CHAPTER 11

Applications of Nanotechnology and Carbon Nanoparticles in Agriculture

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ABBREVIATIONS

Al_2O_3	aluminum oxide
ATP	adenosine triphosphate
AuNPs	gold nanoparticles
CNF	carbon nanofibers
CNPs	carbon nanoparticles
CNT	carbon nanotubes
CP	coat protein
CTV	*Citrus tristeza virus*
CVD	chemical vapor deposition
dsDNA	double-stranded DNA
ELISA	enzyme-linked immunosorbent assay
FRET	fluorescence resonance energy transfer
Gd_2O_3	gadolinium(III) oxide
GQD	graphene quantum dot
HSBM	high-speed ball milling
IP	identity preservation systems
La_2O_3	lanthanum(III) oxide
MWCNT	multiwalled carbon nanotubes
NADPH	nicotinamide adenine dinucleotide phosphate
Pd	palladium
PEG	polyethylene glycol
QD	cadmium-telluride quantum dots
SDS	sodium dodecyl sulfate
Si	silicon
ssDNA	single-stranded DNA
UCP	upconverting phosphors
WsCNO	water-soluble carbon nano-onions
Yb_2O_3	ytterbium oxide

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11.1 INTRODUCTION

In 1959, Richard Feynman, a physicist, opened up a new field named as nanotechnology by his classical lecture entitled "There is plenty of room at the bottom" at the annual meeting of the American Physical Society [1]. In the last 30 years, humankind has achieved extraordinary potential to manipulate materials at extremely small scales [2]. The field of nanotechnology refers to the molecular and submolecular technology on the nanoscale, typically smaller than 100 nm [2]. Any organic or inorganic materials that fall into this small size range can be considered as nanomaterials, and by decreasing the particle dimensions, the surface-to-volume ratio is impacted considerably. This surface-to-volume ratio shifts lead to the important features of nanomaterials, which is its large surface-to-volume ratio. The surface is a critical feature of the material since it provides the interface between the material itself and its surrounding environment. Nanomaterials have been applied in different aspects of biology including biological labeling [3, 4], gene and drug delivery [5, 6], probing of nucleotide structures [7], and tissue engineering [8, 9]. On the other hand, within the last decade, the diagnostic field of study has advanced considerably by utilizing nanomaterials in biology and medicine to develop fast, economic, and sensitive techniques [10].

Carbonaceous nanomaterials are considered as the most widely discussed and utilized nanomaterials within this decade. The discovery of C60 fullerene is recognized as the initial stage of the revolution of carbonaceous nanomaterials [11]. Carbon nanoparticles (CNPs) are classified as a remarkable type of recently developed quasispherical carbonaceous nanomaterials with sizes bellow 10 nm. CNPs, by presenting a strong photoluminescence depending on size and excitation wavelengths, have attracted substantial attention as nascent fluorescent molecule, practically in the fields that cost, size, water solubility, transparency, and biocompatibility of the labels are important. Thanks to the existence of numerous carboxylic moieties on the surface, CNPs present outstanding water solubility and competency for consequent functionalization such as with polymeric, organic, inorganic, and biological molecules. CNP unique properties such as well-defined shape; small-sized dimensions; harmonic and adjustable surface functionalities; and their simple, fast, economic, and nontoxic synthesis procedures make them an encouraging alternative to other nanoparticles especially toxic metal-based quantum dots. The typically useful features of CNP are shown in Fig. 11.1. Evidently, there is a promising chance for nanotechnology to play a profound role in medicine, energy, electronics, physics, mechanics, materials sciences, environment, biotechnology, and agriculture sector. Nanotechnology could provide a profound impact on agriculture by focusing toward agricultural sustainability, improved varieties, increased productivity, disease management, and crop protection [12, 13].

11.2 APPLICATIONS OF NANOTECHNOLOGY IN AGRICULTURE

The extensive range of unique and beneficial nanotechnology finds wide applications ranging from electronics, energy, biology, and even in the agricultural sector.

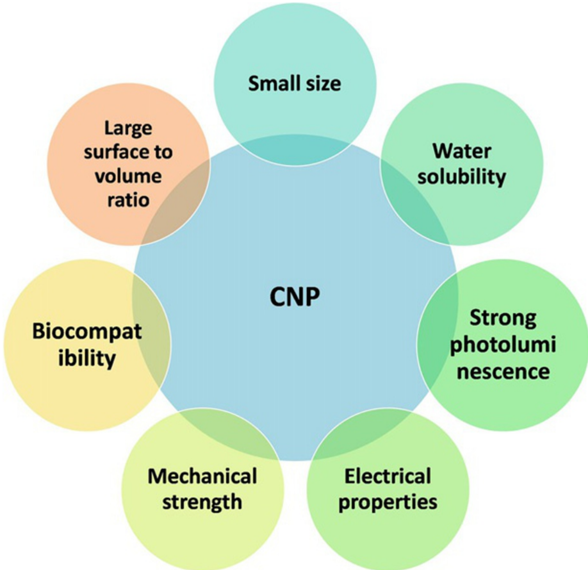

Fig. 11.1 Important features of CNP.

The developments of nanotechnology in agriculture have globally earned an increasing attention in the 21st century, since it is involved in every possible system that is involved with agriculture. Nanotechnology in agriculture was initiated when researchers found that conventional farming technologies were unable to increase agricultural productions and furthermore could save ecosystems by decreasing the amount of water, fertilizers, and pesticides used. In fact, nanotechnology may play a substantial role in sustainable agriculture and precision farming development. The use of nanotechnology in agricultural science is increasing due to the demand for higher agricultural yields by a constantly growing population. In addition, nanotechnology in agriculture may provide precision farming technologies for maximizing the crop yield through the usage of sensors and monitoring devices, thus boosting global food production and showing positive impact in the agricultural sector [14]. Fig. 11.2 illustrates the vast applications of nanotechnology in the agricultural sector. Each application will be discussed briefly in the following subsections.

11.2.1 DNA Sequencing

DNA sequencing is the procedure that is used to determine the order of nucleotides within DNA strands accurately. The most important requirements for DNA sequencing are to improve the accuracy and quantity of analysis per analysis. Nanotechnology is applicable for both advancing the current techniques and developing new approaches for sequencing. Recent studies on DNA sequencing have used nanobiotechnology to advance the sequencing approaches through nanofabricated gel-free systems.

Fig. 11.2 Nanotechnology applications in agriculture.

These newly developed systems would allow fast and accurate multiplex DNA sequencing [15, 16]. By using novel approaches in the molecular genetic analysis of the cultivated crop and the wild relative gene pools, extremely valuable data about molecular markers related to economically and agronomically significant traits can be recorded [17]. Therefore, by using nanotechnology-based techniques, molecular marker-assisted breeding area can be improved significantly.

11.2.2 Microarrays

Developing microchips is one of the main areas that is advanced by applying nanotechnology. In these systems, the immersed biomolecules in fluids are manipulated and immobilized on the chip surfaces, allowing lab-on-chip biochemical processing.

Several biochemical processes like sampling, mixing, amplification, separation, sensing, and analysis could be performed on chips. Nanotechnology can be utilized to pattern the surface of chips for an extensive range of sensing and medical purposes [18–21]. In microarray-based hybridization techniques, the expression level for thousands of genes is measured simultaneously. This process is indicated as "expression profiling," and important data about diverse features of gene function and regulation can be investigated [22]. DNA microarrays as another type of microarray systems are used for screening gene regulation and function, detecting mutations in disease-related genes, determining the important genes for crop production, and improving the monitoring system for microbes used in bioremediation.

Without deep information about the function of genes, gene sequencing and chromosome mapping would not be practical, so protein microarrays are developed to solve this limitation [21]. Protein microarrays are applied in a broad range of purposes including the discovery of protein biomarkers attributed to diseases, studying the relationship between protein structures, assessment of efficiency and toxicity of natural and synthetic pesticides, measuring the protein production and function, sensing of disease-associated proteins, and evaluation of binding between proteins and other molecules.

11.2.3 Sensing of Plant Diseases

Plant diseases often are the most important limiting factor in the agricultural production that leads to a significant economic losses [23]. Due to the fact that detection should be carried out at the exact stage of prevention (viral DNA replication stage or initial viral protein production), managing plant diseases is hard [24]. Mostly, disease management is performed by applying pesticides. Using pesticides leads to toxicity and environmental risks. Moreover, using pesticides after the emergence of disease results in crop losses.

Viruses have been critically identified as a main threat to different plants [25] because of their high level of communicability, virulence, and mutation rate. Moreover, viruses remain intangible via a variety of mechanisms and can often be complicated to be quickly recognized [26]. Unlike virus-infected crops and fodder that can still be consumed, the fruit trees and ornamental plants can be completely eradicated or can cost a significant economic loss by unfavorable fruit quality or productivity [25].

Advances and convergence of molecular biology, nanotechnology, bioanalytical chemistry, and electrochemistry have paved the path for more sensitive, specific, and rapid biosensors with a vast range of applications from bioterrorism to plant diseases repeatedly ascribed as nanobiosensors. Nanobiosensors are usually described as analytic devices that can detect disease by applying biological recognition elements associated with a physicochemical transducer or transducing microsystem including electrochemical, optical, piezoelectric, thermometric, and magnetic transducer [27, 28].

Nanobiosensors can be used for the detection and quantification of various kinds of biological moieties including antibodies, antigens, nucleic acids, or other biologically relevant small molecules, which are used as markers for a particular disease [29–35]. The interaction between the recognition elements and the target molecules causes physical or chemical shifts, which leads to the production of heat, mass, light, electrons, or ions [36]. Nanobiosensors include usage of a numerous nanomaterials, such as gold nanoparticles (AuNPs) [37], magnetic nanoparticles [38], quantum dots (nanocrystals) [39], carbon nanotubes [40], mesoporous silica nanoparticles [41], and bionanoparticles such as virus-like particles [42].

Currently, several nanosensors have been designed for detecting different plant viruses and diseases such as rhizomania [43], tristeza [44], witches' broom disease of lime [45], *Trichoderma harzianum* [46], bacterial spot disease [47], karnal bunt disease [48], maize chlorotic mottle virus [49], *Cymbidium mosaic virus* [50], *Potato virus Y*, cucumber mosaic virus, tobacco rattle virus [51], and *Ganoderma boninense* [52].

11.2.4 Nano-Barcodes

Using barcodes for successful national and international marketing is essential. Barcodes in definition are electronic data illustrating different factors including date and place of production and packaging, chemicals and methods used for its production, and price of products. In order to read the barcodes, an electronic data reader is required. Due to the recent significant increase in the shipment of agricultural products, tracking and controlling of these products is more difficult. Moreover, the lack of resources also prohibits the requirement of inspectors to control the critical points at the borders [22].

By introducing nanotechnology in this area, tracking and controlling the quality of products and monitoring all relevant data in a short period of time have become practical [53, 54] Fluorescent nanoparticles doped with rare-earth materials have been used to develop nanobarcodes. In order to read nanobarcodes, mostly UV lamp and optical microscopes are used.

An identity preservation (IP) system provides data on the methods and chemicals applied to yield agricultural products, place and date of production, and food safety and security for both stakeholders and consumers. Since nano-based IP systems are able to track and record the history of the products continuously, it can advance the entire agricultural industry [55]. Nano-based IP can revolutionize the field of agricultural products by developing biodegradable sensors for both biological and physical factors such as ripening, color, contamination, flavor, stiffness, and texture of agricultural products.

11.2.5 Controlling the Quality of Products

Vitamins and their precursors, as insoluble materials, can be solubilized in water by being formulated as nanosized particles. These formulated nanosized particles show a high value of bioavailability in the blood. Recently, many producers have mixed fruit juices with these formulated nanomaterials to enhance the nutritional factors and also provide a more attractive color [22].

Nanosensors integrated with packaging ingredients have been developed that can examine the freshness of the products. Spoiling of agricultural products can also be monitored by change of the color or by recording the gases released. Several nanosensors have been produced by using silicon or polymer for controlling the quality of agricultural products [56, 57].

Moreover, bioselective surfaces have already been developed to monitor the presence of small amounts of chemical reactions or pathogenic agents on the surface of products. In this field, the surfaces of products are considered as the most important region on which most chemical and biological interactions would take place. These bioselective surfaces could be used for developing biosensors, catalysts, and separator and purifier platforms [58, 59].

In addition, some nanoparticles such as silver nanoparticles (AgNPs), silicon (Si), and ZnO have shown strong antimicrobial activity that is critical for producing high-quality agricultural products. They can also decrease plant disease contingency. Using AgNPs prior to the penetration and colonization of fungal spores has successfully controlled powdery mildew. It can also extend the life span of gerbera flowers by reducing microbial growth and vascular blockage of flower [60]. In the same way, ZnO is able to inhibit the microbial activity *Penicillium expansum* and *Botrytis cinerea* [61]. Moreover, Si could increase disease and stress resistance by absorbing into plants. It inhibited the growth of powdery mildew and enhanced plants physiological activity [62].

11.2.6 Agricultural Waste Management

Shortage of skilled personnel and the lack of mechanization can lead to the production of large amounts of waste throughout any agricultural process, from planting and processing to storage. Due to the limitation in the waste processing, the waste can either become rotten or damaged that would cause crop loss. By using nanobioengineering, the efficiency of enzyme extraction and subsequently energy production could be enhanced. For example, by using nanometallic catalysts, the efficiency of biofuel production from the agricultural wastes such as rice husk, cotton stalk, coconut shell, corncobs, groundnut shell, sugarcane, cotton, vegetable oils, and animal fats was advanced [22, 63, 64].

Bioremediation of waste chemicals such as slowly degradable pesticides has been advanced by using nanotechnology. Nanoparticles could be used as reactant agents to degrade and convert these dangerous wastes to nontoxic materials [65]. In addition, due to the perilous effects of wastewater on the environment, removal of these waste materials is critical [66, 67]. Several strategies including nanotechnology have been developed for the treatment of wastewater. One of the most important nano-based wastewater treatments is by using photocatalysis. It has been applied for purification, filtration, decomposition, and decontamination of either water or air. It also can be used for the removal of pathogenic or destructive agents when semiconductors are used in the photocatalysis. Photocatalysis is a process in which a reaction is taken place by a catalyst in the presence of light. In this reaction, when a nanoparticle is exposed to UV light, the valence electrons in the outer layer are excited to form electron-hole pairs. Several nanoparticles including metal oxides and sulfides such as TiO_2, ZnO, SnO_2, and ZnS have been utilized as catalysts [68–71].

11.2.7 Water Managements

In the last century, the usage of plastics in microirrigation technology has enhanced the application of subsurface irrigation extensively. Subsurface irrigation systems tend to be nonflexible and heavy in weight, and troubleshooting subsurface irrigation can be difficult. In the case of any malfunction or clogs, the water waste in the conventional piping systems will increase dramatically. Therefore, due to the drawbacks of the conventional subsurface irrigation systems, there is continual interest to develop and promote traditional irrigation methods, by introducing new biodegradable, low-cost, flexible, and efficient materials in the subsurface agricultural piping systems for irrigation and water preservation especially in water-limited lands. Nanosized materials by showing high surface-to-volume ratio, flexibility, and toughness could be considered as one of the affordable choices [22]. Moreover, recently, by developing nano-based targeted gel irrigation systems such as silica in the fields of perennial plants, the water consumption decreased significantly. In this scenario, a saturated nanogel is set under individual trees, and the water flows from gel to the plant root systems through osmotic pressure differences [72].

11.2.8 Agrichemical Applications

Agrochemicals refer to all the chemicals used in the agricultural sector including fertilizers, pesticides, herbicides, plant growth regulators, and vaccines. Conventional pest and pathogen management techniques mostly rely on using these chemicals that tend to be expensive and toxic, affecting both the environment and farmers. Practically 90% of used chemicals are evaporated to the air and/or subjected to runoff during application. In addition, frequent usage of these chemicals promotes pathogen and pest resistance and decreases soil biodiversity, nitrogen fixation rate, and plant pollinator [73].

Nanomaterials with large surface-to-volume ratio are able to provide controllable platforms to decrease the amount of agrochemical usages and decline the rate of pathogen and pest resistance. Therefore, nanotechnology has been applied for targeted delivery of agrochemicals and production and application of new effective nano-based pesticides or fertilizers.

Targeted delivery of agrochemicals mostly relies on using nanoscale carriers to increase the efficiency of the delivery. This increase in the efficiency relies on providing a more efficient and controllable release, a better storage capacity, and longer stability over degradation for the agrochemicals. Moreover, these smart platforms are able to control the quantities of agrochemicals required to release by taking accurate decision for their self-adjustment [62]. Nanoscale carriers enhance the efficiency of agrochemicals through several mechanisms including encapsulation and entrapment of chemicals inside the polymers and dendrimers in surface ionic and weak bond attachment manners. For example, porous silicon nanoparticles (SiNPs) with 15 nm shell thickness and 4–5 nm in pore size were able to carry almost 600 g/kg avermectin, a type of pesticides. SiNPs could control the release rate of avermectin up to 30 days after being used [73]. Nanoscale carriers reduce the amount of chemicals to be utilized, their runoff, and environmental problems.

Clay nanotubes have been shown to be a good candidate to control the release of agrochemicals. It enhances the contact between chemicals and plants and reduces the amount and cost of chemicals by 70%–80% [65]. Anionic nanoclay was used to control the release of plant growth regulators and other agrochemicals [74].

Nanoemulsions refer to micelles of herbicides, pesticides, or fertilizers. Nanoemulsions could practically increase the effect of pesticides and fertilizers while decreasing the amount of the agrochemicals used. It can increase the dispersion and moisturizing ability of agrochemicals and reduce undesirable chemical runoff [75]. Nanoparticles and composites show unique features required for formulating nanoemulsions including permeability, high surface-to-volume ratio, solubility, thermal stability, hardness, biodegradability, and crystallinity [76, 77]. Moreover, nanoemulsions are mostly degraded faster in soil but slower in plants [78]. For instance, a nanoencapsulated imidacloprid was developed by using sodium dodecyl sulfate (SDS)-modified Ag/TiO_2 to control soybean pests [79].

11.2.9 Targeted Genetic Engineering

The genetic constitution of crops can be modified by using nanotechnology to enhance the economic and agronomic traits. Nanotechnology provides novel devices to manipulate crop genetic pools. Nanomaterials could be used as carriers to transfer a large quantity of genes and control the release of carried genes in crop genetic pools [60]. Nanotechnology is directing genetic engineering to some level down defined as atomic engineering. DNA can be manipulated to rearrange genes and regenerate a new plant with advanced agricultural and agrieconomical traits [62].

Cases in point, modified chitosan nanoparticles with polyethylene glycol (PEG) have been applied as gene carriers to release genetic materials controllably. Moreover, starch nanoparticles labeled with fluorescent molecules transported genetic materials across the cell wall by promoting immediate aperture channels in cell wall. In another try, silver nanoparticles coated with plasmatic DNA have been used to transport DNA into nucleus.

Recently, a gene gun is one of the widely used tools for plant gene pool improvement. It has been used for direct transport of genes into cell. In this platform, gold as a nontoxic particle is used as bombardment material. Previous results confirmed the successful delivery and expression of plasmatic DNA into tobacco and maize cells when gold nanoparticles were used for bombardment [60].

Both natural and artificial mutations play an imperative role in crop improvement. In the conventional artificial mutation, common chemical compounds and/or physical mutagens are used. Instead of conventional mutation, nanotechnology has shown remarkable ability in the mutation induction. For instance, a new white-grained rice variety is developed from a traditional purple-colored rice variety via nanotechnological approaches [22]. In this attempt, the walls and membranes of the cells were drilled by using a particle beam to create a nanosized hole in the wall. A stream of fast-moving particles was used as a particle beam to drill the hole, and subsequently, nitrogen atoms were inserted to the cell in order to arouse rearrangement of DNA.

11.2.10 Labeling and Imaging

Labeling of different molecules and elements is an important technique in which the transition and the pathway of several molecules and element in both plants and soils can be investigated. Labeling of molecules and elements will give researchers critical information about significance, effectiveness, and the mechanism of action of these important chemicals.

Previously, labeling of molecules was carried out by using organic dyes, but the cost and fast fluorescence degradation limited widespread application of these dyes. Fluorescent labeling of molecules by QD has recently advanced the field of luminescent labeling. Nanosized QD, as a novel generation of fluorescent probes, have been considered as alternative bioanalytical materials because of their exclusive optical features such as photostability, high fluorescence intensity, broad tenability, and narrow emission spectrum [80, 81]. QD have several advantages over conventional fluorescence dyes such as high degree of stability against photobleaching, broad excitation spectrum, high quantum yield, extended fluorescence lifetime, and narrow emission [82].

Molecular imaging, intersection of in vivo imaging and molecular biology, is providing visual representation of the cellular function and the pursuing of the molecular pathways in living organisms without disturbing them [83]. Field of imaging is advanced critically by developing nanotechnology. Fluorescent QD have been widely used for molecular imaging, and magnetic nanoparticles advanced the field of medical imaging significantly as well.

By fluorescent labeling of vaccine, in vivo imaging and mechanism of action of vaccines could be investigated. Vaccine follow-up could give more information about the disease and the tissues that are more affected by the pathogens. In this regard, CNP by providing strong fluorescent intensity, broad absorbance peak, and low toxicological effects can be used as the fluorescent labeling molecules for following up vaccines in vivo and molecular imaging.

11.2.11 Plant Growth and Germination

Plant growth and germination are significantly affected by the surrounding conditions. The presence of a chemical could induce or dissuade growth and germination [84]. Recently, several investigations have considered the effects of nanomaterials on growth and germination of plants in order to advance its application for agriculture. The effects of several nanoparticles including TiO_2, MWCNT, fullerenes, Si, palladium (Pd), Au, Cu, FTIC-labeled silica nanoparticles, QD, aluminum oxide (Al_2O_3), ZnO, Al, Zn, CeO_2, lanthanum(III) oxide (La_2O_3), gadolinium(III) oxide (Gd_2O_3), and ytterbium oxide (Yb_2O_3) on germination of different plants such as spinach, tomato, lettuce, rice, radish, rape canola, ryegrass, corn, cucumber, wheat, and cabbage have been studied frequently. These studies confirmed the positive effects of nanoparticles on germination rate, dry weight, photosynthetic rate, and chlorophyll formation of plants. Mostly seed germination rate is inversely correlated to the nanoparticle size in which smaller nanoparticles provide the higher rate of germination. This increase in the germination rate is due to the enhancement in the photosterilization and photogeneration of active oxygen, for example, superoxide and hydroxide anions. This active oxygen will enhance the stress resistance and shell penetration level of the seeds. Increase in capsule penetration of the seeds will result in higher rate of water and oxygen intake into the seeds and subsequently faster germination rate. Moreover, nanoparticles might have improved the absorption level of inorganic nutrients, stimulated the organic substance disintegrations, and enhanced the photosynthetic rate [78]. The effects of CNP on plant growth and germination are described in more detail in the final subsection of this chapter.

11.3 CARBON NANOPARTICLES AND THEIR PREPARATION METHODS

The importance and widespread use of carbon materials have now been extended to carbon nanomaterials. As various exciting carbon nanomaterials are emerging, they have attracted incredible interest, and due to their unique electric, chemical, and optical characteristics, they have been extensively used in a wide range of applications including hydrogen storage, water filtration, electronics, energy, biomedical, and agricultural applications [85].

Carbon nanomaterials show vast diversity in structure that include fullerenes, nanodiamonds, nano-onions, nanofibers, nanorings, nanotubes, and quantum dots (QD). In the context of this chapter, carbon nanoparticles (CNPs) are a class of nanomaterials, typically a magnitude smaller than the 100 nm size range, which cover nanoparticles either spherical or faceted in shape. Their minute size renders them with a whole set of unique properties, especially optical and electric in nature. Their inert nature has opened up possibility for biological applications that could not have been done before due to the toxic nature of their metal and semiconductor counter parts.

CNPs have superior sp^2 configuration that is representative of nanocrystalline graphite and considered as close relatives to the graphene quantum dots (GQD) that are planar in shape. CNPs contain large amounts of oxygen in their molecular structure, and because of their small size, they may be referred to carbogenic QD or simply carbon quantum dots (CQD). CNPs show spectrally unstructured broad photoluminescence emission with strong λ_{max}. The CNP photoluminescent emission occurs because of the radiative recombination of excitons placed at the energy traps on the surface.

Various techniques from high degree of complexities to simple methods have been presented for synthesizing CNP including laser ablation of graphite [86], arc discharge [87], microwave-based pyrolysis [88], carbonization of carbohydrates [89–91], chemical vapor deposition (CVD) [92], hydrothermal carbonization of waste materials [93, 94], oxidation of candle soot [95], and alkali-assisted electrochemical method [96].

In the first two methods, a solid piece of graphite carbon is heated to a high temperature where carbon atoms are separated and reassembled on a cathode in the arc-discharge method or on a chilled plate surface in the laser ablation method. In the reassembling procedure, highly ordered carbon nanomaterials are produced. In CVD, instead of a solid piece of carbon, hydrocarbon gas is applied as a carbon source that separates either thermally or in the presence of plasma. Moreover, recently, some other techniques have advanced for the synthesis of carbon nanostructures from renewable resources. Among physical methods, ball milling has recently raised as a proficient technique for the decrystallization of cellulose and synthesizing carbon nanoparticles. Since the laser ablation, arc-discharge, and CVD techniques are comprehensively explained in an earlier chapter, it will not be covered in the current chapter.

11.3.1 Carbonization-Based Procedures

Carbonization is the thermal process in which organic materials are converted into CNP via extreme pyrolysis or destructive decomposition. Carbonization consists of several reactions including dehydration, condensation, hydrogen transformation, and isomerization. It has been used for centuries in fossil fuel production by converting plants to fuels. Recently, carbonization of several carbohydrates is applied to synthesize CNP and other carbonaceous materials in a one-step manner. Due to its economic, easy handling, and nontoxic nature, carbonization is considered as a useful technique to produce CNP [97].

Carbonization of Carbohydrates

Carbohydrates are biological molecules composed of carbon, hydrogen, and oxygen atoms. Saccharide is a commonly used synonym for carbohydrates that include sugars, starch, and cellulose. Due to strong sustainability of carbohydrates, they have been widely used for producing carbonaceous materials, and some of them have strong fluorescence characteristics [98, 99]. Various carbohydrates such as glucose, sucrose, and chitosan have been used to synthesize CNP. In these techniques, mostly a carbohydrate source is carbonized at high temperature; then, alkali or acid treatment is performed as surface passivation. These surface-passivated CNPs are generally photoluminescent water-soluble materials. The passivation procedure and the source of carbon will affect the solubility and optical properties of produced particles.

Microwave-Based Pyrolysis

Pyrolysis is the irreversible thermal disintegration of materials in an environment with oxygen deficiency or when considerably less oxygen is present than needed for complete combustion. It has been used since ancient Egyptian times when tar was produced by pyrolysis and used for caulking boats and protecting agents [100]. Pyrolysis has recently advanced and is broadly applied for the production of charcoal and coal. The pyrolytic breakdown of wood generates a variety of solid, liquid, and gas chemical substances during the process [100]. Conventional pyrolysis procedure has extensively been used for producing CNP at high temperature. In this technique, a carbon source and a functionalizing agent are treated for several hours at high temperature [101].

In microwave-based pyrolysis, a microwave is used as the heating source to catalyze the thermochemical decomposition reactions. It has been used widely for the recycling of several waste materials like agricultural waste, tires, plastics, wires, and cables. Generally, organic materials have poor heat conductivity; therefore, using conventional pyrolysis for decomposition of carbohydrates is not an easy procedure. The quality of the CNP produced during the pyrolysis procedure critically depends on the capability to control the temperature. Microwave will induce high temperature into the organic source. Moreover, the temperature can be controlled by exciting the individual molecules in the organic source. For instance, microwave-assisted pyrolysis technique has been used to produce biocompatible, water-soluble photoluminescent CNP [84]. However, in this one-step synthesis procedure, inorganic ion was required to be used, but no surface passivation process was needed, and the reaction was finished in a few minutes. In another study, 1,2-ethylenediamine and citric acid were used to synthesize fluorescent CNP by using a one-step microwave-based pyrolysis [102]. The synthesis of water-soluble photoluminescent CNP, 12 nm in size, by using low-temperature microwave-assisted pyrolysis of citric acid in the presence of polyethylenimine (PEI) has also been reported [103].

Carbonization of Waste Materials

Various waste materials such as pomelo peel, banana juice, paper, sago starch, rye straw, coffee grounds, grass, and facial tissue have been used to produce CNP. Waste-derived CNPs have shown promising electrochemical features similar to CNT, CNF, graphene,

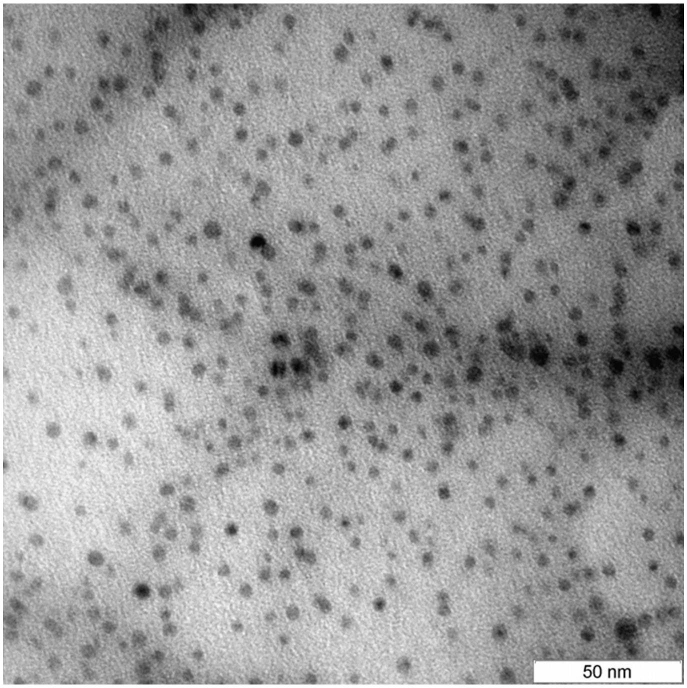

Fig. 11.3 TEM image of synthesized CNPs from waste facial tissue.

and activated carbons [97]. In these researches, the waste materials were treated with acids at high-temperature condition followed by purification and filtration. Furthermore, some facile techniques have recently been developed in which CNPs were synthesized by using regular burning procedures. For instance, Shojaei and colleagues simply burn facial tissues under ambient conditions to produce water-soluble CNP (Fig. 11.3). The synthesized CNPs were successfully functionalized with carboxyl and carbonyl groups in a one-step synthesis procedure. The produced CNP showed strong blue photoluminescence. The effect of different important variables including concentration of HNO_3, pH, sonication time, and temperature on the mean diameter of CNP was investigated. The results showed that the mean diameter of CNP is pH-sensitive while it was not affected by temperature significantly. The results confirmed the effects of HNO_3 in the addition of the carboxylic groups on the surface of CNP, but it did not affect the size of CNP [104].

11.3.2 Oxidation of Soot

In this method, soot obtained from the combustion of odorless candles or natural gas burners is used as the carbon source. The oxidation process is mostly performed by refluxing derived soot with acidic solution for a long time. This approach was first used by Mao when candle soot was used as the carbon source [11]. Derived CNPs were slightly soluble in water without the need for surface passivation. Until now, several researchers have used candle soot or combustion soot of natural gas to produce CNP [95, 105, 106].

11.3.3 Electrochemical Method

In the electrochemical techniques, electric charges are transferred between electrodes and an electrolyte. In this technique, carbonaceous electrodes are used as working electrodes, and metals are used for both counter and reference electrodes. Moreover, a solution, mostly phosphate buffer solution (PBS), is used as the electrolyte in electrochemical cells. This technique was first designed by Zhou and coworkers [107] to synthesize CNP. In their study, multiwalled carbon nanotubes (MWCNT) derived from rolled layers of graphene were deposited onto carbon paper. The MWCNT, a Pt wire, and Ag/$AgClO_4$ were served as working, counter, and reference electrodes, respectively. In another study, water-soluble long-term homogeneous photoluminescent CNPs with 3–6 nm in size were produced when graphite rod, Pt wire, and Ag/AgCl were utilized as working, counter, and reference electrodes, respectively [108].

11.3.4 Ball Milling

Ball milling as a mechanochemical technique has been extensively used for grinding of materials to fine particles and for the formation and modification of inorganic solids. Mechanochemistry is a branch of solid-state chemistry in which intramolecular bonds are broken mechanically by using an external mechanical energy followed by additional chemical reactions [109]. Its use in synthetic organic chemistry is comparatively limited but has attained more attention during the last decade. A study proposed the importance of ball milling in synthetic organic chemistry, which has been widely documented [110]. Many reports in the literature have shown that high-speed ball milling (HSBM) is appropriate for a variety of organic transformations and for the expansion of environmentally benevolent chemical reactions [111, 112]. HSBM in solvent-free circumstances is considered as a feasible alternative to wet chemistry. It is based on the similar principles as that of mortar and pestle, which utilizes mechanical actions to convert reactants to products during the course of the reaction [113, 114]. The mills are effective at creating small particle sizes, which has allowed them to demonstrate their amazing characteristics. The ball milling time is an important factor in nanostructure materials synthesis. It has been demonstrated that an increase in the milling time increases microhardness of synthesized materials [115]. Different numbers, sizes, shapes, and materials of the ball bearings used could influence mixing and impact energy and thus the efficiency of the reaction. Using no ball bearing predictably gave the least amount of mixing and energy resulting in the lowest percent conversion to product.

11.4 CARBON PRECURSORS USED FOR SYNTHESIS OF CNP

Depleting petroleum resources and environmental concerns have led to the search in finding substitute sources for producing carbon nanomaterials. In general, CNP synthesis techniques require carbon-based resources to form an underlying precursor. The commonly used petroleum-based precursors include rayon, ethylene gas, oil pitches, coal, polyacrylonitrile, and polyvinyl alcohol.

Due to the global shortages of mineral resources and energy and deterioration of the environment, synthesis of CNP from bio-based feedstocks and waste materials has attracted intense attention. Up until now, different waste materials including growing part of plants, fruit juice and skin, candle soot, and hydrocarbonaceous waste have been used to synthesize environmentally friendly and low-cost CNP. This is shown in Table 11.1.

So far, nanotechnology has been used in a broad range of applications including electronics, energy, automation, materials sciences, physics, mechanics, and life sciences. Using nanotechnology in the field of life sciences is limited to the pharmaceuticals, diagnosis, cancer therapy, and imaging. The areas where nanotechnology could have critical

Table 11.1 Summary of studies performed on the synthesis of spherical shape carbon nanoparticles from waste materials

Source of waste	Achievement	Process	References
Sago starch	Spherical shape water-soluble carbon nanodots at 20–100 nm size	Carbonization, surface oxidation, and dehydration process performed by using concentrated sulfuric acid and nitric acid in 2 h	[116]
Candle soot	CNP with 10 nm in size	The candle soot was treated by using triton X-100, dry benzene, sodium methoxide, and sonication. The disperse solution then was refluxed at 60°C for 48 h	[95]
Pomelo peel	CNP dispersed in water	Hydrothermal treatment in Teflon-lined autoclave at 200°C for 3 h. Dried under vacuum for 48 h	[93]
Banana juice	Water-soluble carbon nanodots with nominal size of 3 nm	By heating banana juice at 150°C in an oven for 4 h	[94]
Glucose	Water-soluble CNP of <5 nm	Alkali- and acid-assisted ultrasonic for 4 h. CNP was then treated by adding $MgSO_4$ for 24 h	[117]
Facial tissue	Water-soluble spherical shape CNP	Simple burning of tissue followed by HNO_3 treatment and purification. Production process takes just 1 h	[104]

influence on the agricultural sciences are limited to the food security, pathogen treatments and detections, delivery methods, and public education [22]. By this time, nanotechnology has been commonly applied in the agricultural sector theoretically, but it has begun and is expected to continue to show a critical impact in the field [13, 22, 118]. In the following section, the impact of CNP on agriculture and the expected methods for managing far-reaching advances in this field of science are discussed.

11.5 APPLICATIONS OF CNP IN AGRICULTURE

11.5.1 CNP in Nanosensors

In recent years, CNP has been used in the field of clinical diagnostic methods as an immobilizing surface [119, 120]. Moreover, they have been used widely in the detection of ions and chemical agents such as mercury(II), Sn(II), and silver(I) as shown in Table 11.2.

CNPs offer various advantages over conventional inorganic fluorescent molecules such as low toxicity, biocompatibility, low level of photobleaching, outstanding water solubility, harmonic surface immobilization, and economic synthesis procedure. This makes them appropriate alternative materials as building blocks for optoelectrical, biological, and other advanced functional platforms. The great interest in employing CNP for biological applications is critically related to this fact that the main component of CNP is carbon, a nontoxic element.

Recently, by taking advantage of the CNP, a new FRET-based nanosensor was developed for detecting *Citrus tristeza virus* (CTV). Cadmium telluride QD was conjunct with a specific antibody against CTV, and the coat protein (CP) was immobilized on the surface of CNP to investigate the efficiency of CNP in quenching mechanism of QD and subsequently develop a specific and sensitive FRET-based nanosensor for detecting CTV. With reference to the mechanism of the developed nanosensor, based on the antibody-antigen interaction phenomena, the QD-Ab and CNP-CP formed an immunocomplex. The vicinity of the QD-Ab and CNP-CP resulted in the FRET phenomena to happen. Subsequently, when CNP-CP was presented in the mixture, the emission spectrum of the QD-Ab was decreased. Meanwhile, when an infected sample was added to the mixture, the fluorescence intensity of QD was recovered into the original quantity as illustrated in Fig. 11.4. The developed nanosensor showed higher sensitivity and specificity over ELISA with a limit of detection at 0.22 μg/mL. The sensitivity and specificity of CNP/QD nanosensor were estimated to be 93% and 88%, respectively, while the sensitivity and specificity value of ELISA were found to be 80% and 88%, respectively [104].

11.5.2 CNP for Plant Growth and Germination

Agriculture is the backbone of most of the developing countries where it supplies food for human directly and indirectly, with more than 60% of the global population depending

Table 11.2 Summary of studies that apply carbon nanoparticles for detecting various targets

Target molecules	CNP role	Method	Limit of detection	References
Sn(II) ions	Fluorophore	The CNP fluorescence intensity is quenched in the presence of Sn(II) ions	0.36 μM	[116]
ssDNA	Quencher	The FAM-labeled ssDNA is adsorbed onto the surface of CNP quenching the FAM, while in the presence of target, dsDNA is formed recovering the fluorescence	33 nM	[121]
Hg(II) ion	Fluorophore	By adding Hg(II) ion, the fluorescence intensity of CNP is quenched	430 nM	[102]
CTV	Quencher	The fluorescence intensity of QD is quenched by CNP. In the presence of target, the fluorescence intensity is recovered	220 ng/mL	[104]
Silver(I) ion	Quencher	A ROX-labeled specific nucleotide for Ag^+ is quenched in the absence of Ag ion, while in the presence of Ag, the probe is induced to form a hairpin structure that prohibits the probe to adsorb on CNP and thus retains the dye fluorescence	500 pM	[122]
Thrombin	Quencher	FRET between upconverting phosphors (UCP) and CNP in the absence of target. In the presence of target, the aptamer on the surface of UCP forms a hairpin structure that prohibits the CNP to place in the vicinity of UCP and thus retains the UCP fluorescence	0.18 nM	[123]

on it for their livelihood [124]. The agricultural sectors also contribute to the major part of the human's income. As the world population is increasing, a large proportion of those livings are facing food shortages and stagnation in crop yields; thus, it is necessary to employ the modern technology such as nanotechnologies in order to attain a sustainable growth in agriculture to meet the food security challenges [125]. Nanotechnology plays a vital role in the development of the agricultural sector with an abundance of public

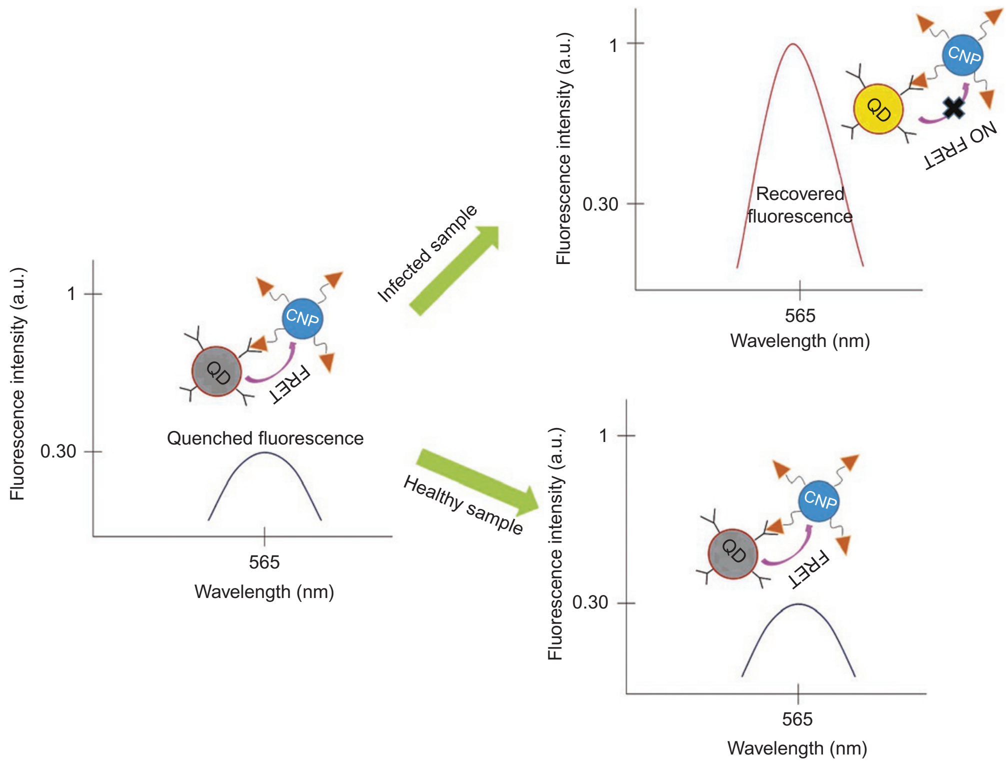

Fig. 11.4 Schematic of the sensing system for developed nanosensor by using CNP and QD.

funding, but the pace of development is modest. In the emergence of recent discoveries of the unique effects of nanosized materials, CNP on nanotechnology in agriculture has begun and will continue to impart some significant effects especially on the physiological processes in plants toward crop productivity. The metabolic functions of plants can be affected by the optimum concentrations of nanoparticles that penetrate into the plant system, resulting in beneficial effects on plant growth [13, 126]. There have been several reports on the effects of CD on germination and growth with the goal to promote their use of agricultural applications.

A study by Sonkar et al. [127] revealed that gram (*Cicer arietinum*) plant from its germination to seed formation is grown in an aqueous medium containing different concentrations of water-soluble carbon nano-onions (WsCNO). Treatment of plants with the concentration of WsCNO that ranged between 0.01 and 0.03 mg/L can enhance the overall growth rate of plant by the adsorbing of nanoparticles onto the xylem and phloem vessels of the plant in comparison with the control plant. WsCNO was synthesized by the pyrolysis of wood wool without the presence of any metal catalyst. The effect of WsCNO on the growth of gram plants can be determined in terms of shoot length,

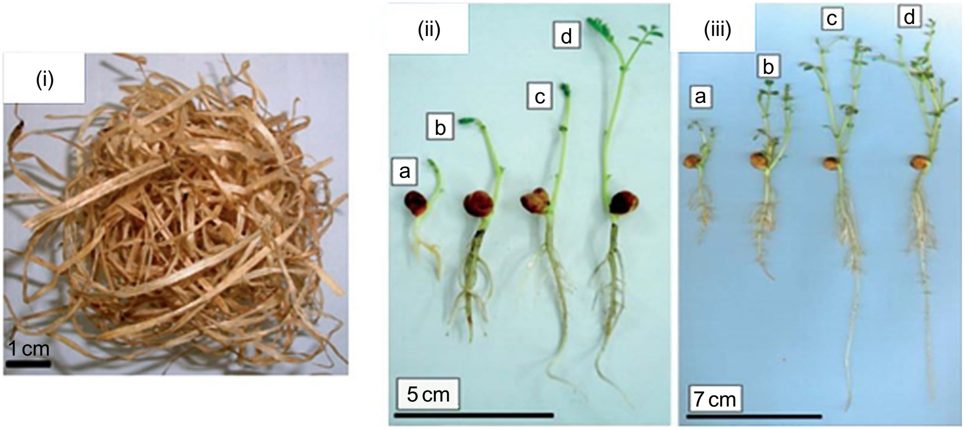

Fig 11.5 (i) Photograph of wood wool and images of gram plants treated with different concentrations of WsCNO: (a) control plant and (b–d) plants treated with 0.01, 0.02, and 0.03 mg/L WsCNO with the exposure durations of (ii) plants after 5 days and (iii) plants after 10 days. *(Reproduced with permission from S.K. Sonkar, et al., Water soluble carbon nano-onions from wood wool as growth promoters for gram plants, Nanoscale 4(24) (2012) 7670–7675. Royal Society of Chemistry.)*

branching, number of roots, and length in comparison with the control plant. The difference in the growth of plants with the number of roots and length is shown in Fig. 11.5 where it (i) displays the photograph of wood wool used to synthesize WsCNO, (ii) shows the growth of plants after 5 days, and (iii) shows the growth of plants after 10 days with different concentrations of WsCNO ranges from 0.01 to 0.03 mg/L (b–d) in comparison with the blank (a). As a result, the addition of WsCNO significantly shows the positive effect to the enhancement growth of plant.

The relationship between CQD or more simply carbon dots (CD) and the electron transfer study of mung bean plants exposed to CD have been studied systematically in detail by Chandra et al. [128]. In this study, a microwave-assisted method was used for the synthesis of amine-functionalized CD using ascorbic acid and 2,2′-(ethylenedioxy)bis(ethylamine) as the starting precursor. The high luminescence property of CD is thought to be able to promote the photosynthesis process by means of electron transfer from CD to chloroplast of mung beans where it can act as an electron donor and speed up the conversion of light energy to electric energy and eventually to chemical energy as assimilatory power adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH). The whole mechanism of the process is proposed in Fig. 11.6. In addition, the presence of CD also enhances the oxygen evolution, noncyclic photophosphorylation, and ATP synthesis in isolated chloroplast of mung beans.

In a separate work, biochar-derived CD was synthesized by the method reported in Chapter 5 (Section 5.5.2) by Jamaludin, Abdul Rashid, and Tan. The effects of CD exposure at concentrations of 100 (low), 300 (medium), and 500 μg/mL (high) on the

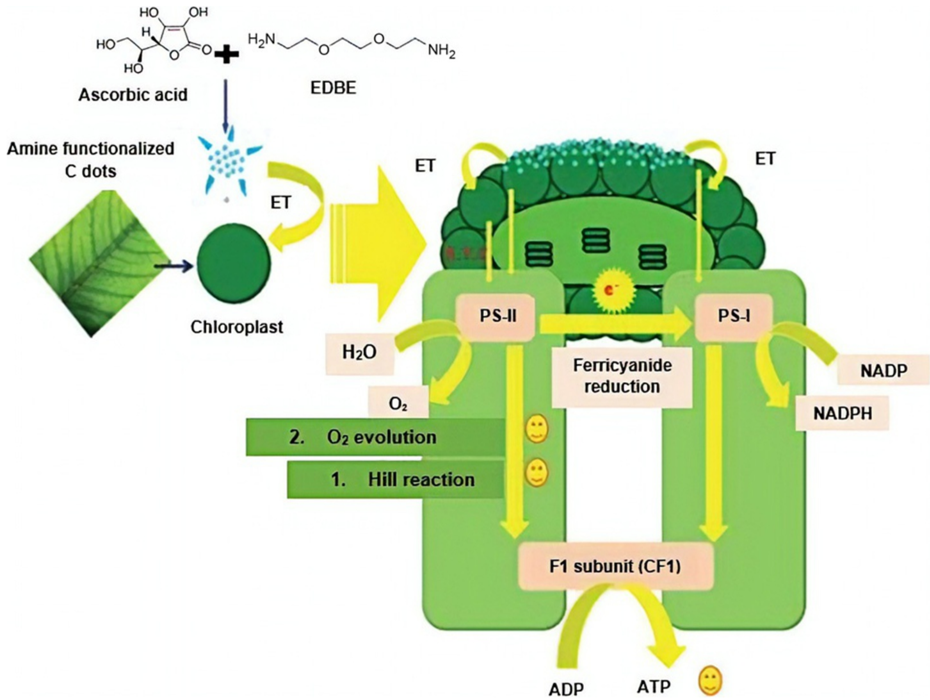

Fig. 11.6 Schematic representation illustrating the whole mechanism process between CD and chloroplast of mung beans. *(Reproduced with permission from S. Chandra, et al., High throughput electron transfer from carbon dots to chloroplast: a rationale of enhanced photosynthesis, Nanoscale 6 (7) (2014) 3647–3655. Royal Society of Chemistry.)*

photosynthesis of mung bean plants were investigated. Initially, the mung bean seeds were planted in small polybags and kept at room temperature. CD solutions with the desired amount of concentration were sprayed onto the leaves of mung bean (approximately 5 mL per plant), and the growth was monitored. As expected, the role of CD as a plant growth enhancer was demonstrated as indicated by the increase in the height of the plants as compared with the untreated plants as shown in Fig. 11.7. The highest concentration of CD resulted in the tallest plant. Moreover, the lengths of the stems of mung bean plants treated with CD were longer compared with untreated mung bean plants. The number of leaves observed in mung bean plants treated with CD were also observed to be greater compared with that of untreated plants as a function of time (~6 weeks).

Saxena et al. [129] reported beneficial effects on crop productivity of wheat plants germinated on cotton clothes of 1 ft^2 size after the addition of CNP ensuring the increased shoot lengths and growth rate. The raw CNPs are isolated from biochar, while the water-soluble CNP can be prepared by the introduction of COOH and OH groups following chemical oxidation of raw CNP in biochar. They indicated that the growth of

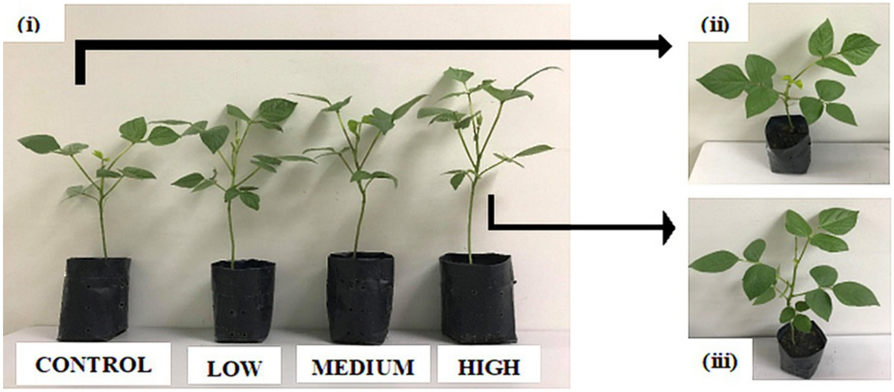

Fig. 11.7 (i) Image of treated mung bean plants with varying concentrations of CD (low, medium, and high) in comparison with control. Top part of the mung bean plant leaf image for (ii) control and (iii) high concentration of CD treated, respectively.

the shoot part of the wheat plant increases with the presence of water-soluble CNP in comparison with the control. The concentration of CNP involved in this study varied in the range from 10 to 150 mg/L, while the optimum growth rates found to obtain with 50 mg/L CNP, as the highest concentrations of CNP may have a deteriorate effect on the plant growth.

On the other hand, the use of graphene quantum dot (GQD) for growth enhancement in coriander (*Coriandrum sativum* L.) and garlic plant (*Allium sativum*) has been reported by Chakravarty et al. [130]. The effect of GQD on the physiological response of coriander and garlic plants including leaves, roots, shoots, flowers, and fruits with seeds is investigated. For GQD-treated coriander plants, the size of the leaves and the number of flowers are observed to be increased. The average length of coriander roots was also observed to be increased with GQD as compared with the plant treated without GQD. For garlic plants, the length of garlic root and the number of garlic leaves are also observed to be increased as compared with untreated plant.

Li et al. [131] demonstrated that CD synthesized from phenylenediamine showing the uptake and translocation of CD promoted the overall growth rate of mung bean plants as illustrated in Fig. 11.8. Mung bean plants were treated with CD at a concentration range of 0.1–1.0 mg/L, induced seed germination and seedling elongation, and imposed no phytotoxicity on mung bean growth. Another study by Zheng et al. [132] indicated that pollen-derived blue fluorescent CD to enhance plant production and promote absorbance efficiency of nutrients in *Brassica parachinensis* L. CD with the concentration ranges from 1.75 to 7 mg/L can increase the yield of *B. parachinensis* L., improve the photosynthesis, and affect the accumulation of energy for plant growth. The elemental contents of nutrient solutions can also be tracked by the fluorescence properties of pollen CD.

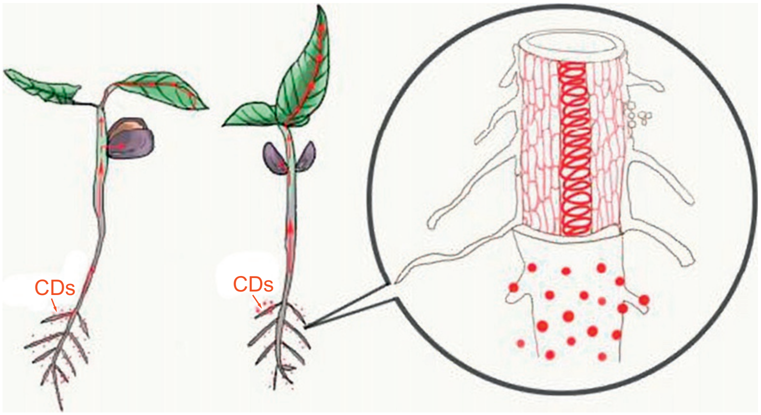

Fig. 11.8 Schematic representation illustrating the uptake, transport, and accumulation of CD by mung bean plant. *(Reproduced with permission from W. Li, et al., Phytotoxicity, uptake, and translocation of fluorescent carbon dots in mung bean plants, ACS Appl. Mater. Interfaces 8(31) (2016) 19939–19945. American Chemical Society.)*

In a study published in the journal of ACS Omega, a cost-effective and biocompatible fertilizer with CD derived from rapeseed pollen by a hydrothermal method for growing lettuce and increasing crop yields is explored by a team of researchers from China. In the study, the researchers discovered that for the 30 mg/L treated sample, the CD increased plant biomass by 48.09% compared with plants that did not receive the CD. A nearly linear positive correlation is observed in the shoot fresh weight and dry weight, leaf width, and leaf areas as the concentration of CD increased from 10 to 30 mg/L, resulting in the best production yields at 30 mg/L as shown in Fig. 11.9. Further analysis also revealed that the CD would not alter the composition of vitamin C, soluble sugars, and proteins in the lettuce as this research highlights a safe method to increase crop yields for future demands [133]. The positive effects of CNP on plant growth and development described above are summarized in Table 11.3.

11.6 FUTURE DIRECTIONS AND CONCLUSIONS

Nanotechnology has shown great potential in agricultural applications as it can enhance the quality of life and world's economy. The focus of this chapter is based on the provision of basic knowledge about the applications of nanotechnology and carbon nanoparticles (CNPs) in agriculture for the welfare of humans and sustainable environment. Through advancement in nanotechnology, there are a number of state-of-the-art techniques available for a variety of agricultural nanotechnology applications, including DNA sequencing, nanosensors, nanobarcodes, and nanocatalysts.

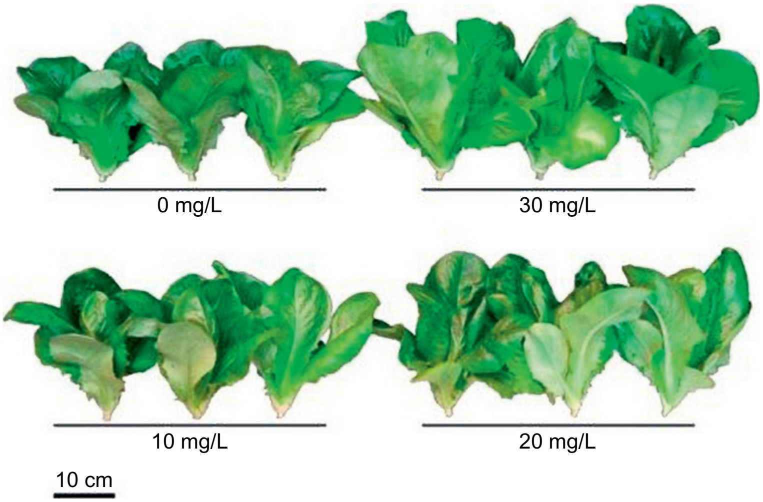

Fig. 11.9 Effect of the concentrations (0, 10, 20, and 30 mg/L) of CD on the yield and leaf width of the Rome lettuce. *(Reproduced with permission from Y. Zheng, et al., Bioimaging application and growth-promoting behavior of carbon dots from pollen on hydroponically cultivated Rome lettuce, ACS Omega 2(7) (2017) 3958–3965. American Chemical Society.)*

CNP nanotechnology is a rapidly growing area of research that is widely used in plants. CNP with their unique physiochemical properties can be easily synthesized from different methods and can be applied in agriculture. From the above discussion, it is clearly shown that CNPs have potential to enhance plant growth, seed germination, and root elongation. Plenty of studies have been conducted to explore the effect of CNP on the plant growth activities, yet how and why different plant species display different resistance to CNP remains unexplored. Although many studies report positive effects from CNP exposure, however, most of the work is focused on short-term studies with high levels of CNP exposure, while the relevance of CNP exposure to actual agricultural conditions is still comparably marginal and has not yet made it to the market to any large extent. The potential that nanotech solutions offer in agricultural field is investigated by large companies, but the products for the agricultural sector have not reached the market so far, considering the costs involved in large-scale production. Besides, there are a very limited number of studies evaluating the phytotoxicity of CD under environmentally relevant conditions; hence, more studies on toxicity are required for future commercial food crop applications. In addition, a detailed understanding of the mechanism studies between the interactions of CD with plants is necessary to be further investigated.

Table 11.3 Influence of carbon nanoparticles on plant growth

Type of carbon	Sources of carbon	Plant species	Size of CNP (nm)	Concentrations (mg/L)	Exposure durations (days)	Effects	References
CNO	Wood wool	Gram (*Cicer arietinum*)	~30	0.01–0.03	5, 10	• The addition of CNO leads to an increase in plant growth in comparison with the control plants	[127]
CD	Ascorbic acid 2,2′-(ethylenedioxy) bis(ethylamine)	Mung bean	1–2	0.01–0.2	N/A	• The photosynthesis of mung bean plants can be enhanced by CD by modulating the electron transfer process	[128]
CNP	Biochar	Wheat (*Triticum aestivum*)	20–50	10–150	5–20	• CNP-exposed wheat seeds germinate faster than the control • The shoot lengths of treated wheat plants are longer compared with the control	[129]
GQD	Graphene	Coriander and garlic plant	~5	0.2	7–90	• The growth rate in terms of length and size of leaves of both plants increased with the presence of GQD	[130]
CD	Phenylenediamine	Mung bean	4	0.1–1.0	5	• The treated mung bean shows an increased root and stem elongation as compared with the control	[131]
CD	Bee pollen	Chinese cabbage (*Brassica parachinensis* L.)	2.01	1.75–7.00	20	• The treated plant grew rapidly with the fresh weight of the shoots that were higher than the control • CNPs improve ammonium nitrogen absorption and increase the plant yield	[132]
CD	Rapeseed pollen	Rome lettuce	3.1–5.1	10–30	25	• The biomass of lettuce increased by 48.09% over that of untreated lettuce • The addition of CNP will increase the leaf number and enlarge the leaf area	[133]

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