



Review article

Current and emerging nanotechnology for sustainable development of agriculture: Implementation design strategy and application

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ABSTRACT

Recently, agriculture systems have faced numerous challenges involving sustainable nutrient use efficiency and feeding, environmental pollution especially heavy metals (HMs), infection of harmful microorganisms, and maintenance of crop production quality during postharvesting and packaging. Nanotechnology and nanomaterials have emerged as powerful tools in agriculture applications that provide alternatives or support traditional methods. This review aims to address and highlight the current overarching issue and various implementation strategies of nanotechnology for sustainable agriculture development. In particular, the current progress of different nano-fertilizers (NFs) systems was analyzed to show their advances in enhancing the uptake and translocations in plants and improving nutrient bioavailability in soil. Also, the design strategy and application of nanotechnology for rapid detection of HMs and pathogenic diseases in plant crops were emphasized. The engineered nanomaterials have great potential for biosensors with high sensitivity and selectivity, high signal throughput, and reproducibility through various detection approaches such as Raman, colorimetric, biological, chemical, and electrical sensors. We obtain that the development of microfluidic and lab-on-a-chip (LoC) technologies offers the opportunity to create on-site portable and smart biodevices and chips for real-time monitoring of plant diseases. The last part of this work is a brief introduction to trends in nanotechnology for harvesting and packaging to provide insights into the overall applications of nanotechnology for crop production quality. This review provides the current advent of nanotechnology in agriculture, which is essential for further studies examining novel applications for sustainable agriculture.

1. Introduction

The visions of sustainable agricultural development and food security have remained global difficulties regarding various factors that impact plant growth and crop production [1]. Agricultural growth and crop production are globally influenced by food security demand, climate change, soil health, and water availability [2,3]. Cropland and food demand are predicted to increase in the future

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due to the world population outbreak in 2050 and 2100 [4]. The present situation requires the longstanding sustainable development goals of agricultural systems that are facing several challenges. For instance, the long-term effects of overuse of agrochemicals (fertilizers, pesticides, and other plant-protection chemicals) may bring the risk of environmental pollution and soil and water system destruction that directly influence the agricultural ecosystem [5,6]. The application of traditional chemical fertilizers in the wrong ways is likely to reduce nutrient use efficiency (NUE) and increase nutrient excess and nutrient degradation [7]. On the other hand, environmental pollution, especially heavy metals (HMs) contaminated in soil and water, can have negative effects not only on plants but also on animals and humans. Arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), and nickel (Ni) are classified as Group 1 carcinogens by the International Agency for Research on Cancer [8]. HMs can be released and accumulated through the manufacturing industry, agrochemicals, and other production activities. They can cause retardation in plant growth and harmful effects on human beings if they intake foods that contaminated HMs [9]. The monitoring and remediation of contaminated HMs in croplands is challenging due to the heterogeneity and complexity of soil components. Plant pathogens are critical threats that cause major diseases and reduce crop production. The influence of these microorganisms is intensified by global trade, developing induced invasive pathogens and damage to crop production [10]. According to the Food and Agriculture Organization (FAO), total global finance of about \$220 billion per year has been used for plant disease problems causing 20–40 % of yield loss [11,12]. Pathogenic microorganisms can attack the whole plant growth period, postharvest, and packaging process. It is a requirement to develop novel approaches to the detection and treatment of disease agents in the early stages to prevent the big lesions of plants and ensure substantial crop production.

As these present situations, the emerging implications of nanotechnology open the way to overcoming the remaining agricultural problems. The development of nanotechnology has provided novel nanomaterial and technology applications in many fields, such as pest management [13], food packaging and preservation [14], and pesticide and fertilizer formulation [15]. Typically, nanomaterials, with their small size range of less than 100 nm and high surface-to-volume ratio, can offer opportunities to develop nano-fertilizers (NFs) with bioavailability nutrients and high absorption and intake efficiency in both ways foliar spraying or soil amendment due to their nanoscale dimension. Advancements in nanomaterials have unique chemical, physical, and optical features that allow them to be designed and developed as chemical and biological sensing systems that can rapidly detect various analytes such as HMs and pathogens. Taking quantum dots as an example, the implementation of quantum dots (QDs) - based biosensors relates to the ability photostability, narrow emission bands, and broad excitation wavelengths. The emission spectra of QDs can be tunable due to size changes called quantum confinement. QDs are probably based on the Stoke luminescence shift in which the energy of the emission is lower than that of the excitation. Due to exceptionally large Stoke shifts, QDs can be used for multicolor analysis and bioanalysis applications. The implication of nanotechnology-based sensors and pathogen detection is to improve the sensitivity, selectivity, signal-to-noise, and time response [16]. Also, the properties and functional surface of nanomaterials can possibly be designed and altered to immobilize with biorecognition and analyses. For instance, metal nanoparticles (MNPs) involving silver, gold, copper, platinum, and other metal oxide and metal-based nanostructure compositions have been widely used in biosensor platforms [17,18]. Noble metals exhibit unique physiochemical properties that are useful in signal transducer components for the enhancement of sensitivity detection and analysis [19]. Generally, nanomaterials can interact effectively with numerous bioanalysts and biorecognition receptors such as antibodies, nucleic acids, and enzymes for the selective detection of plant pathogenic microorganisms. Nanotechnology can be applied to various aspects of agriculture. The implementation design and strategy application of various types of nanomaterials are comprehensively discussed. Different applications of nanotechnology in agriculture have been updated and highlighted, involving nano-fertilizers (NFs), assessment of heavy metals (HMs), pathogen diagnosis, anti-microbiology, and postharvest and packaging (Fig. 1).

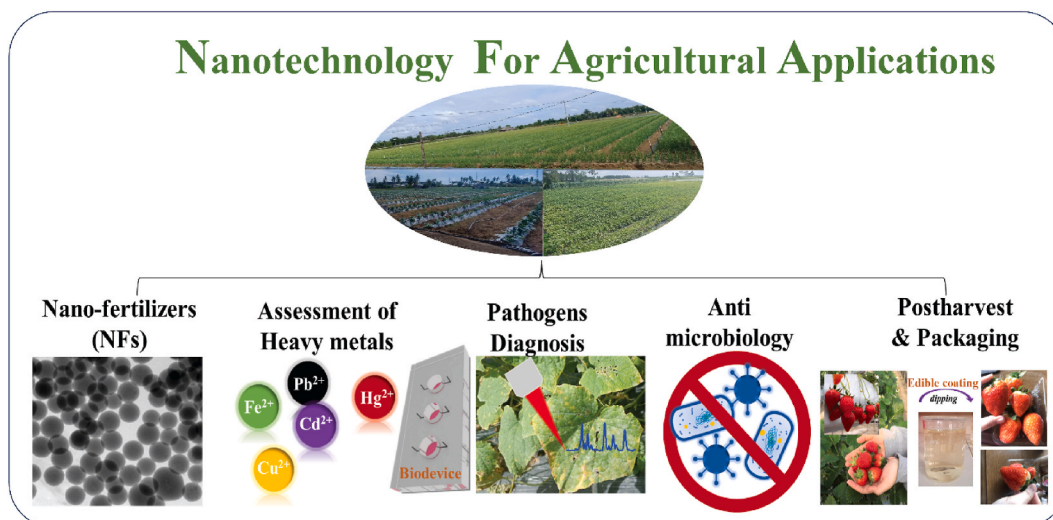


Fig. 1. Implications of nanotechnology for agricultural applications.

2. Nano-fertilizers (NFs)

Recently, several fabrication methods have been proposed in both top-down and bottom-up approaches for the fabrication of different types and structures of NFs [20]. Many NFs are developed based on bottom-up, but the top-down methods have been considered more beneficial in industrial manufacturing in terms of large scale and cost-effectiveness [21]. Advanced nanotechnology can provide novel nanosystems that encapsulate and control the release of active ingredients such as macro- and micro-nutrients [22, 23]. These NFs can effectively improve nutrient availability and enhance the physiology and quality of crops [24]. The behaviors of the absorption, uptake, transport, and penetration of nanoparticles in plants have been proposed (Fig. 2A) [25].

Typically, plants can uptake NFs by foliar or root feeding. In the foliar approach, NFs can be entered inside the plant mainly through stomata or trichomes in leaves and transported within the plant through phloem and xylem [26,27]. The translocation of NFs in plants has also been reported to occur via the two apoplastic and symplastic pathways [28–30]. The apoplast involves intercellular space, the

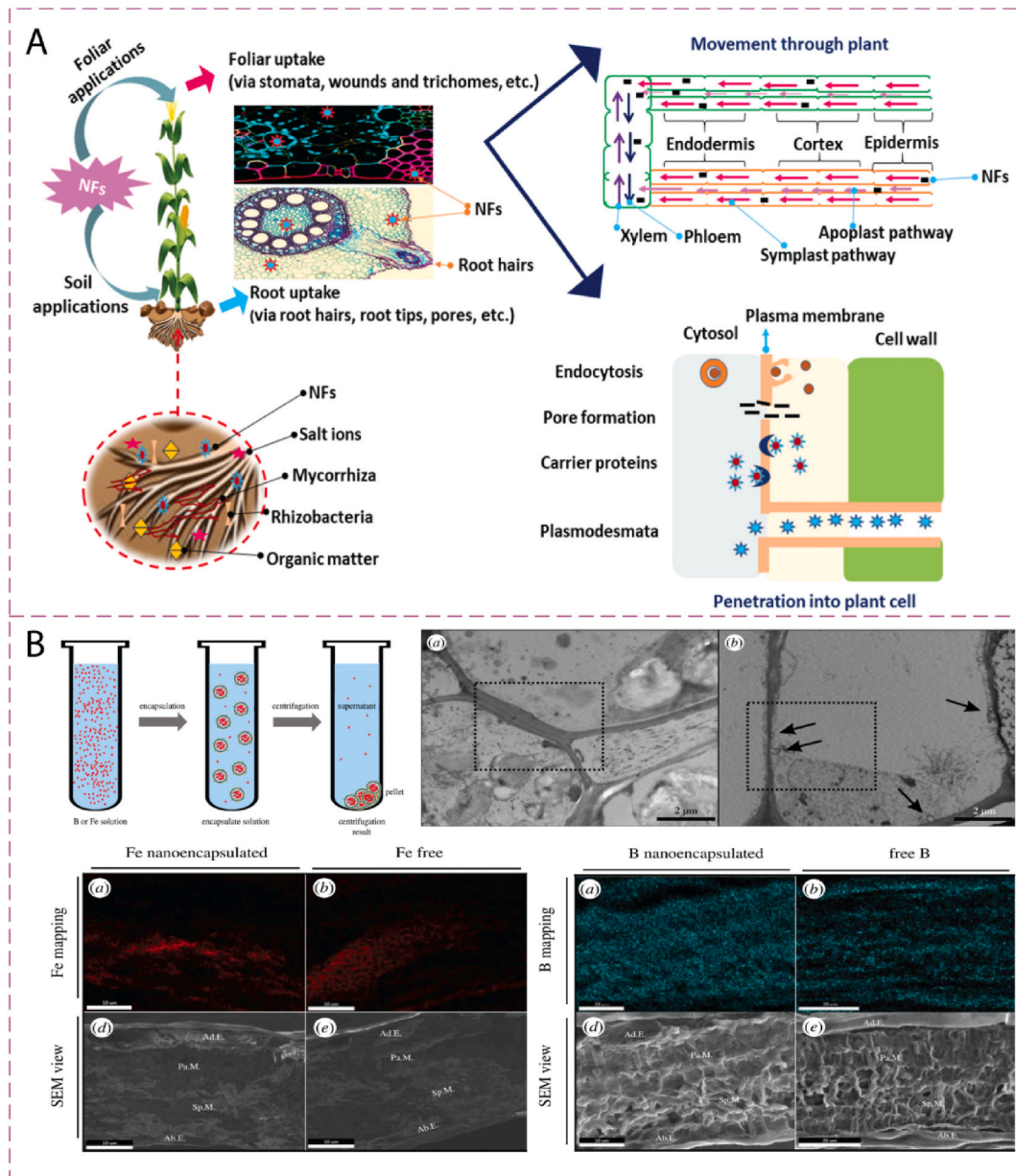


Fig. 2. (A) The uptake of NFs through various channels and their translocation pathways in different parts of a plant, including the NFs traits, translocation mechanism, and strategy (A). Reprinted from Ref. [25], Copyright 2022 MDPI. (B) The schematic of encapsulation process of Fe and B-based NFs and their vesicle application in plant cell. The FESEM-X-EDS and element mapping images indicate Fe and B distribution after foliar application. Reprinted from Ref. [34], Copyright 2020 RSC Publishing.

cell wall, and the xylem. It takes an important role in nutrient and water transport and allows radial movement and nanomaterials to enter the vascular tissue [31]. The uptake and translocation of NFs in plants are affected by several factors such as size, shape, chemical and physical properties of nanomaterials, and biophysical properties of plants [32]. The transmembrane transports of NFs by plant cells have been hypothesized by the mechanism of aquaporin, interconnected ion channels, endocytosis, and altered membrane intubation [33]. Recently, various types of NFs have been developed. Rios and coworkers have reported a nanosystem of iron (Fe) and boron (B) based NFs for foliar applications in almond tree *Prunus dulcis* L. (Fig. 2B) [34]. The penetration of both Fe and B-based NFs through the stomatal system was more effective than the conventional foliar fermentation. The utilization of NFs offered higher

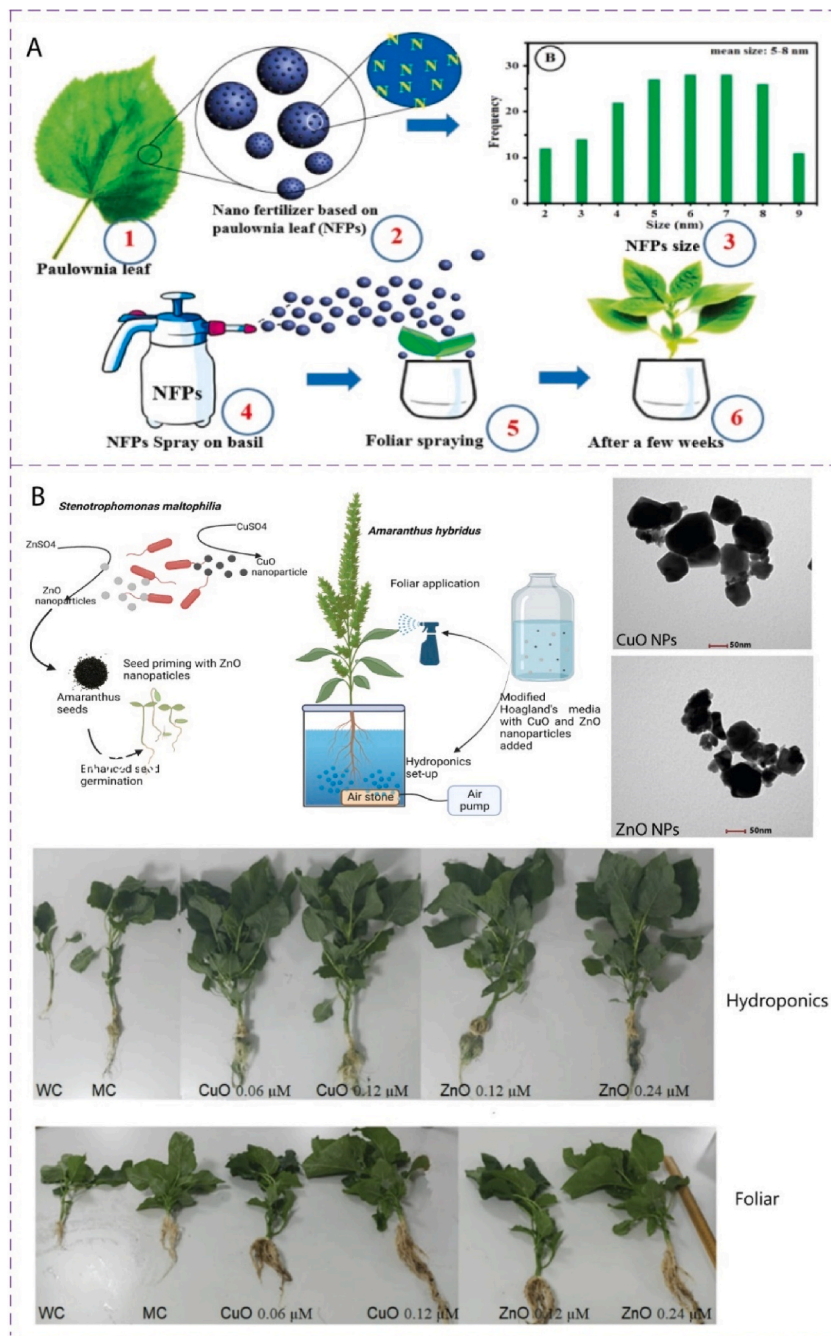


Fig. 3. (A) The schematic of plant-based green synthesis of nanoparticles and its application as NFs. Reprinted from Ref. [40], Copyright 2022 Springer Nature. (B) Biogenetically fabrication of CuO and ZnO NPs using soil bacterium, *Stenotrophomonas maltophilia*, and their evaluation in the growth of *Amaranthus hybridus* in a hydroponics system. Reprinted from Ref. [42], Copyright 2022 MDPI. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

concentration, distribution, and movement of Fe and B than relative free forms of the two elements. The study also indicated that the applied NFs can generate areas with several invaginations of the plasma membrane after foliar treatment. To reduce the loss of phosphorus fertilizer in the surrounding environment through irrigation activities, Salama and coworkers have proposed to use phosphorus NFs as foliar application [35]. Hydroxyapatite NPs (HA-NPs) were applied on two cultivars of sweet corn (yellow and white) during two seasons. HA-NPs have positively enhanced the growth characteristics and yield production as phosphorus sources to achieve agricultural sustainability.

To reduce the overdosage and accumulation of fertilizer elements in soil, the novel conceptual development of new NFs regards the combination of NFs with superabsorbent hydrogels to propose the regulate nutrient releases and retained water in the complex structures as smart NFs. The NFs complex structures of ZnO and CuO nanoparticles on the alginate matrix were developed to study the release behavior of the micronutrients in the nanosystems [36]. In this study, the NPs were reacted with sodium alginate to form a hydrogel matrix where the alginate chains cross-linked with the Zn(II) and Cu(II), allowing the metal oxide NPs to crystallize on the hydrogel. The size of ZnO NPs was 80–100 nm, and that of CuO NPs was 80–90 nm. The experimental-based tea bag was used to evaluate the release behavior of Zn and Cu in NFs. The results indicated that 50 % of Zn and Cu were released after 24h in water and after ten days in soil. The uptake of NPs by tomato suggested that a reduced uptake of Cu has occurred but the amounts of Zn in the leaves were undetected, which can be explained by its uptake inhibited by soil phosphorous or the antagonistic nature in the uptake of Zn and Cu.

We obtain that the green synthesis of nanomaterials has been considered and studied for NFs applications these days. The bio-synthesis techniques mainly utilize biological objectives such as plants, algae, bacteria, and fungi to prepare the nanomaterials, offering opportunities to limit chemical accumulations in the environment [37–39]. Recently, Sohrabi and coworkers have proposed to prepare carbon dots-based NFs using *Paulownia Tomentosa* and the green hydrothermal method (Fig. 3A) [40]. The as-synthesis NPs achieved the size range of 5–8 nm for NFs that successfully applied and increased the biological yield of *Ocimum basilicum* by protecting the photosynthesis pigments or cell organelles and providing the nutrients that support the generation of protein and antioxidant compounds. In a similar study, MnO₂ NP-based NFs were eco-friendly and successfully synthesized using potato leaf extract [41]. The as-green synthesized MnO₂ NPs obtained a size range of 26 nm and. The MnO₂ NPs-based can be applied directly through soil or spraying as foliar feeding with the ability to increase the growth, photosynthesis pigments, and antioxidant activities of cowpea (*Vigna unguiculata*). The green synthesis of NF methods is considered a sustainable, and environmentally friendly technique to produce various types of nutrients NFs that could replace conventional fertilizers. Bacteria also can be used as potential green synthesis techniques to create several types of nanomaterials. For instance, CuO and ZnO NPs have been successfully achieved using a soil bacterium, *Stenotrophomonas maltophilia* (Fig. 3B) [42]. In this study, the sizes of biogenetically synthesized NPs were obtained at 38.96 nm (± 5) and 42.64 nm (± 3) for CuO NPs and ZnO NPs, respectively. The green-synthesized NFs were demonstrated to positively

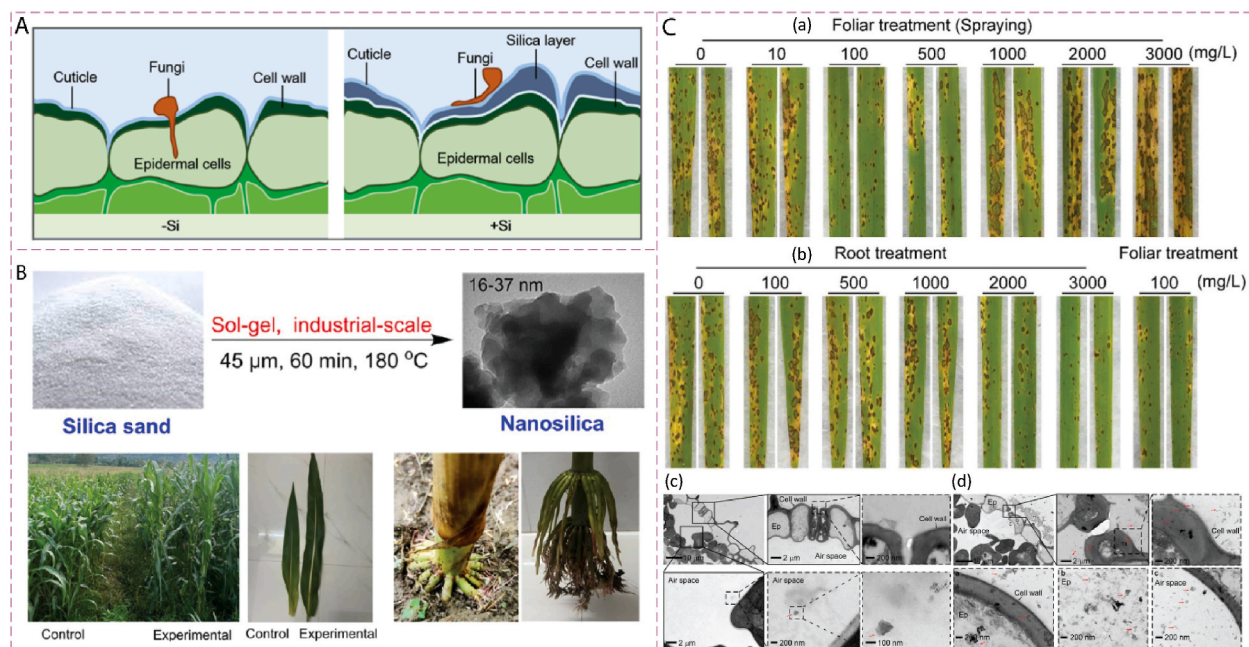
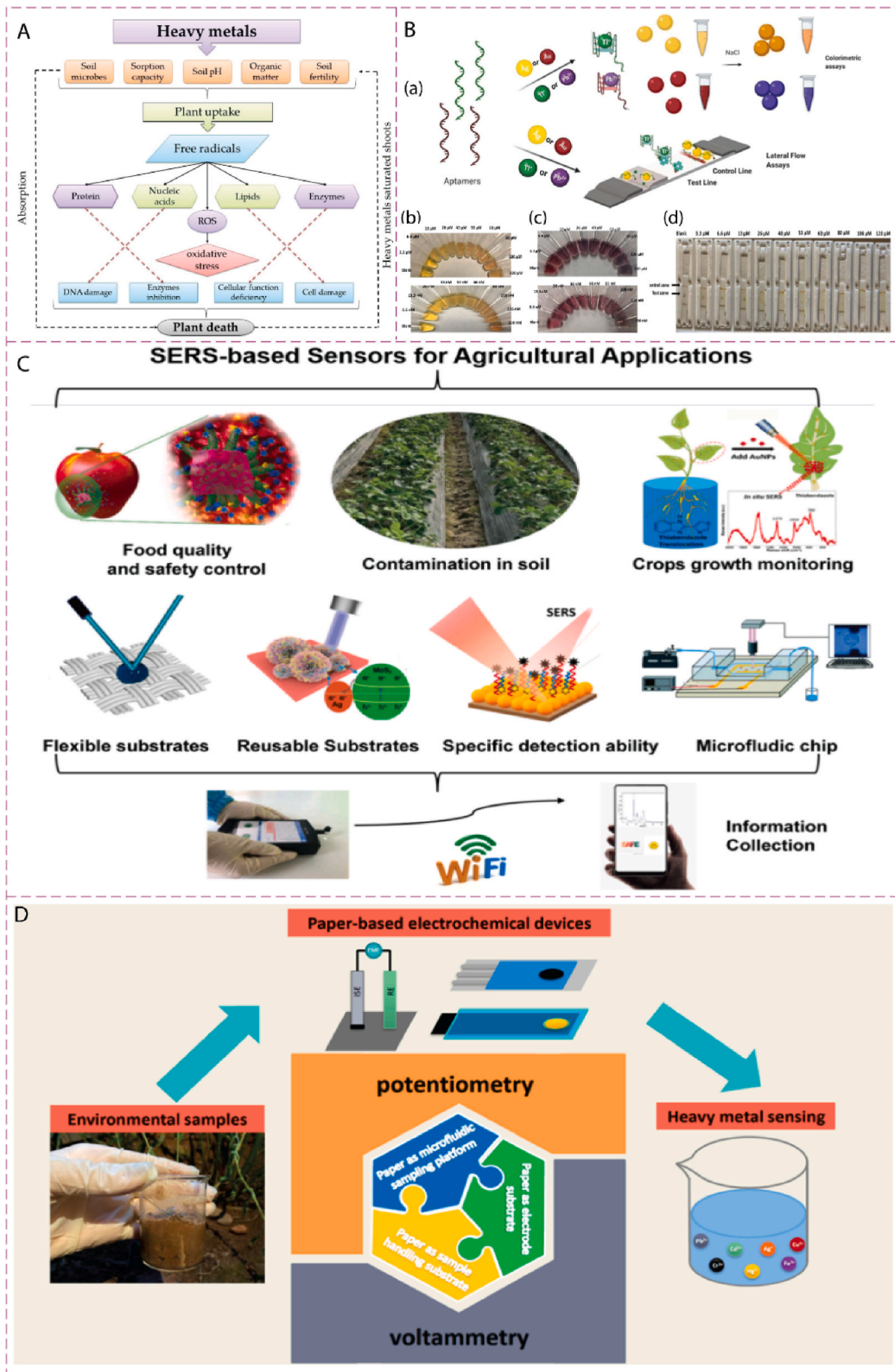


Fig. 4. (A) Schematic of the role of Si in plant cells to enhance plant resistance through physical barrier formation. Reprinted from Ref. [51], Copyright 2017 Frontiers. (B) Large-scale fabrication of SiNPs (16–37 nm in size) from silica sands using sol-gel methods and their evaluation in maize plants. Reprinted from Ref. [56], Copyright 2022 ACS. (C) SiNPs stimulate the immunity of rice plants to resistance to biotic and abiotic stress. (a, b) Symptomatic disease response of rice at different SiNPs concentration treatments via foliar treatment and root treatment, respectively. (c, d) TEM image of SiNPs distribution in rice leaves through foliar treatment of 100 mg/L and 3000 mg/L respectively. Reprinted from Ref. [57], Copyright 2022 Springer Nature.



(caption on next page)

Fig. 5. (A) Schematic of pathways and mechanisms that HMs toxicity in soil and plant. Reprinted from Ref. [61], Copyright 2021 MDPI. (B) Colorimetric detection of Tl(I) and Pd(II) ions by AgNPs, AuNPs, and FLA-AuNPs based colorimetric detection. (a) Schematic illustration of the nanosensing systems, (b) The behavior of color change of AgNPs-based sensing under concentration series of metal ions, (c) The behavior of color change of AuNPs-based sensing under concentration series of metal ions, and (d) behaviors of FLA (AgNPs base) for Tl(I) ions detection from 0 to 120 μM . Reprinted from Ref. [66], Copyright 2023 RSC. (C) Applications of SERS in agriculture. Reprinted from Ref. [71] (which has been adapted from Refs. [85–90], Copyright 2022 Elsevier. (D) Schematic illustrations of paper-based electrochemical devices for HMs sensing. Reprinted from Ref. [84], Copyright 2021 ACS Publications. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

affect the plant growth of *Amaranthus hybridus* in a hydroponics system.

Soil nutrient bioavailability can be defined as the soil-plant system's capacity to supply/absorb nutrients. This is the ability of the soil-plant system to supply essential nutrients for plant crops, and plant association mainly through the release of nutrients from the solid phase to the solution phase [43]. It is reported that the design structures and properties of NFs can enhance nutritional bioavailability [44]. For instance, Zn is one of the most important microelements that contribute to many cellular and physiological activities of plants, improving plant growth, development, and crop yield. Also, it takes the response in structural, enzymatic, and regulatory substains of several proteins and enzymes [45]. However, the amount of Zn usually is low on agricultural land and many solutions have been proposed to increase the Zn bioavailability in soil, including nanotechnology. The implementation of ZnO NPs can significantly increase availability of Zn content and soil nutrient availability [46–48]. ZnO NPs were also investigated to effectively support the grain Zn fortification in wheat and rice crops [49,50]. Similarly, Si is important in plant cell wall structure, strengthening, and immune systems. Plants use Si to stimulate antioxidant metabolism and enhance the hardening of cell walls and plant resistance, such as fungi infection, and environmental adaption (Fig. 4A) [51–53]. The availability and solubility of Si influence the Si absorption efficiency of plants. SiO₂-based NFs are a powerful tool to provide high bioavailability Si content in agricultural soil [54,55]. Recently, the sol-gel methods have been reported potential for industrial-scale manufacturing of SiNPs from silica sands (Fig. 4B) [56]. The size range of SiNPs was obtained from 16 to 37 nm with high purity and their evaluation in maize plants showed a significant enhancement of plant growth in terms of blase height and plant height. The treated SiNPs plant had more hardness and tenacity, and no root rot was obtained. SiNPs have been investigated to help crops compact with biological and abiotic stresses. SiNPs can induce plant immunity in rice to improve resistance to *Magnaporthe oryzae*, a rice blast fungus, that causes destructive disease and loss of rice production. The dose of SiNP use is an essential factor in determining SiNP performance behaviors. In a previous study, a suitable concentration of SiNPs could substantially reduce the infectious fungal growth and limit the lesion area (Fig. 4C) [57]. It was also found that the combination of NFs and conventional fertilizers practically can offer a synergistic phenomenon. For instance, Rahman and coworkers have proved the use of mixed NFs (MNFs) and commercial fertilizers (CFs) can offer a number of advancements involving nutrient use efficiency (NUE), producibility, and nutritional features of the fruits [58]. The balanced and controlled distribution of MNFs and CFs allowed higher growth and development of plants and the proximal constituents contents of the tested fruits. Also, this combination can attributed to inducing more bioactive compounds and antioxidant activity. In this case, the use of CFs was significantly reduced and the combination of NFs and conventional fertilizers can be considered a promising approach for sustainable nutrient feeding.

3. Assessment of heavy metals (HMs)

The risk of hazardous contamination in agroecosystems involves several substances such as heavy metals, pesticides, insecticides, herbicides, and many other toxic pollutants in soil and water during agricultural activity. In this section, we focus on the detection and assessment of HMs due to their huge impact on the environment, and plant, animal, and human health. HMs can be classified in many ways and according to the toxicity, HMs can be divided into groups of metabolism fundamental and essential metals: e.g., Fe, Na, Zn, Ca, K, Cu, Mo, Mg; toxic heavy metals: e.g., Cd, Ph, As(III), As(V), Hg, Cr(III), Cr(VI), Sr, Al; radioactive metals: e.g., Am, V, Tc, Th, Ra, R; and pseudo-metal for biological effective detection: e.g., Se, Si, B, Ge, At, Sb, Po, Te [59]. The development and implementation of metals in industrial manufacturing, food processing, agriculture, pharmaceutical, energy, and other fields in our daily lives led to the wide distribution and contamination of HMs on the earth. The global demand for metals has been proposed to continuously increase over the 21st century [60]. The pathways and mechanisms that toxicity HMs accumulate and exposure to agricultural soil and plants have been proposed (Fig. 5A) [61]. These toxic HMs can generate free radicals and reactive oxygen species (ROS) that lead to several disorders and damage to different parts, such as oxidative stress and biological molecular denaturation, leading to the dysfunction or inhibition of enzyme activity and other physiological problems. Moreover, human health can be at risk through the dietary intake of food crops that contaminate HMs when the roots uptake toxic HMs in the soil. In the past decade, the rapid development of nanotechnology has provided various nanomaterials, sensing mechanisms, and techniques for the detection of trace HMs in agroecosystems and their production. The advances of these nanosensing systems include the high sensitivity, selectivity, producibility, and the ability to develop a portable device. For example, colorimetric, surface-enhanced Raman scattering (SERS), and electrochemical-based detection methods are widely developed and applied [62–64].

3.1. Colorimetric-based sensor

Colorimetric assay is one of the common methods for the detection of HMs due to its cost-effective, simple, easy operation, and on-site analysis. Chen and coworkers have proposed the main conceptional colorimetric sensing of trace HMs involving dye-based chemosensors, organic materials-based sensors (LSPR, QDs, and MOFs), and photonic crystal or cation selective optode-based colorimetric

sensors [62]. Colorimetric LSPR detection is typically associated with the optical property change of plasmonic nanomaterials such as silver and gold nanoparticles [65]. Recently, Srinivasan and a coworker have proposed two colorimetric nanosensing systems based on metallic NPs (AgNPs and AuNPs) and lateral flow assay (FLA) integrated NPs for the detection of Tl(I) and Pd(II) ions [66]. The first sensor concept was based on the adsorption/desorption mechanism. When the target was absent, the aptamer-NPs complex was formed due to the electrostatic interaction between the aptamer and NPs. The addition of metal ions led to the desorption process of aptamers from the NP's surface to release NPs. NaCl persuaded and the color changed from red (monodispersed AuNPs) to blue (aggregated AuNPs) and from yellow (monodispersed AgNPs) to orange (aggregated AgNPs) (Fig. 5B) [66]. The second sensor concept was developed based on biotin and streptavidin interactions due to the aptamer functionalized NPs (AgNPs/AuNPs) on FLA. The colorimetric sensors were rapid and had the potential for the development of biosensor devices. Reticular nanomaterials are widely used for colorimetric sensors. For example, Zn-MOFs have been synthesized and applied to nanosensing systems for the detection of Fe^{3+} [67], and Ag^+ [68]. A colorimetric sensor-based COFs nanosheet has been constructed for ultrasensitive detection of trace Hg^{2+} [69]. In this study, bipyridine-containing COFs nanosheets (Tp-Bpy NSs) were fabricated to provide functional groups of nitrogen for AuNPs growth. The synergist of AuNPs@Tp-Bpy allowed the ultrasensitivity of Hg^{2+} with an LOD of 0.33 nM.

3.2. SERS-based sensor

SERS is a spectroscopic technique that is widely applied for ultrasensitive monitoring and assessment applications in foods [70], agriculture (Liu et al., 2022), and environment [72]. Typically, SERS relies on inelastic light scattering by molecules adsorbed onto plasmonic nanoparticles or plasmonic active substrates [73]. That can detect a single molecule without the requirement of complex sample pretreatment [74]. In agriculture, SERS has exhibited powerful tools for various applications, such as the detection of residues of pesticides, insecticides, and several other toxic substances, including HMs (Fig. 5C) [71]. The development of nanotechnology provides diverse plasmonic nanostructures for SERS enhancement, such as AuNPs, AgNPs, and 3D plasmon substrates. In practice, the aggregated Au and Ag colloids have been the classic SERS-active substrates, but they remain challenging in stability and reproducibility [75]. The self-assembly of plasmon particles such as Au and Ag colloid has been a typical model for SERS active substrate through its multi-dimensional structure and highly intense local field enhancement. We observe that the development of highly

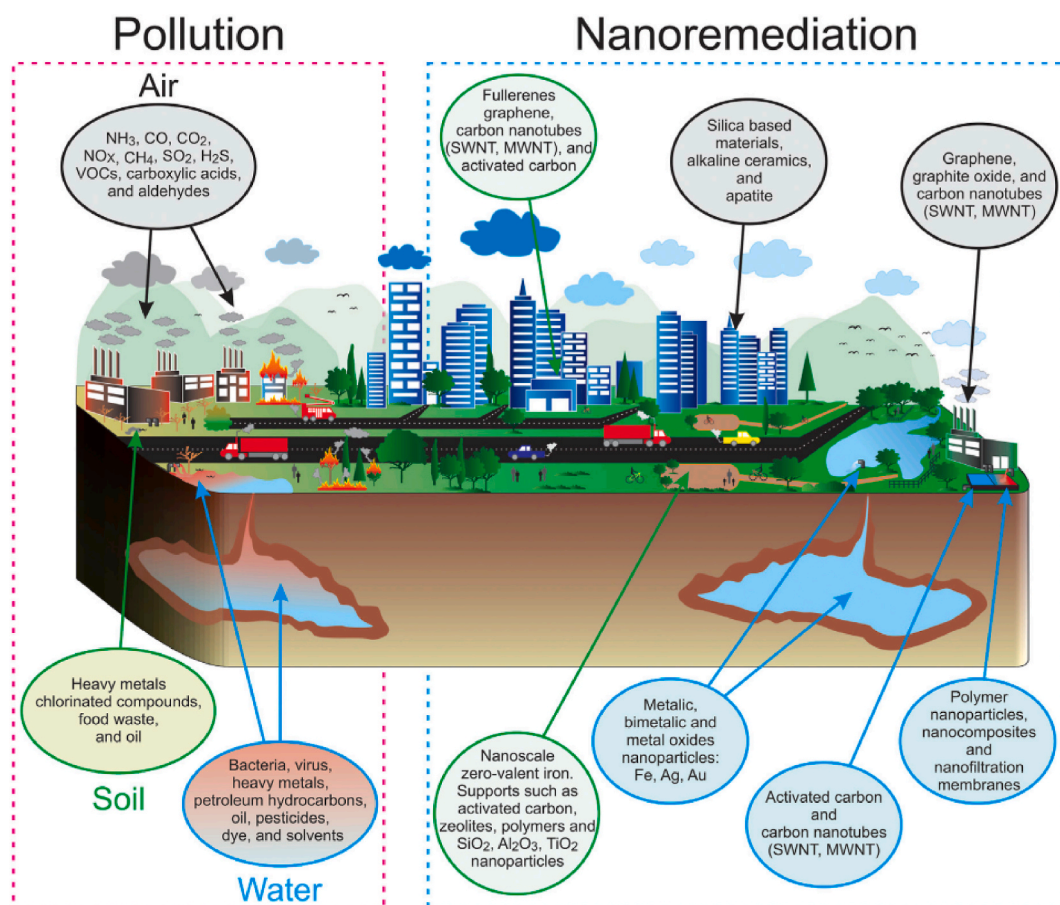


Fig. 6. Application of nanomaterials for remediation of the environment. Reprinted from Ref. [91], Copyright 2021 Frontier.

ordered SERS substrates with deterministic geometries and reproducibility is concerned with the routine application of trace-level analytes. A 3D Au and Ag nanoarrays template has been considered for SERS applications [76].

3.3. Electrochemical-based sensor

The electrochemical analysis techniques also are considered in situ techniques for detection of HMs with high sensitivity, cost-effectiveness, and easy operation [77]. Typically the electrochemical sensors are based on the monitoring of potential, charge, current, power output, or electrochemical impedance to identify the analytes according to their chemical reactivity. Consequently, the chemical-modified electrodes are based on combined electrochemical methods which can be classified as amperometric, potentiometric, impedimetric, photoelectrochemical, and electrogenerated chemiluminescence [78]. Diverse types of nanomaterials have been developed to incorporate electrodes to enhance HMs electrochemical detection. The common nanomaterials-modified electrodes are QDs, carbon nanotubes, graphene oxide, and metal and oxide nanoparticles [79–82]. Recently, Shen and coworkers have proposed a novel boron-modified bio-carbon (B-bioC) electrode for simultaneous electroanalysis of HMs of Cd, Pb, and Cu using differential pulsed anodic stripping voltammetry (DPASV) [83]. The sensing system exhibited sensibility of 10.54, 509.96, and 22.38 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ for Cd^{2+} , Pb^{2+} , and Cu^{2+} , respectively. In another study by Liu and coworkers, electrochemical detection of Pd^{2+} was developed based on carbon quantum dots (CQDs) and zeolitic imidazolate framework-8 (ZIF-8). The integration of CQDs and MOF was successfully used to detect Pd^{2+} , Cd^{2+} , and Cu^{2+} by DPASV. It was found that the presence of CQDs could enhance the electrical conductivity of ZIF-8 electrode. The LOD of Pd^{2+} detection was obtained at 0.04 nM and the limit of quantification (LQD) was 0.14 nM. Recently, the implementation strategy to increase functionality of electrodes by paper substrate and depictions of potentiometry and voltammetry behaviors have been considered and developed (Fig. 5D). [84]. Many electrochemical devices and sensor systems can interact with the designed paper substrate with heavy metals to improve the sensitivity and accuracy of the device.

Nanoremediation is used to describe the application of nanotechnology and nanomaterial for remediation of the contaminants in polluted environments such as soil and water. Nanoremediation of HMs is considered a great potential and cost-effective method for the detoxification of HMs contaminated in agricultural lands and other agroecosystems. Nanoremediations help to recover the polluted agricultural soil and water to enhance the quantity and quality of crop production, NUE, and nutrient loss. Many different types of nanomaterials have been studied and applied to reduce the HMs in the environment (Fig. 6) [91]. Recently, nanotechnology

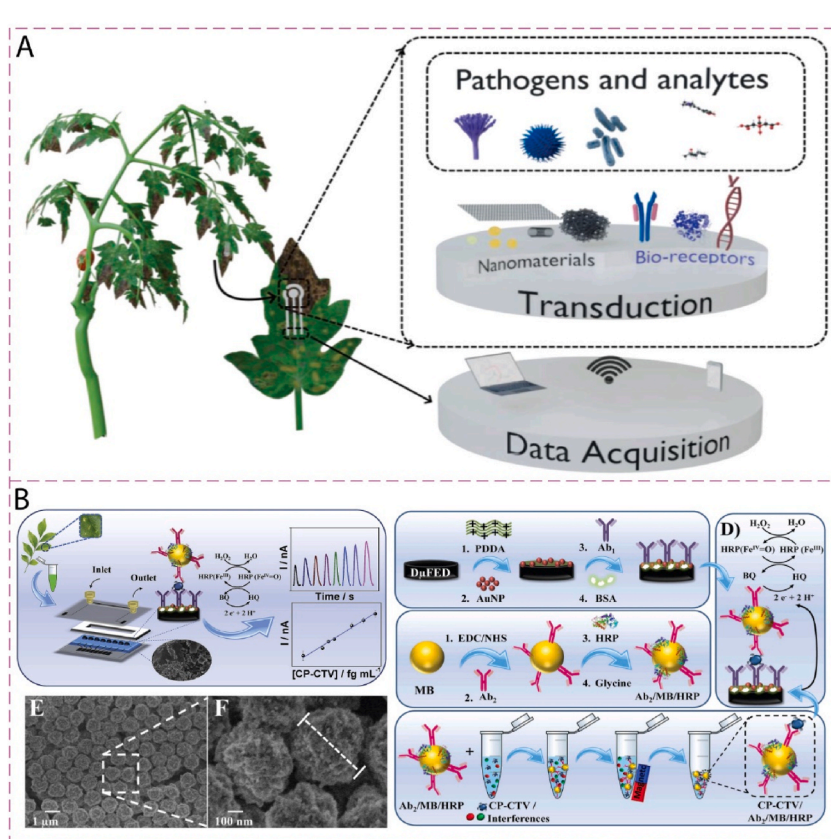


Fig. 7. (A) Scheme of nanomaterials based sensor for plant disease diagnostics. Reprinted from Ref. [100], Copyright 2022 Elsevier. (B) Scheme of design strategy of AuNPs in disposable microfluidic electrochemical device for ultrasensitive immunoassay detection of CTV and SEM images of AuNPs distributed on the electrode surface. Reprinted from Ref. [126], Copyright 2019 Elsevier.

has offered great potential and cost-effective remediation techniques for the detoxification of HMs in agricultural lands. The implementation strategy for the ultimate of nanomaterials due to their high reactivity, high ratio surface to volume, and surface modification ability that lead to the interaction between nanomaterials and HMs in different ways. The most common nanomaterials for the removal of HMs involve metallic NPs, polymeric NPs, carbon-based NMs, and nanocomposites [92]. The design strategy of nanotechnology and nanomaterials for remediation applications due to their own nanomaterial traits and the ability to surface structures and properties modification for specific targets.

Taking advantage of chemical and physical properties, iron NPs have been widely exploited for the remediation of several pollutants in water, soil, and sediments. The detoxification mechanism based on iron NPs includes the adsorption, redox, and coprecipitation pathways [93]. The transformation and mobility of HMs are typically related to HMs' solubility which is regulated through various behaviors and reactions such as the adsorption/desorption, redox reactions, ion exchange, photocatalysis, and precipitation/dissolution processes. These types of reactions support controlling the bioavailability of both biotic and abiotic in soil [94]. Baragaño and coworkers have reported using graphene oxide NPs (nGOx) and zero-valent iron NPs (nZVI) to study the remediation of Cu, Pb, Cd, As, and P [95]. The study found that nGOx actively can immobilize Cu, Pb, and Cd, but mobilized As and P. Whereas, nZVI exhibited rapid immobilization of As and Pb, and increased availability for Cu. Recently, the integrated nanostructure has been concerned and developed due to its impact on the practice of sustainable agriculture. A combination of biochar treated with Fe was proved to minimize the amount of HMs in paddy-rice crops and prevent the accumulation of hazardous HMs in rice grain [96]. The combination of nZVI and biochar can improve the reduction reaction of nZVI and improve removal efficiency [97].

4. Pathogen diagnosis

The pathogens that cause plant diseases extremely affect the quality and quantity of crop production. The fast, accurate, and on-site diagnostics of plant disease is essential for the development of sustainable agriculture. The main concept of nano-biosensors involves several approaches, such as chemical, physical, and biological properties [98]. The analysis and detection of pathogen-based nanomaterials can be constructed from the combination of nanomaterials and biorecognition ligands such as antibodies, oligo, DNA, and protein (Fig. 7A) [99,100]. The advances in nanomaterials that have a high surface-to-volume ratio and the ability to surface functionalization enable binding sites for bio-recognition immobilization. The design of the nanosensor systems and immobilization strategies play a crucial role in the sensing performances that involve sensitivity, selectivity, and reproducibility. The two commons for bio-recognition immobilization have been proposed to be absorption (van der Waals forces, electrostatic forces, hydrophobic interactions, and hydrogen bonds) and the covalent bonding of the functional groups or cross-linker [100]. The identification of disease causes can be carried out by the detection of pathogens or biomarkers. Table 1 presents the employment of nanomaterials for the detection of bacteria, fungi, and viruses as plant disease agents. Nanomaterials can incorporate various techniques to enhance the sensitivity and selectivity of sensing systems such as SERS, ELISA, LSPR, PCR, LAMP, and other electrochemical sensors [98]. For instance, Rana and coworkers recently described electrochemical sensors comprised of DNA probes and oxidized graphene-based geno-biosensors on paper electrodes for the detection of race false smut caused by *Ustilagoidea vires*. The DNA-based electrochemical biosensor exhibited high selectivity to target DNA and sensitivity with an LOD of 10 fM. Similarly, Chaudhary and coworkers have presented a graphene oxide-based electrochemical immunosensor for the rapid detection of groundnut bud necrosis ortho-topovirus (GBNV) in plant crops [101]. The design strategy of deposited GO on the electrode and anti-GBNV allowed the electrochemical response a sensitivity with a LOD of 5.7 ± 0.7 ng/mL.

Table 1
Nanotechnology in the diagnosis of plant diseases.

Nanomaterials	Analytes (pathogens or biomarkers)	Sensing systems	LOD	Ref
AuNPs	MeSA Biomarker	SERS	0.608 ppm	[102]
AuNPs	<i>Botrytis cinerea</i> , <i>Pseudomonas syringae</i> , <i>Fusarium oxysporum</i>	SERS-RPA (recombinase polymerase amplification)	2 copies of pathogen genomic DNA	[103]
AuNPs	Potato virus Y	LFIA	5.4 ng/mL	[104]
AuNPs, MWCNTs, and CTSNTs	<i>Ganoderma boninense</i>	Electrochemical	7.87–18.54 ppb	[105]
SWCNT	<i>Candidatus Liberibacter</i>	Chemoresistive biosensor	5 nM	[106]
GQDs and AuNPs	<i>Xanthomonas oryzae</i> pv. <i>oryzae</i>	Fluorescence-based immunoassay	22 CFU/mL	[107]
AuNPs	<i>Pseudomonas syringae</i>	Colorimetry	15 ng/ μ L	[108]
CdSe QDs	Banana bunchy top virus	Electrochemical ELISA	N/A	[109]
ZnO	Grapevine virus A-type proteins	Luminescence	1 pg/ml to 10 ng/ml	[110]
AuNPs and CdTe QDs	<i>Citrus tristeza virus</i>	FRET	0.13 μ g/mL	[111]
AuNPs	Tomato yellow leaf curl virus	LSPR	5 ng/ μ L	[112]
AuNPs	<i>Fusarium</i> mycotoxins • Deoxynivalenol, • zearalenone (ZEA) • T-2	iSPR	15 μ g/kg, 24 μ g/kg, 12 μ g/kg	[113]

AuNPs: gold nanoparticles, CTSNTs: chitosan nanoparticles, MWCNTs: Multi-walled Carbon nanotubes, SWCNTs: Single-walled carbon nanotubes
GQDs: graphene quantum dots, SERS: surface-enhanced Raman scattering, RPA: recombinase polymerase amplification, LFIA: lateral flow immunoassay, ELISA: enzyme-linked immunosorbent assay, FRET: fluorescence resonance energy transfer, LSPR: localized surface plasmon resonance, iSPR: imaging surface plasmon resonance.

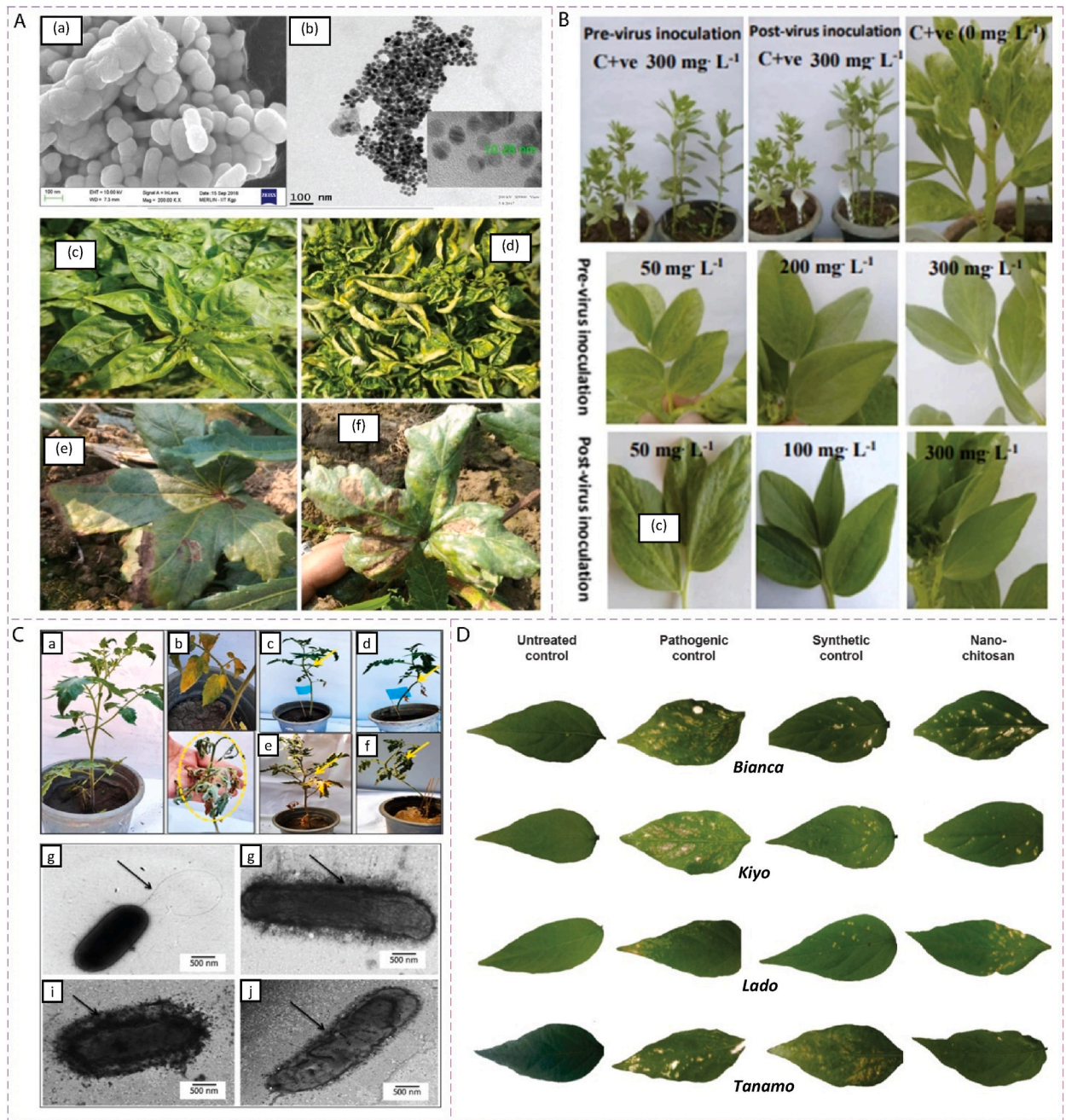


Fig. 8. (A) The use of AgNPs as foliar spray to defend leaf curl diseases in chili (*Capsicum annuum*) and leaf spot disease in okra (*Abelmoschus esculentus*). (a,b) The SEM and TEM images of as-prepared AgNPs with an average size of 28 nm. (c,d) treated and untreated of AgNPs in chili leaf curl. (e,f) treated and untreated of AgNPs in okra leaf spot disease. Reprinted from Ref. [128], Copyright 2022 Springer Nature. (B) AgNPs for preventing and curing of bean yellow mosaic virus (BYMV) in faba bean. Digital images of a healthy faba bean plant, infected one, and treated with different concentrations of AgNPs. Reprinted from Ref. [129], Copyright 2021 Springer Nature. (C) Nano chitosan for management of potato and tomato bacteria wilt diseases. Symptomatic response the efficacy of chitosan nanoparticles on (a) heavy control, (b) infected control, (c,d) spraying and soil amended, respectively, of chitosan nanoparticles 100 $\mu\text{g}/\text{mL}$, (e,f) spraying and soil amended, respectively, of chitosan nanoparticles 200 $\mu\text{g}/\text{mL}$. The TEM images of morphology and structure of *Ralstonia solanacearum* (g) un-treated and (h, i, j) 2 days after being treated with chitosan nanoparticles. The bacterial cell and flagella were destructed and lysis by the role of the nanomaterials. Reprinted from Ref. [131], Copyright 2022 Elsevier. (D) Nano chitosan against *X. campestris* infected in chili pepper (*Capsicum annuum* L.). Leaves of four chili pepper cultivars Bianca, Kiyo, Lado, and Tanamo after 12 days after inoculation with *X. campestris* and treatment with synthetic bactericide and nano chitosan. Reprinted from Ref. [132], Copyright 2020 Agrivita. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

We found that Raman and SERS also pay attention to the field of plant disease monitoring. They can be applied not only to determine bacterial, fungal, and viral diseases, pests, and mycotoxins but also to distinguish healthy and infected plant crops. A number of research on plant disease detection of various crops have been summarized by Weng and coworkers [114]. Huanglongbing (HLB) causes the most common diseases in citrus (known as citrus greening) and remains the biggest challenge of economic loss around the world [115]. Early detection of HLB can be obtained by Raman. Pérez and coworkers have reported a portable field Raman spectroscopy (RS) to recognize HLB on Sweet Orange, which is caused by *Candidatus Liberibacter asiaticus*, in the early stage [116]. The indicator peaks were demonstrated and combined with statistical analysis to exhibit a sensitivity of 86.9 % of HLB-positive, a specificity of 91.4 % of HLB-negative, and a precision of 89.2 % in discriminating between the healthy plant and HLB-infected plant. Most recently, Son and coworkers have developed nanosensor-based SERS for the real-time monitoring of stress signaling molecules in plants that are related to the onset of plant disease. In this work, a non-constructive nanoprobe composed of Si nanosphere surrounded by a corrugated Ag shell. The nanosystem was modified with a water-soluble cationic polymer that can interact with plant signaling molecules. As-prepared SERS platform has successful multiplex detection of different abiotic and biotic stress related to plant diseases such as salicylic acid, extracellular adenosine triphosphate, cruciferous phytoalexin and glutathione in *Nasturtium officinale*, *Triticum aestivum* L. and *Hordeum vulgare* L. In other work, SERS-based gold nanorods (AuNRs) have been proposed to detect deoxynivalenol (DON) residues in *Fusarium* head blight (FHB) infected wheat kernels that are caused by fungi *Fusarium graminearum* and *Fusarium culmorum*, and extremely influence the wheat yields [117]. The SERS system of AuNRs could exhibit good producibility with a relative standard deviation (RSD) of 4.2 % and a LOD of 0.11 mg/L.

In addition, microfluidic and lab-on-a-chip (LoC) technologies have rapidly developed in fields of biological and diagnostic applications, especially for the detection and identification of pathogens, due to their benefits such as high-throughput signal, minimization of material and energy consumption, designable conditions and reaction chambers, and precise sampling process [118–120]. Nanomaterials meet microfluidic and LoC technologies to create multifunctional and intelligent platforms and enhance the sensitivity and selectivity of the analytical systems [121,122]. Smart and portable sensor devices allow rapid on-site detection of plant disease infections with low cost and simplicity without expert knowledge and skills [123–125]. Fretias and coworkers have described a disposable microfluidic electrochemical device for the detection of the *Citrus tristeza virus* (CTZ), a common infection virus in citrus around the world (Fig. 7B) [126]. AuNPs were applied to immobilize monoclonal antibodies via EDS coupling on the carbon electrode surface. The electrochemical response of the modified electrodes integrated microfluidic systems to achieve the ultralow detection limit of 0.3 fg/mL.

5. Anti-microbial application

Agriculture systems and development are faced with huge problems in terms of economics and stability due to the wide infection of several pathogenic agents. Plant pathogens generally comprise viruses, bacteria, fungi, nematodes, and parasitic plants. In the past decade, a number of techniques and methodologies have been developed for the rapid detection of plant pathogens. Nanotechnology has the potential to be implemented to manage harmful microorganisms. Typically, the anti-microbial nanomaterials can be classified into inorganic and organic-based nanomaterials. The inorganics nanomaterials may include metal-based nanostructures such as AgNPs, CuNPs, TiO₂, and ZnO₂. Organic nanomaterials may consist of the nano and micro-emulsions of natural compounds and biomolecules such as secondary plant metabolites, chitosan, and chitin. Yin and coworkers have recently summarized the antibacterial mechanisms of silver nanoparticles (AgNPs) [127]. The main mode of action is due to their ability to the ability of AgNPs can anchor and accumulate to the cell surface to denature the cell membrane. Due to their small size, AgNPs can penetrate and cause structural changes in the cell membrane. AgNPs with a diameter of smaller than 10 nm can directly alter cell permeability to damage the cell. They can also denature the cytoplasmic membrane and break the inside organelles, leading to cell lysis. AgNPs can also influence the microbial signal transduction that leads to cell apoptosis. Moreover, the cell wall can be disrupted and damaged by the Ag⁺ generated by AgNPs and reactive oxygen species (ROS), which induce production by AgNPs after they adhere and pass through the cell wall and cytoplasmic membrane. Ag⁺ can also denature the ribosome and interrupt the ATP production process. AgNPs, Ag⁺, and ROS typically can interfere with the DNA replication process.

Anti-microbial nanomaterials can be applied as foliar spray or soil amendment. Kumar and coworkers have reported using AgNPs as a foliar spray to control leaf curl diseases in chili (*Capsicum annuum*) and leaf spot disease in okra (*Abelmoschus esculentus*) (Fig. 8A) [128]. Leaf curl and leaf spot are common diseases caused by *Alternaria alternata* that extremely damage crops and reduce yields. In this study, a solution of 50 ppm AgNPs has been demonstrated to significantly reduce the average disease severity in chili and okra plants by 29.05 and 23.3 %, respectively. Also, the crop yield of chili and okra was increased by 0.985 kg and 1.656 kg per plant, respectively. The anti-microbial mechanisms were proposed due to the high reactivity of AgNPs to release Ag⁺ and ROS due to their reaction with oxygen, which damages the protein, lipids, and nucleic acids of the cells. AgNPs also exhibit the capacity to prevent viral plant diseases. For example, the bean yellow mosaic virus (BYMV) in faba bean could be controlled by AgNPs (Fig. 8B) [129]. In this case study, AgNPs exhibited both preventing and curing agents. The mechanism of antivirals was demonstrated due to their high bio-activity, which can bind to viral particles and suppress viral replications and accumulation within plant tissue. The study also revealed that the AgNPs exhibit curative viricidal activity by interacting with the virus coat protein and interfering with the virus vector. Most recently, Giri and coworkers have developed chitosan fabricated biogenic silver nanoparticles (Ch@BSNP) that can against *Xanthomonas campestris* (*X. campestris*) caused bacterial leaf spot (BLS) disease in tomatoes [130]. As-prepared Ch@BSNP obtained a size of 30–35 nm and exhibited the ability to increase photosynthesis efficiency, increase water use, decrease transpiration rate, and stomatal conductance. Also, Ch@BSNP could fight the biotic stress to reduce the stress marker response of plants. The nanostructure of Ch@BSNP was demonstrated to reduce the disease lesions of the nano-treated plants under the infection of

X. campestris by staining of trypan blue dye.

Chitosan is a natural cationic biopolymer well-known to act as an anti-microbial agent. The mode of action of chitosan to inhibit microorganisms has been reported [130]. The anti-microbial mechanism of chitosan-based nanomaterials is due to their binding ability to the charged surface of the cell wall and DNA to cause the disruption of the cell and nuclei of microorganisms, respectively. Also, chitosan can work as chelate agents which can selectively bind to trace metals (Zn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) to inhibit cell growth. In some cases, chitosan can cover and isolate bacterial cells with nutrients and block to oxygen path to kill the bacteria. Recently, Khairy and coworkers have demonstrated the role of nano-chitosan in defense of *Ralstonia solanacearum*/*Pseudomonas solanacearum* which normally causes potato and tomato bacteria wilt diseases (Fig. 8C) [131]. Nanochitosan can be applied by spraying or soil-amended curative treatments at the concentration of 100 $\mu\text{g}/\text{mL}$ can have positive effects on preventing and curing the infected plants. The TEM analysis revealed extreme damage to bacteria cells in terms of cell lysis and cell flagella loss. In a similar study, nano chitosan exhibited intensity against *X. campestris* infected in chili pepper (*Capsicum annuum* L.) [132]. The results revealed that foliar spraying of nano chitosan could create a layer as a thin film on the leaf surface to protect the plant from pathogen infection (Fig. 8D). Also, the formation of nano chitosan thin film reduced the stomatal opening and limited *X. campestris* penetrate to the plant cell wall. The role of nanomaterials has been demonstrated to be a powerful tool for plant pathogen diagnostics and disease management. Together with the implementation vision of nanomaterials, the design and fabrication strategies of nanostructure to meet a circular economy and sustainable development of agriculture [133]. Micro-/nano-emulsion of botanical compounds has been exploited for pesticides, bactericides, and fungicides. Essential oils (EOs) are one of the most prominent active ingredients that have been widely used and studied. The mode of action of EOs for control of pests and microorganisms typically depends on their chemical and components. Nazzaro and coworkers have deeply described the anti-microbial activities and mechanisms of EOs and their components [134]. The hydrophobicity of EOs allows their ability to disrupt bacterial cell walls. The increased permeability of EOs through the cell membrane and cytoplasm leads to intense interference, interaction, and damage to the structure and inside organelle, pathways, and biomolecules of the cell. To increase the stability and reactivity of these natural compounds, nanoemulsion technology, and synergic design strategies have been applied. The combination of two or more biologically active ingredients in suitable ways allows for obtaining the synergistic phenomena. For example, in the combination of carvacrol and p-cymene, carvacrol's chemical function with the hydroxyl group could couple with the delocalized electron to be less apt to portioning in the hydrophobic phase of the bilayer membrane. While the p-cymene, lacking those features, has higher portioning potential, occupies more space between fatty acid chains, and further expands the membrane p-cymene might synergize with carvacrol via its membrane destabilizing activity, helping the penetration of carvacrol into the cytosol to take action [135].

6. Postharvest and packaging

In the full picture of agricultural systems, postharvest and packaging are also important aspects that impact the quantity of crop productivity to the customers. Good postharvest and package techniques can attack microorganisms, cause loss of nutrients, and damage the crop products. Nanotechnology has provided novel materials and techniques to maintain the good quality of crop production. For instance, nanotechnology-based edible coating and thin film deposition are studied to prevent the damage of microorganisms and environmental disorders. Typically, edible thin films are formed from diverse types of biopolymers and biomolecules that are non-toxic and environmentally friendly [136]. The materials involve polysaccharides (cellulose, starch, pectin, chitosan), protein (gelatin, whey, soy), and lipids (wax, oil, resins) [137]. In practice, the most common coating method is dipping. We obtained that several chitosan-based commercial coating products have been developed and used dipping methodology for fruit and vegetables. Other techniques are spraying, planning, and fluidized bed process [138]. To ensure anti-microbial activity, the edible coating can involve nano-emulsion of natural compounds in their polymeric structure [139,140]. In light of nanotechnology development, the implementation strategies of post-harvesting and packaging may intensify to the intelligent packing systems not only maintain the quality of the crop production by selective control of the gas permeability and anti-microbial activity but also integration with nanosensing system in one manner platforms.

7. Conclusion

This work summarizes and highlights comprehensive applications of nanotechnology in agriculture. Different implementation strategies and concepts have been proposed to use nanomaterials for the formulation of NFs which can have positive effects on the absorption and uptake pathways of nutrients by plants, enhancement of NUE, and bioavailability nutrients of cropland soils. Engineering nanomaterials have great potential for the high-sensitivity detection of HMs and pathogenic microorganisms through various detection approaches such as Raman/SERS, colorimetric, biological, chemical, and electrical sensors. Accordingly, the implications strategies of nanomaterials can be improved by the immobilization and interaction of nanomaterials' surface with the bio-receptors. Nanotechnology-based sensors can be designed to obtain high selectivity and sensitivity, high signal throughput, and reproducibility. Especially, the flexibility and integration ability of microfluidic technology allows for the construction of multi-function nanosystems that possibly exhibit on-site, portable, and real-time monitoring on a manner platform. Anti-microbial nanomaterials have substantial impacts on the prevention and treatment of plant diseases. We classified two main types of anti-microbial nanomaterials organic and inorganic nanostructures. The strategy combination of these anti-microbial agents can achieve synergic behaviors that significantly enhance the anti-microbial activity. We anticipate that a suitable combination of modern nanomaterials and conventional agro-chemicals can meet sustainable ways for agricultural cultivation activity in the future. In addition, further investigation regarding the nanomaterial fate and their clinical effects on the nanomaterials to human beings needs to be more studied. At this point, we believe

that green synthesizing of nanomaterials, especially organic nanomaterials such as nano- and micro-emulsion of natural compounds, will be more concerned, with not only providing a complete eco-friendly and safe nanomaterials but also obtaining circular economy and sustainable agricultural development.

CRedit authorship contribution statement

Nguyen Nhat Nam: Writing – review & editing, Writing – original draft, Conceptualization. **Nguyen Ngoc Trai:** Writing – original draft, Conceptualization. **Nguyen Phuong Thuy:** Writing – original draft, Conceptualization. **Phan Quoc Nam:** Writing – original draft, Conceptualization. **Le Truc Linh:** Writing – original draft, Conceptualization. **Hoang Dang Khoa Do:** Writing – review & editing, Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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