



Carbon Nanomaterials towards Transformation in Agriculture : A Review

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ABSTRACT

Population problem is a global crisis. It is a challenge to ensure supply food towards massive population through the utilization of limited resources. Nanotechnology is a potential tool in employ in attaining sustainability in food and feed production. Thus, with advancement in nanotechnology, application of carbon nanomaterials (CNMS) has become a promising technique in enhancing agricultural production. CNMs with their excellent physico-chemical properties, possess various positive impacts in growth and development of crop plants through regulation of different processes of plant physiology and genetics. Despite some challenges, there is potentiality of carbon-based nanomaterials application in agricultural and environmental aspects regarding climate changing issue. Therefore, this review paper evaluate firstly, the impact of CNMs plant biotechnology for developing of crop species with desired gene; secondly promoting crop tolerate against different stresses; and finally pledging a better environment with some prospects of transformation crop production in a sustainable way.

Key words: Nanotechnology, Plant biotechnology, stress tolerance, yield and sustainability

Introduction

Feeding the future is becoming a challenge day by day. Because the population of the world is increasing rapidly whether the production of agricultural commodities is need to rise in parallel way. By 2050, the world population is assumed to raise about 9.1 billion, thus it is expected to reduce the cultivable land due to non-agricultural activities. Moreover, climate changing extent, biotic and abiotic stresses act as obstacles in sustaining agricultural production. Agriculture is always indispensable sector as it provides the raw materials to food and feed industries. However, agricultural productivity is confronted by the insufficient space, disease-pest infestation, and alteration in agro-climatic circumstances. Therefore, this loads need to reduce by adopting modern technologies for improving agricultural production. Thus, the sustainable progress in agriculture can be enhanced greatly through the adoption of smart and innovative techniques such as nanotechnology (Saranya et al. 2019, Giller et al. 2021).

With potential of application, more than 1300 commercial nanomaterials are currently available. The synthesis of nanomaterials with specific size, configuration and properties has extended their effective application in several fields of agriculture. However, NMs used in agriculture may be of natural origin or engineered particles. Engineered nanomaterials (ENs) can roughly be categorized into organic, inorganic, and combined materials including surface-modified clay (Saranya et al. 2019). Thus, Carbon nanomaterials (CNMs), a group of engineered nanomaterials (ENMs) having exceptional versatile properties (like optical, electrical, mechanical, and thermal) have been applied in agriculture sector for enhancing productivity (Srivastava et al. 2015).

Exposure of CNMs in terrestrial plants, have been observed stimulatory and beneficial impacts on the growth and development crop plants. These outcomes have amplified the interest in the potential applications in agricultural production as well as food manufacturing process (Serag et al., 2015). However, CNMs have revealed promising effects on plants, starting from low to moderate high doses of CNTs to improve over-all plant growth. In addition, CNMs have potential to increase seed germination, nutrient uptake, and fruit quality. Besides germination and growth enhancement due to CNMs exposure; CNMs have been demonstrated to affect physiological parameters in plants positively. However, results from several studies illustrate that the beneficial responses are largely depend on concentration/types of CNMs, nature of the growing medium and growth conditions, and plant species (Mukherjee et al. 2016). In spite of having some challenges in adopting nanotechnology in crop production, it has created immense scope of ensuring food security for mankind. Therefore, this review article clearly depicts the aspects of CNMs exposure in the field of plant biotechnology for improving plant genetic make-up, and subsequent build-up of plant vigor towards sustaining during different stress conditions and finally ensuring a clean environment through application of CNMs adopted different technologies with some potential prospects towards a better world in future.

What is carbon nanomaterials (CNMs)?

CNMs are materials that are deliberately manufactured with a size range from 1 to 100 nm in diameter and starting from a few μm to mm in length, and they may be used as a single particle or in the form of aggregates (Wang et al., 2013). They have different physical, chemical, and electrical properties than their bulk counterparts which open a new roads in the arena of science, including the agricultural sector (Khan and Upadhyaya 2019). The most frequently manufactured CNMs for several applications include carbon nanotubes (CNTs), graphene, graphene oxide (GO), fullerenes (C_{60}), full erols, carboxyfullerenes, carbon nanoparticles (CNPs), carbon nanohorns (CNHs), carbon nanodots (CNDs), nanocarbon sol (CNS), carbon nanofibers (CNFs), fluorescent carbon dots (FCDs) etc (Verma et al., 2018). Among these CNMs, the most frequently used ENPs are CNTs including single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs), GO, fullerene and fullerol in agricultural sector.

Interestingly, in spite of the above listed forms, CNTs are among the ten most manufactured ENMs, and also along with graphene, CNTs are regarded worthwhile for extended use in commercial applications (De Volder et al. 2013, Keller et al. 2013). The worldwide production of CNTs were reported from 55-3,300 tons and fullerenes from 0.6-1620 tons (Sun et al., 2014). However, the actual impact of carbon nanomaterials largely reliant their composition, size, surface charge, concentration, and physic-chemical properties along with the vulnerability of the plant species (Ma et al., 2010; Lambrea et al., 2015). Therefore, depending on the purposes, varirious forms of CNMs are being used with diverse size, concentrations and so on.

CNMs in agriculture

The necessity for nanotechnology in the agriculture is to improve crops, investigate plant health, enhancing plant nutrient absorption capacity, monitor soil quality and diagnose diseases-pest infestation, which ultimately will contribute in enhancing plant performance, those are maintained in all breeding programs (Sertova, 2015). The incorporation of carbon-based nanomaterials such as nano biosensors, nano encapsulated agrochemicals have the potential to enhance the nutritive value and yield of crop (Yashveer et al., 2014). Moreover, CNTs acts as a pore and assist the uptake of water by the seed coat and channelize water from substrate to the seeds. Thus, it can improve germination in rainfed agriculture (Reddy et al., 2017). Crop production can be intensified (35 to 40%) through the application nano-fertilizers. For instance, using carbon nanoparticles along with fertilizer can improve grain yields of rice (10.29%), wheat (28.81%), soybean (16.74%), maize (10.93%) and vegetables (12.34–19.76%) (Shang et al. 2019). However, the performance of plant due to application of CNMs may vary according the variation in nanomaterials properties. Apart from overall improvement of CNMs in agriculture, some specific areas are included here.

CNMs in advancement of plant biotechnology

Application of CNMS in plant and agricultural research is still in recent progress in regards of nanobiotechnology (Majeed et al. 2020). CNMs have been revealed to improve germination and growth of various plant species, which extends their applicability of emerging nano-biotechnology arena towards crop science (Martínez-Ballesta et al. 2016). However, various promising results in delivery of genes for transformation as well as transfection, resulting advances of agricultural production, increasing crop yield (Kashyap et al., 2015). In addition, carbon nanoparticles are easier to deploy, have high affectivity, low toxicity and faster rates of action. Fluorescent nanoparticles are being used as a gene carriers in plants since 2012 (Jiang et al., 2014). These nanoparticle-based gene carriers' possess high stability and solubility (Lachowicz et al., 2017). They may enter plant cells to carry DNA and dsRNA, which were successful in knocking down expressions of developing genes, and thus implementing the classic RNAi in plants may happen. Moreover, several studies indicated that CNMS such as graphene/CNTs were applied for gene transfection with a green fluorescent protein (GFP) of pIRES- plasmid conjugated in different cell lines; for delivering small genomic substances by conjugation with chitosan. Moreover, the attachment of oxygen groups on the MWCNTs surfaces by applying plasma treatment while the composites are physically mixed and being used for gene transfection, with great transfection efficiency and low cytotoxic levels (Zanin et al. 2014).

In the field of nanobiotechnology, with the improvement of bionic plants by implanting nanoparticles into the cells or chloroplasts of living plants with a view to imaging or sensing objects in their growing environment and to interconnect as self-powering of plants as light sources which has huge potentials in precision farming (Ghorbanpour and Fahimirad et al. 2017, Kwak et al. 2017). For example, result from a study it is observed, through the insertion of SWCNTs in plants enhances the rate of electron transfer of light-adapting chloroplasts by 49% under in vivo growing conditions by increasing photoabsorption (Giraldo et al. 2014). They also stated that these nanoparticles contributed to the capacity of light-harvesting and suppress the generation of ROS (reactive oxygen species) in chloroplast and influenced the process of sensing in plants; resulting an increased efficiency of photosynthesis and quantum yield in crop plants. Moreover, MWCNTs are used proficiently in plant growth studies through regulation of hormones like auxin which can assist researchers to explore how roots of plants acclimatized to the environment, mostly to the marginal/polluted soils (Dimri et al. 2020).

A crucial potential of nanotechnology is the development of genetically modified (GM) crops with enhanced performance and yield augmentation, which is the utmost need to meet the demand of increasing produce. Thus, it can be achieved by application of several principles of nanobiotechnology, like natural or induced mutation, transgenic breeding etc. (Adlak et al., 2019).

Another essential potential of nanotechnology is the advancement of adisease-pest resilient varieties through suitable breeding programs which integrate nano-based carbonaceous materials. However, it can be obtained by incorporating nanoparticle mediated genes or specific DNA of our desired interest into a targeted crop plant (Prasad et al., 2017). Thus through application of CNMs, it is possible to insert desired gene in crop plant to attain specific goal.

CNMs in stress tolerance of plants

The responses of abiotic stress in plants are complex which includes changes in morphology, physiology and also plant metabolism. For efficient biotic and abiotic stress management, engineered nanomaterials especially CNMs can be applied in plants in the state of nanosized fertilizers, herbicides,

pesticides and systems of smart delivery, sensors by expending little money and energy. Abiotic stresses like flood, drought, nutrient deficiency, metal stress, light and heat are the key constraints affecting growth and productivity. The research community with a major concern in overcoming loss in crop production induced via abiotic stress. Therefore, several carbon NPs are being considered to evaluate their potentiality to protect plants from abiotic stresses, modifying various plant processes to improve plant growth (Khan and Upadhyaya 2019).

Several strategies are followed to increase the tolerance level of plants to abiotic stresses, which include the development of genetically-engineered crop varieties comprising various gene paradigms supposed to augment the plant performance under stress conditions. Moreover, by application of carbon nanoparticles, increases in seed germination, seedling growth and also physiological activities such as photosynthesis and metabolism, activities of POX, APX, CAT, chlorophyll contents in leaf, and overall carbohydrate contents, protein, and yield occur. And also changes in gene expression positively indicate the potential usage in crop improvement. Moreover, these particles enhance the water stress tolerance via increasing water uptake and hydraulic conductance of roots; thus possess differential profusion of proteins included in ROS detoxification, oxidation-reduction, hormonal pathways and stress signaling in plants. As these nanoparticles are highly mobile in nature, this clues to quick transport of nutrients towards the whole plant parts (Das and Das 2019). For example, the rate of germination, seedling growth, and physiological aspects were improved in watermelon by application of different concentrations of CNMs, and such exposure increased the activities of SOD, POD and CAT comparing to control treatments which facilitated mitigation of various abiotic stresses of watermelon. Moreover, CNTs, can be served as a synthetic antennae for chloroplast which would assist the chloroplast to capture green light, infrared and ultraviolet (UV) (Giraldo et al., 2014; Shweta et al., 2016). In another study, in salt stressed crop like broccoli (*Brassica oleracea*) positive effects of MWCNTs were examined, which showed uptake and transportation of water improved (Martínez-Ballesta et al. 2016). Similarly, in *Hyoscyamus niger* seedlings, SWCNTs at a low concentrations can boost up plant tolerance against lower to moderate levels of drought (Hatamiet al. 2017). Application of polyhydroxyfullerene (PHF), a water-soluble carbon nanomaterial, can reduce the toxicity level in plants induced by heavy metal like Cd (cadmium) (Pradhan et al. 2017). Similarly, in *Arabidopsis thaliana* plant, application of MWCNTs reduced the paraquat toxicity and promoted the plant growth (Fan et al. 2018).

Research reports have explained the potential application of nanocarbon in plant pathology, mentioning as a significant tool for disease-pest control. For example, graphene oxide sheets having a single cylindrical wall or multiple walls at the nanoscale, can be a potential antimicrobial motion has been found. The antimicrobial action of carbon nanomaterials has been observed against fungi and bacteria, accompanied by positive impacts on plant growth (Wang et al. 2014). Fast detection of pathogens is crucial for successful crop production during disease infestation. For diagnosing, nanotechnology offers key advances in identification of pathogen (more sensitive one). However, carbon nanoparticles can be used as a rapid diagnostic tools for pathogens like fungi, bacteria, nematode and virus causing disease to plants. In addition, the superior antimicrobial activity of CNMs and the certain forms can be produced in a large scale at comparatively low cost and this can be expanded as a disease management tool and also as agricultural amendment in deed (Elmer and White 2018). Thus the usage of CNMs can be a potential tool in plant abiotic and biotic stress management to sustain crop growth and yield.

CMNs in reducing environmental pollution

Now a days, one of the major global challenges is environmental pollution since pollutants of diverse nature pollute agricultural and urban areas. Thus, to lessen the contamination extent, proper remediation approaches to get a sustainable environment, it is essential to increase the efficiency to introduce innovative methodologies. In this regard, nanotechnology, and especially carbon-based nanomaterials can largely contribute as they have a massive absorption potentiality due to their high surface area than conventional ones (Song et al. 2019). For example, several conventional wastewater managements used activated charcoal as an adsorbent earlier; and it can adsorb a large variety of organic and inorganic pollutants, while the adsorption rate is very poor and it is ineffective and nonspecific towards microorganisms. Thus, wastewater management techniques can be upgraded by using various forms of CNMs instead of conventional methods (Majeed et al. 2020).

Carbonaceous nanosorbents possess well controlled pore size distribution, higher surface area to volume ratio and manipulated surface chemistry. Because of their greatly porous and hollow structure with big specific surface area, having light bulk density and strong interface between CNTs and toxic molecules, the applications of CNTs for the exclusion of hazardous pollutants from large scale aqueous solutions and gas streams, have been experimented widely via theoretical and experimental extents with molecular simulations. Thus, numerous studies have been done already on the adsorption of several organic chemicals, heavy metal ions, small molecules and radionuclides (Lee et al. 2016). Consequently, CNMs play a significant role in wastewater treatment and monitoring air pollution. In the wastewater treatment plants, different forms of CNMs act as nanofilters, sorbents, and antimicrobial agents to eradicate organic and inorganic contaminants, and also pathogenic microorganisms. In case of monitoring air pollution, advances in carbon nanotube-based gas sensors resulting great sensitivity with quick sensor response towards pollutant gases (Peng et al. 2020). Therefore, CNMs in sensing of Air Pollution is important for various environmental applications, and there are a huge number of sensor materials has been developed till now. The outstanding optical and electrochemical properties of CNTs stimulated the interest of scientists to explore the potential of CNTs application as sensing component to monitor and detect the concentration of poisonous gases released in the environment. Moreover, CNTs grounded gas sensors provide a number of advantages than conventional sensors with low operating temperature and power consumption as well as high sensitivity (Elhaes et al 2016). Therefore, with the advances in nanotechnology and its proper application, it is possible to maintain a clean ecosystem through the whole universe.

Harmful aspects of CNMs

In recent days, the use of nanotechnology in plant breeding and other prospective agricultural fields has prompted concerned authorities, including breeders, agriculturists, environmentalists, researchers, and even the general public, to express concerns about the initial and long-term safety of beings, the environment, and environmental parameters (Ndlovu et al., 2020). Every potential technology possess to some drawbacks to an extent. Likely, in

spite of having wide scope of CNMs application in agriculture, there are various limiting aspects impeding the extensive use of CNMs. Many studies have also reported the negative impact of using carbon and metal oxide nanoparticles on plant growth and seed germination, hence causing phytotoxicity, cytotoxicity, and genotoxicity (Prasad et al., 2017). For example, though carbon nanotubes facilitated better root elongation in cucumbers and onions, it was found that they significantly decreased the root length in tomatoes (Mishra et al., 2017). Researchers have shown that in artificial plant cultures with selected CNMs have solidified toxicity at cellular (physiological), and genetic levels (Ghosh et al. 2015). The strength of the CNMs in a complex media, involved contaminants and heavy metals from CNMs (Bennett et al. 2013). Moreover, toxic heavy metals (such as Ni, Fe and Co) related with CNMs (mostly CNTs) could also change the whole toxicological profile. The phytotoxicity of five different kinds of nanomaterials (multiwalled carbon nanotubes, aluminum, alumina, zinc, and zinc oxide) have been stated on seed germination and development of plants. Studies have observed a potential of fullerenes to enhance accumulation of organic pollutants in plants and caused inhibitory impact on maize and soybean crops (De La Torre-Roche et al 2013). Therefore, an inclusive knowledge of the degradation kinetics of the CNMs in the environment is essential to understand the primary mechanistic pathways. Moreover, direct physical contact has been revealed to modify plant physiological and biochemical parameters such as germination rates, growth, ROS production and biomass production. Result of several studies in the literature representing CNM mediated modification of pesticide toxicity in terrestrial plants like soybean, zucchini, lettuce, tomato, etc. (Hamdi et al., 2015).

Improper application of this technology can pose a greater risk to living organisms. The negative influence of nanomaterials on plants and soil organisms has been need to identify broadly. The accumulation of carbon nanomaterials in food crops may give rise to several human health concerns and also environmental issues (Ghouri et al., 2020). Moreover, these tiny particles with different properties may transfer from soil to plants and subsequently to higher trophic levels is required to known in large scale as it possess a greater potentiality in obtaining maximum crop yield.

Prospects CNMs in attaining sustainability

Nanotechnology can bring a succeeding agri-tech revolution, transmuting agriculture to more efficient and sustainable way. This technology in agricultural production will continue to spread along with advance in nanotechnology and understanding of plant- carbon nanomaterial interaction (Lowry et al., 2019). Apart from, the advancement of plants through nano-biotechnology, tolerance of plants towards stresses and protecting the environment from varying degrees of pollution, CNMs are crucial with future prospects. CNMs may create an immense scope of generating renewable energy sources. Global consumption of marketed energy is predicted to increase by 57% between 2004 and 2030. This phenomenon anticipates the requirement for advance renewable energy source technologies in order to meet the long term energy demand challenge and protect the environmental balance. However, carbon sources for preparing CNMs largely focus on non-renewable petroleum and coal products, such as methane (CH₄), ethylene (C₂H₄) and benzene, which is giving an arise of many serious problems like energy scarcity and environmental catastrophe. Thus, for seeking, environmentally friendly, low-cost and renewable carbon sources and exploring the consistent methods towards CNMs preparation are the key factors. As, biomass originated from the photosynthesis (carbon dioxide, water and solar light) is the richest renewable source of carbon in nature. The world's yearly biomass production is around 146 billion tons where carbon accounts for 20 billion tons (Abnisa and Daud 2014). Moreover, biomass as a by-product of agriculture, forestry and industry (like grain planting, forest mining, pulp and paper manufacturing, and bioethanol fermentation) has largely produced each year (Kumar et al. 2009). Thus, researches have revealed the latest advancement in synthesis of CNMs (such as CNTs, CNFs, graphene) from biomass. This will also provide an efficient waste management way to make the environment clean. In addition, porous-activated carbon (PAC) materials have also been playing a vital role in meeting the challenges of the ever-increasing demand for alternative clean and sustainable energy technologies. In the present scenario, a facile approach is suggested to generate hierarchical PAC at various activation temperatures by using cow dung (CD) waste (Rajabatharet al. 2020). Thus, production CNMs from collective biomass and its usage in various fields of agriculture will provide a new era of attaining a sustainable ecosystem.

Conclusion

In consideration with the potential challenges, particularly, due to rapid growth of population globally and the impact of climate change, the application of nanotechnology and specifically the introduction of carbon nanomaterials in agriculture may contribute greatly to attain sustainability in global food production. Therefore, the exposure of carbon nanomaterials for improving plant genetical properties, enhancing plants capacity towards combating biotic and abiotic stresses, and also protecting our environments from noxious pollutions. However, studies have revealed both the positive as well as negative effects of usage of carbon nanomaterials. Further advancement in research on carbon nanomaterials is required regards the issue of agricultural crop species, properties of nanomaterials as well as the environmental conditions.

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