal of Agricultural and Food Chemistry. 2011;**59**(8):3485-3498

[82] Aslani F et al. Effects of engineered nanomaterials on plants growth: An overview. The Scientific World Journal. 2014;**2014**:28

[83] Priyanka N, Venkatachalam P. Biofabricated zinc oxide nanoparticles coated with phycomolecules as novel micronutrient catalysts for stimulating plant growth of cotton. Advances in Natural Sciences: Nanoscience and Nanotechnology. 2016;7(4):045018

[84] Tan W, Peralta-Videa JR, Gardea-Torresdey JL. Interaction of titanium dioxide nanoparticles with soil components and plants: Current knowledge and future research needs–A critical review. Environmental Science: Nano. 2018;**5**(2):257-278

[85] Shen CX et al. Induction of programmed cell death in Arabidopsis and rice by single-wall carbon nanotubes. American Journal of Botany. 2010;**97**(10):1602-1609

[86] Liu Q et al. Carbon nanotubes as molecular transporters for walled plant cells. Nano Letters. 2009;**9**(3):1007-1010

[87] Zhu Z-J et al. Effect of surface charge on the uptake and distribution of gold nanoparticles in four plant species. Environmental Science & Technology. 2012;**46**(22):12391-12398

[88] Kamaly N et al. Degradable controlled-release polymers and polymeric nanoparticles: Mechanisms of controlling drug release. Chemical Reviews. 2016;**116**(4):2602-2663

[89] Mout R et al. Surface functionalization of nanoparticles for nanomedicine. Chemical Society Reviews. 2012;**41**(7):2539-2544

[90] Demirer GS et al. High aspect ratio nanomaterials enable delivery of functional genetic material without DNA integration in mature plants. bioRxiv. 2018;**14**:179549

[91] Abdallah NA, Prakash CS, McHughen AG. Genome editing for crop improvement: Challenges and opportunities. GM Crops & Food. 2015;**6**(4):183-205

[92] Joldersma D, Liu Z. Plant genetics enters the nano age? Journal of Integrative Plant Biology. 2018;**60**(6):446-447

[93] Zhao X et al. Pollen magnetofection for genetic modification with magnetic nanoparticles as gene carriers. Nature Plants. 2017;**3**(12):956-964